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Synthesis and structural characterization of well-defined anionic aluminium alkoxide complexes supported by NON-type diamido ether tridentate ligands and their use for the controlled ROP of lactide[†]

Frédéric Hild,^a Pierre Haquette,^b Lydia Brelot^c and Samuel Dagorne^{*a}

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The tridentate proligands (RNH-o-C₆H₄)₂O (**1a**, R = C₅H₉; **1b**, R = Cy) were found to readily react with LiAlH₄ to yield the corresponding lithium aluminium dihydrido salt species [η^2 -N,N-{(RN-o-C₆H₄)₂O}AlH(μ -H)Li(THF)]₂ (**2a**, R = C₃H₉; **2b**, R = Cy) in 50% and 42% yield, respectively. The solid-state structure of both complexes **2a** and **2b** were determined by X-ray crystallographic studies. Compounds **2a** and **2b** readily react with one equivalent of benzaldehyde to afford the corresponding mono-benzyloxide species η^2 -N,N-{RN-o-C₆H₄)₂O}Al(H)(μ -OCH₂Ph)Li(THF)₂ (**4a**, R = C₄H₉; **4b**, R = Cy), as confirmed by X-ray studies in the case of **4b**. In a similar manner, when compounds **2a** and **2b** are reacted with two equivalents of benzaldehyde the bis-benzyloxide derivatives **5a** and **5b** η^3 -N,N,O-{RN-o-C₆H₄)₂O}Al(μ -OCH₂Ph)₂Li(THF)₂ (**5a**, R = C₄H₉; **5b**, R = Cy) may be prepared. While the lithium Al mono-alkoxide species **4a**-**b** are inactive in the ring-opening polymerization (ROP) of lactide, their bis-alkoxide Al analogues **5a**-**b** polymerize *rac*-lactide and (*S*)-lactide at room temperature, which is rather uncommon for Al-based alkoxide systems. Kinetic studies of the lactide ROP initiated by compound **5a** suggest a strong preference for racemic enchainment during the ROP chain growth; the resulting PLAs are however moderately heterotactic due to detrimental transesterification processes occurring as the chain grows.

Introduction

The ring-opening polymerization (ROP) of rac-lactide, a dimer of the renewable resource lactic acid, initiated by well-defined metal alkoxide complexes has been the subject of numerous studies over the past fifteen years as the derived polymers, poly(lactic) acid (PLA), are biodegradable and biocompatible.¹ Among these metal alkoxide species, neutral aluminium derivatives supported by various tetradentate ligands such as, for instance, Salen- and Salantype chelate ligands have been widely investigated and several of these systems were found to stereoselectively polymerize raclactide to afford highly stereoregular polylactide materials, which are of particular interest as they exhibit improved thermal and mechanical properties versus those of atactic PLA.² Nevertheless, lactide polymerization initiated by Al alkoxide compounds is usually slow compared to other metal alkoxide initiators, which greatly limits the potential usefulness of these systems despite the low cost of aluminium.2e

To improve the catalytic performance of Al-based ROP initiators of *rac*-lactide, we have become interested in the synthesis of formally charged aluminium alkoxide complexes. In this regard, while *cationic* aluminium alkoxides may be too Lewis acidic for the ROP chain-growth step to proceed, thereby precluding the polymerization process to occur,³ the expected enhanced nucleophilicity of the Al- OR^- alkoxide moiety in *anionic* aluminium alkoxide derivatives should favour both the polymerization initiation and subsequent chain-growth steps. Also, in such anionic systems, a counteranion such as Li⁺ may well act as a weak Lewis acid able to activate the lactide monomer toward nucleophilic attack by the Al- OR^- alkoxide.

In general, despite their interesting features, well-defined anionic metal alkoxide complexes have rarely been used as ROP initiators of rac-lactide.4 For aluminium, the use of the commercially available reagent Red-Al, formulated as Na⁺[AlH₂(OCH₂CH₂OCH₃)₂]⁻, for the ROP of (L)-lactide constitutes the only example on this matter. In the latter case, rather harsh conditions are however required for the ROP to proceed (110-130 °C, 2-3 days), which may result from a high level of aggregation in Red-Al.⁵ The use of an appropriate supporting ligand for coordination to Al may provide access to well-defined species, limit aggregation processes, and thereby be beneficial to catalytic activity. The potentially N,O,N tridentate bis(amido)ether ligand of type A (Scheme 1) appeared suited for the synthesis of aluminium alkoxide anions of the type $\{LX_2\}Al(OR)_2^-$ because its steric nature may easily be tuned via the N-R substituent and the central oxygen ether atom may provide an extra-electronic stabilization of the N,N-chelated Al metal centre and thus disfavour aggregation. In addition and apart from their straightforward

^aLaboratoire DECOMET, Institut de Chimie (UMR CNRS 7177), Université de Strasbourg, 4 rue Blaise Pascal, 67000, Strasbourg, France

^bLaboratoire Charles Friedel, UMR CNRS 7223, Ecole Nationale Supérieure de Chimie de Paris, 11 rue Pierre et Marie Curie, 75005, Paris, France

^cService de Radiocristallographie, Institut de Chimie (UMR CNRS 7177), Université de Strasbourg, 4 rue Blaise Pascal, 67000, Strasbourg, France † Electronic supplementary information (ESI) available: The MALDI-TOF mass spectrum of a PLA sample and an ORTEP drawing along with a summary of crystallographic data for compound **2b**. CCDC reference numbers 735904–735907. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b911802k



Scheme 1

synthesis, ligands of type A have been shown to be effective ancillary ligands for high-oxidation-state and oxophilic group 4 metals.⁶

Here we report the synthesis, structures of anionic aluminium alkoxide complexes bearing a bis(amido)-ether ligand of type **A** as well as their applications in the controlled ROP of *rac*-lactide. Along the way, the synthesis and characterization of a couple of anionic hydrido Al species were carried out and are thus also discussed herein.

Results and discussion

Access to Al alkoxide anionic species chelated by a dianionic chelating ligand of type **A** was achieved through the synthesis of the corresponding Al hydrido anions, which were then subsequently converted to the Al alkoxide derivatives.

Synthesis and structure of the lithium Al hydrido complexes 2a-b

The proligands (RNH-*o*-C₆H₄)₂O (**1a**, R = C₅H₉; **1b**, R = Cy, Scheme 2) were readily synthesized in a one-step procedure according to a literature report from the commercially available bis(amino)-ether (NH₂-*o*-C₆H₄)₂O.⁶ The reaction of proligands **1a–b** with one equivalent of LiAlH₄ (THF, -35 °C to room temperature) affords the corresponding lithium Al hydrido complexes $[\eta^2-N,N-{(RN-o-C_6H_4)_2O}AlH(\mu-H)Li(THF)]_2$ (**2a**, R = C₅H₉; **2b**, R = Cy, Scheme 2) in 50% and 42% yield, respectively. The molecular structures of both **2a** and **2b** were determined by X-ray crystallographic studies and that of **2a** is depicted in Fig. 1, (see Table 1 for a summary of crystallographic data and ESI† for the molecular structure of **2b**). As expected, compounds **2a** and **2b** exhibit very similar structural features in the solid-state and these will only be discussed for **2a**.



As illustrated in Fig. 1, the salt compound **2a** is dimeric in the solid state and is best described as two $[\eta^2 - N, N - \{((C_5H_9)N - O - C_6H_4)_2O\}AlH_2Li(THF)]$ units connected by two Al–H–Li bridges. This results in the formation of a central four-membered Li₂H₂ ring, a frequently observed structural element in lithium hy-



Fig. 1 Molecular structure (ORTEP drawing) of the lithium aluminium hydrido species **2a** with partial atom labelling. The hydrogen atoms, except those bonded to Al and Li, are omitted for clarity. Selected bond distances (Å): Al–N(1) = 1.865(1), Al–N(2) = 1.908(1), Al–H(1) = 1.55(2), Al–H(6) = 1.59(2), Li–O(1) = 2.025(3), Li–O(2) = 1.930(3), Li–N(2) = 2.246(3), Li–H(6) = 2.21(2); selected bond angles (°): N(1)–Al–N(2) = 114.17(5), N(1)–Al–H(1) = 110.4(9), H(1)–Al–H(6) = 109.2(11), O(2)–Li–O(1) = 114.15(14), O(1)–Li–N(2) = 75.82(9).

drido aluminate dimers.⁷ Within each $[\eta^2 - N, N - \{((C_5H_9)N - o - n)\}$ $C_6H_4)_2O$ AlH₂Li(THF)] moiety, the Al atom adopts a distorted tetrahedral structure and is effectively η^2 -N,N-chelated by the supporting NON²⁻ ligand with a relatively large bite angle (N(1)– $Al-N(2) = 114.17(5)^{\circ}$). The coordination sphere of the Al centre is then completed by a terminal and a bridging hydride; the Al metal centre apparently does not interact with the central oxygen donor atom of the NON²⁻ ligand. The Al-N bond distances (1.886(1) Å average) as well as both the terminal and bridging Al-H distances (1.57 Å average), albeit of low accuracy for the Al-H distances, are consistent with other examples reported in the literature.8 Both Li atoms are η^2 -N,O-chelated by a NON²⁻ ligand with a rather acute O(1)–Li–N(2) bite angle $(75.82(9)^{\circ})$, which results in the formation of a Al–(μ -N)–Li bridge. The sphere of coordination of the Li atoms is completed by two bridging hydrides and a THF molecule, both exhibiting normal bonding parameters to Li.

The NMR data for both salt compounds **2a** and **2b** (CD₂Cl₂, room temperature) are consistent with effective C_{2v} -symmetric structures under the studied conditions, implying some degree of fluxionality that was not further investigated. Compound **2b** is unstable in CD₂Cl₂ solution at room temperature and reacts with the solvent to slowly and quantitatively yield the corresponding neutral Al hydrido complex {(CyN-o-C₆H₄)₂O}AlH(THF) (**3b**) along with formation of CHD₂Cl and LiCl. Thus, apart from resonances assigned to **3b**, the ¹H NMR spectrum of the reaction mixture exhibits a quintet signal ($\delta 2.99$, ²J_{HD} = 1.6 Hz) assigned to the proton resonance in CHD₂Cl.⁹ Compound **3b** was synthesized on a preparative scale allowing its isolation; IR and elemental analysis data further confirmed its identity. Although not studied, it appears very likely that the closely related salt species **2a** undergoes a similar decomposition.

One should mention that the nature of the tridentate supporting ligand NON²⁻ may play a crucial role in the relatively good stability of the lithium hydrido Al species 2a and 2b; as a

| Table 1 | Summary | of crystallographic | data for compounds 2a | i, 4b and 5a |
|---------|---------|---------------------|-----------------------|--------------|
|---------|---------|---------------------|-----------------------|--------------|

| Compound | $2\mathbf{a}\cdot \mathbf{CH}_{2}\mathbf{Cl}_{2}$ | 4b | 5a | | | |
|--|---|---|---------------------------------------|--|--|--|
| Formula | C ₂₇ H ₃₈ AlCl ₂ LiN ₂ O ₂ | C ₃₀ H ₅₄ AlLiN ₂ O ₄ | C44H56AlLiN2O5 | | | |
| Formula weight | 527.41 | 648.76 | 726.83 | | | |
| Crystal system | triclinic | monoclinic | monoclinic | | | |
| Space group | P-1 | C 2/c | $P 2_1$ | | | |
| a (Å) | 9.531(1) | 23.5757(14) | 8.7739(4) | | | |
| $b(\mathbf{A})$ | 12.933(1) | 22.3191(16) | 20.3007(11) | | | |
| $c(\dot{A})$ | 13.383(1) | 17.1128(7) | 11.7890(6) | | | |
| α (°) | 102.921(2) | 90 | 90 | | | |
| β (°) | 109.009(2) | 124.518(3) | 107.960(3) | | | |
| γ (°) | 107.777(2) | 90 | 90 | | | |
| $V(Å^3)$ | 1386.31(9) | 7419.3(8) | 1997.49(17) | | | |
| Z | 2 | 8 | 2 | | | |
| Density (g cm ⁻³) | 1.263 | 1.162 | 1.208 | | | |
| μ (Mo K α) (mm ⁻¹) | 0.292 | 0.095 | 0.098 | | | |
| F(000) | 560 | 2800 | 780 | | | |
| Crystal Size [mm] | $0.10 \times 0.10 \times 0.10$ | $0.50 \times 0.50 \times 0.30$ | $0.30 \times 0.15 \times 0.10$ | | | |
| Data collection | | | | | | |
| Temperature (K) | 173(2) | 173(2) | 173(2) | | | |
| Radiation (Å) | ΜοΚα-0.71073 | ΜοΚα-0.71073 | ΜοΚα-0.71073 | | | |
| Theta min-max | 1.72-30.00 | 1.39-27.46 | 1.82-27.47 | | | |
| Dataset $[h, k, l]$ | -13/13, -17/18, -18/17 | -20/30, -26/28, -22/17 | -11/8, -26/24, -11/15 | | | |
| Tot., Uniq. Data, <i>R</i> (int) | 11345, 8002, 0.0170 | 21934, 8428, 0.0889 | 10906, 4707, 0.0807 | | | |
| Observed data $(I > 2\sigma(I))$ | 6720 | 4825 | 2780 | | | |
| Refinement | | | | | | |
| $\overline{N_{\mathrm{reflections}},N_{\mathrm{parameters}}}$ | 8002, 324 | 8428, 381 | 4707, 467 | | | |
| $R2(all), R1(I>2\sigma(I)), wR2(all), wR1(I>2\sigma(I)), Goof$ | 0.0614, 0.0476, 0.1588, 0.1359, 1.114 | 0.1556, 0.0920, 0.2899, 0.2436, 1.058 | 0.1554, 0.0890, 0.2392, 0.2010, 1.026 | | | |
| Max. and Av. Shift/Error | 0.002, 0.000 | 0.000, 0.000 | 0.000, 0.000 | | | |
| Min, Max. Resd Dens. (e Å ⁻³) | -0.608, 0.927 | -0.703, 1.138 | -0.412, 0.675 | | | |
| | | | | | | |

comparison, the reaction of tridentate triamino proligands of the type $(RNHCH_2CH_2)_2NR'$ with LiAlH₄ directly yields the corresponding diamido amino Al neutral hydrido species { η^3 -N,N,N-($RNHCH_2CH_2)_2NR'$ }AlH;¹⁰ in the latter case, the flexibility of the ligand backbone along with the L-type amino central donor atom apparently strongly favour the formation of the neutral Al hydrido derivative.

Synthesis and structure of the lithium Al alkoxide complexes 4a-b and 5a-b

While the reaction of the lithium Al hydrido species **2a** and **2b** with one or two equivalents of an alcohol source such as PhCH₂OH consistently yielded untractable mixtures of species, that with benzaldehyde afforded the corresponding Al mono- and bis-alkoxide derivatives. Thus, both compounds **2a** and **2b** readily react with one equiv. of benzaldehyde (THF, -35 °C to room temperature) to afford the corresponding lithium Al monoalkoxide species η^2 -*N*,*N*-{RN-*o*-C₆H₄)₂O}Al(H)(μ -OCH₂Ph)Li(THF)₂ (**4a**, R = C₄H₉; **4b**, R = Cy; Scheme 3).

The solid-state molecular structure of **4b** was determined by X-ray crystallographic studies. As depicted in Fig. 2, compound **4b** crystallizes as associated Al anions and Li cations and may be formally seen as a "Li(THF)₂+" cationic fragment being *O*,*O*- η^2 chelated by the " η^2 -*N*, *N*-{RN-*o*-C₆H₄)₂O}Al(H)(OCH₂Ph)-" Al anionic moiety. The Al atom adopts a distorded tetrahedral



structure as a result of the rather wide {NN}Al bite angle (N(1)–Al(1)–N(2) = 116.8(1)°) and is connected to the Li cation *via* a μ -O benzyloxide bridging moiety, with an Al–O bond distance (Al(1)–O(2) = 1.790(2) Å) in the expected range for Al alkoxides.¹¹



Fig. 2 Molecular structure (ORTEP drawing) of the lithium aluminium hydrido mono-benzyloxide species **4b** with partial atom labelling. With the exception of H(1a), the hydrogen atoms are omitted for clarity. Selected bond distances (Å): Al(1)–N(1) = 1.892(3), Al(1)–N(2) = 1.882(3), Al(1)–O(2) = 1.790(2), Al(1)–H(1a) = 1.44(3), Li(1)–O(1) = 2.096(7), Li(1)–O(2) = 1.877(7), Li(1)–O(3) = 1.942(8), Li(1)–O(4) = 1.899(8); selected bond angles (°): N(2)–Al(1)–N(1) = 116.85(12), Al(1)–O(2)–Li(1) = 113.5(2), O(1)–Li(1)–O(2) = 83.2(3), O(3)–Li(1)–O(4) = 102.2(3).

The coordination sphere of Al is completed by a terminal hydride (Al–H(1a) = 1.44(3) Å). The Li atom is bonded to four oxygens: two THF molecules (O(3) and O(4)), the central donor oxygen of the NON²⁻ chelating ligand (O(1)) and the Al- μ -O-Li benzyloxide oxygen (O(1)). The geometrical constraints imposed by the NON ligand backbone most likely account for the distorted tetrahedral geometry at Li(O(1)–Li(1)–O(2) = 83.2(3)°) as well as the longer Li(1)–O(1) bond distance (2.096(7) Å) *versus* other Li–O distances (1.91(1) Å average). Such constraints are likely to result from the significant ring strain associated with the eight-membered-ring {NON)Al metallacycle, forced to adopt an unpreferred "boat-like" conformation for coordination of both the central NON and the μ -O benzyloxide oxygens to Li (Fig. 2).¹²

The NMR data for compounds **4a** and **4b** (CD₂Cl₂, room temperature) agrees with the overall C_s -symmetric structures, which implies, given that **4b** adopts a C_1 -symmetric structure in the solid state, a fluxional behaviour of these species in solution under the studied conditions; this was not further investigated. The identity of **4a** and **4b** was confirmed by elemental analysis and IR data. In particular, the IR spectra of **4a** and **4b** exhibit an absorption peak at 1805 and 1811 cm⁻¹, respectively, characteristic of an Al–H bond.

The lithium bis-alkoxide Al derivatives η^3 -*N*,*N*,*O*-{RN-*o*-C₆H₄)₂O}Al(μ -OCH₂Ph)₂Li(THF)₂ (**5a**, R = C₄H₉; **5b**, R = Cy; Scheme 3) were synthesized in an analogous manner to that used for **4a** and **4b**, but using two equivalents of benzaldehyde. The molecular structure of **5a** was determined by X-ray crystallographic studies and is illustrated in Fig. 3. The solid-state structure of the lithium bis-alkoxide Al species **5a** is quite different to that of its mono-alkoxide analog **4b**. In compound **5a**, the Al anionic fragment is connected to the "Li(THF)₂+" cationic moiety *via* two μ -O benzyloxide oxygens, resulting in the formation of a nearly planar AlO₂Li structural motif. The geometry at the Al center



Fig. 3 Molecular structure (ORTEP drawing) of the lithium aluminium bis-benzyloxide species 5a with partial atom labelling. The hydrogen atoms are omitted for clarity. The disordered part of the carbon atoms C(20), C(21) and those in the two THF molecules are also omitted for clarity. Selected bond distances (Å): Al(1)-O(1) = 2.177(4), Al(1)-O(2) = 1.808(4), Al(1)-O(3) = 1.769(4), Al(1)-N(1) = 1.892(5), Al(1)-N(2) = 1.893(5), Li(1)-O(2) = 1.918(12), Li(1)-O(3) = 1.897(11), Li(1)-O(4) = 1.968(13), Li(1)-O(5) = 1.935(13); selected bond angles (°): N(1)-Al(1)-N(2) = 121.1(2), O(2)-Al(1)-O(3) = 87.9(2), O(2)-Li(1)-O(3) = 81.2(5), O(5)-Li(1)-O(4) = 103.9(6).

is best described as trigonal bipyramidal with the NON²⁻ amido nitrogens (N(1) and N(2)) and a bridging μ -O benzyloxide (O(3)) located at the equatorial positions, while the other μ -O benzyloxide oxygen (O(2)) along with the NON central donor atom (O(1)) occupy the axial coordination sites. Thus, despite an expected decreased Lewis acidity for the formally anionic Al metal center, the Al centre is penta-coordinated, which is presumably favoured by the presence of the NON central donor oxygen atom O(1) in its vicinity. Nevertheless, while the Al alkoxides and amido bond distances (1.89(1) Å and 1.892(9) Å average, respectively) are in the expected range, the Al(1)–O(1) bond distance (2.177(4)) Å) is much longer than the classical Al–ether bond distance (from 1.85 to 2 Å).¹³

The NMR data for analytically pure compounds **5a** and **5b** (CD₂Cl₂, room temperature) are consistent with C_{2v} -symmetric structures under the studied conditions. In particular, the ¹H and ¹³C NMR spectra each contain one set of resonances for the NON²⁻ chelating ligand, a singlet signal for the Ph*CH*₂O moiety and agree with the presence of two molecules of THF. Based on the solid-state structure of **5a**, the observed C_{2v} -symmetry for **5a** and **5b** may result from a fast face exchange (*via* decoordination/coordination) of the Al-coordinated NON-oxygen atom (O(1) in Fig. 4) on the NMR time scale.

ROP of lactide by the lithium Al benzyloxide species 5a and 5b

As stated in the Introduction, the use of well-defined anionic metal alkoxide complexes as initiators of the ROP of lactide has not been much studied despite the potential higher activity. The synthesized



Fig. 4 Plot of monomer (*rac*-lactide) conversion *versus* M_n values of PLAs. Conditions: complex **5a** as the initiator, 230 equiv. of *rac*-LA, [*rac*-LA]₀ = 1.6 M, CH₂Cl₂, room temperature.

NON-supported Al alkoxide complexes **4a–b** and **5a–b** were thus tested for their activity in lactide ROP.

While the mono-alkoxide Al derivatives 4a and 4b were found to be inactive in rac-lactide (rac-LA) ROP in CH₂Cl₂ at room temperature, both bis-alkoxide Al species 5a and 5b are active under these mild conditions (CH2Cl2, room temperature, 16 h, 230 equiv. of rac-LA, 82% and 85% conversion to PLA for 5a and 5b, respectively). As initiators 5a and 5b are structurally close and thus exhibit a similar lactide ROP activity, the polymerization of lactide was thoroughly studied only in the case of 5a; all experimental data support a rather well-controlled rac-LA ROP process; these include: (i) all PLAs, isolated at different monomer conversions, exhibit a narrow polydispersity as deduced from SEC data (Table 2); (ii) the monomer conversion linearly correlates with the $M_{\rm p}$ values of PLAs (Fig. 4) and (iii) the polymerization is first order in the monomer (Fig. 5). As estimated from SEC data and shown in Table 2, the M_n values of the PLAs are lower than those expected for a "living"-type ROP proceeding in ideal conditions, which is most likely due to transesterification sidereactions during the present polymerization process. This was substantiated by MALDI-TOF mass-spectrometric analysis of one PLA sample; its mass spectrum primarily exhibits metal ions peaks $(M + Na^{+} and M + K^{+})$ that are equally spaced by 72 a.u. and with exact masses consistent with a linear PLA bearing a benzyloxide group at the ester end (see ESI[†]). In addition, the MALDI-TOF spectrum also contains ion peaks corresponding



Fig. 5 Plot of $\ln([M]_0/[M])$ versus time with *rac*-lactide as the monomer M. Conditions: complex **5a** as the initiator, 230 equiv. of *rac*-LA, [*rac*-LA]₀ = 1.6 M, CH₂Cl₂, room temperature.

 Table 2
 Polymerization of rac-lactide initiated by compound 5a^a

| Conv. (%) ^b | Time (h) | $M_n(obsd)^c$ | PDI | $M_{\rm n}({\rm calcd})^d$ |
|------------------------|----------|---------------|------|----------------------------|
| 35 | 5 | 3950 | 1.04 | 5800 |
| 50 | 7 | 5530 | 1.05 | 8290 |
| 60 | 8 | 5790 | 1.06 | 9950 |
| 70 | 10 | 6730 | 1.04 | 11600 |
| 82 | 16 | 8060 | 1.03 | 13590 |

^{*a*} Polymerization conditions: CH₂Cl₂, room temperature, [*rac*-LA]₀/Al = 230, [*rac*-LA]₀ = 1.6 M. ^{*b*} As determined by ¹H NMR spectroscopy. ^{*c*} Measured by SEC at 25 °C in THF relative to polystyrene standards with Mark–Houwink corrections for M_n [M_n (obsd) = 0.56 M_n (SEC)].¹⁶ ^{*d*} Calculated for two growing chains per aluminium atom and thus from [(MW_{*rac*-LA} × 230 × conversion)]/2.

to cyclic PLAs, which suggests that back-biting reactions take place, to some extent, during chain growth. One should however point out that all SEC chromatograms of the synthesized PLAs display a symmetrical peak with no shoulder, which suggests that the generated cyclic PLA chains have very similar hydrodynamic radii to those in linear PLAs. As for their stereoregularity, the formed PLAs are moderately heterotactic ($P_r = 0.67$ and 0.65 at 60% and 85% conversion, respectively), as determined by ¹H-homodecoupled NMR experiments.¹⁴ This apparent preference for racemic enchainment was further confirmed by comparing the relative conversion rate of rac-LA versus (S)-LA to the corresponding PLA materials. Thus, as illustrated in Fig. 6, the ROP of rac-LA initiated by 5a proceeds much faster than that of (S)-LA ($k_{rac}/k_s \sim 20$). Thus, the moderate heterotacticity of the isolated PLAs (from rac-LA) is certainly to be ascribed to detrimental transesterification processes. One should finally mention that the ROP of (S)-lactide initiated by compound 5a only yielded the obtainment of poly-(S)-lactide, indicating the absence of epimerization during polymerization.



Fig. 6 Plots of $\ln([M]_0/[M])$ versus time with *rac*-lactide and (*S*)-lactide as the monomer M. Conditions: complex **5a** as the initiator, 230 equiv. of monomer, $[M]_0 = 1.6 \text{ M}$, CH₂Cl₂, room temperature.

Thus, while Al-based metal alkoxides classically require heating to initiate the ROP of lactide, the well-defined lithium Al alkoxide species **5a** and **5b** readily undergo such a polymerization at room temperature. To rationalize this difference of activity, it was conjectured that **5a** and **5b**, which are of the type {(RN-o-C₆H₄)₂O}Al(μ -OCH₂Ph)₂Li(THF)₂, may well dissociate, at least partially under catalytic conditions, to yield the neutral Al alkoxide complex {(RN-o-C₆H₄)₂O}Al(OCH₂Ph), likely to be stabilized by the monomer, and LiOCH₂Ph; the latter Li species may then, on Published on 22 September 2009. Downloaded by University of Frankfurt on 22/08/2014 13:52:27.

its own, initiate the ROP of *rac*-lactide.¹⁵ To gain an insight into this matter and taking the case of **5b**, the synthesis of {(CyN-o-C₆H₄)₂O}Al(OCH₂Ph)(THF) (**6b**, see Experimental section) and of LiOCH₂Ph, generated by deprotonation of PhCH₂OH with "BuLi, were carried out. Both compounds were found to be inactive in the ROP of *rac*-LA under conditions found suitable for complexes **5a** and **5b** (CH₂Cl₂, room temperature, 16 h). The latter results are consistent with an active ROP species in which both the Al and Li fragments may be involved and co-operate.

Summary and conclusions

Tridentate diamido-ether dianionic ligands of the type NON²⁻ are suitable ligands for coordination to Al and the synthesis of the derived lithium Al hydrido and alkoxide species 2a-b, **4a–b** and **5a–b**, which, formally, are of the type $\{LX_2\}AlX_2^-$, Li⁺. All these salt species crystallize as associated Al and Li fragments and may be structurally different depending on the nature of the X ligand (hydrido or benzyloxide), as illustrated by the observed structural variation when going from 2a-b to 4b and then 5a. While the lithium Al mono-alkoxide species 4a-b are inactive in the ROP of lactide, their bis-alkoxide Al analogues 5a-b polymerize rac-lactide and (S)-lactide at room temperature, which is rather uncommon for Al-based alkoxide systems. Kinetic studies of the lactide ROP initiated by compound 5a suggest a strong preference for racemic enchainment during the ROP chain growth; the resulting PLAs are however only moderately heterotactic due to detrimental transesterification processes occurring as the chain grows. Future studies will focus on the use and screening of various dianionic and trianionic chelating ligands for coordination to Al so as to probe the potential of the derived anionic Al complexes as lactide ROP initiators.

Experimental

General procedures

All experiments were carried out under N₂ using standard Schlenk techniques or in a Mbraun Unilab glovebox. Toluene, pentane, diethyl ether and tetrahydrofuran were collected after passage through drying columns (SPS apparatus, MBraun) and stored over activated molecular sieves (4 Å) for 24 h in a glovebox prior to use. CH₂Cl₂, CD₂Cl₂, C₆D₆ and THF-d⁸ were distilled from CaH₂, degassed under a N₂ flow and stored over activated molecular sieves (4 Å) in a glovebox prior to use. All deuterated solvents were obtained from Eurisotop (CEA, Saclay, France). All other chemicals were purchased from Aldrich and were used as received with the exception of rac-lactide, which was twice sublimed prior to use. NMR spectra were recorded on Bruker AC 300 or 400 MHz NMR spectrometers, in TeflonTM-valved J-Young NMR tubes at ambient temperature, unless otherwise indicated. ¹H and ¹³C chemical shifts are reported vs. SiMe₄ and were determined by reference to the residual ¹H and ¹³C solvent peaks. ¹⁹F and ⁷Li chemical shifts are reported versus BF₃-Et₂O in CD₂Cl₂, LiCl (1M) in D₂O, respectively. Elemental analysis for all compounds were performed at the Service de Microanalyse of the Université Pierre et Marie Curie (Paris, France) and the Université de Strasbourg (Strasbourg France). SEC analysis of poly(lactic) acid were performed at the Institut

Charles Sadron (Strasbourg, France) on a system equipped with a Shimadzu RID10A refractometer detector using dry THF (on CaH₂) as an eluant. Molecular weights and polydispersity indices (PDIs) were calculated using polystyrene standards. MALDI-TOF mass spectroscopic analysis were performed at the Service de Spectrométrie de Masse of the University of Strasbourg and run in a positive mode; samples were prepared by mixing a solution of the polymers in CH₂Cl₂ with a 0.5 mg/100 mL concentration; α -HCCA (in saturated acetone) was used as the matrix in 5/1 volume ratio.

Proligands (RNH-*o*-C₆**H**₄)₂**O (1a, R = C**₅**H**₉; **1b, R = Cy).** Compounds **1a** and **1b** were synthesized according to a literature procedure involving the reaction of $(NH_2-o-C_6H_4)_2O$ with two equivalents of cyclopentanone or cyclohexanone in the presence of a Zn/CH₃COOH mixture.⁶ The analytical data obtained for **1b** matched those reported in the literature while those for **1a** are listed below.

Data for $[(C_5H_9)$ **NH-***o***-C_6H_4]_2O (1a).** ¹H NMR (300 MHz, C_6D_6): δ 1.21–1.37 (m, 12H, C_5H_9), 1.68–1.76 (m, 4H, C_5H_9), 3.58 (septet, ³ J_{HH} = 6.6 Hz, 2H, N–*CH*), 4.30 (br. d, ³ J_{HH} = 6.3 Hz, 2H, N*H*), 6.58 (dt, ³ J_{HH} = 7.2 Hz, ⁴ J_{HH} = 1.5 Hz, 2H), 6.70 (dd, ³ J_{HH} = 7.5 Hz, ⁴ J_{HH} = 1.5 Hz, 2H), 6.90 (dd, ³ J_{HH} = 7.5 Hz, ⁴ J_{HH} = 1.5 Hz, 2H), 7.01 (dt, ³ J_{HH} = 7.5 Hz, ⁴ J_{HH} = 1.5 Hz, 2H), 7.01 (dt, ³ J_{HH} = 7.5 Hz, ⁴ J_{HH} = 1.5 Hz, 2H), 7.01 (dt, ³ J_{HH} = 7.5 Hz, ⁴ J_{HH} = 1.5 Hz, 2H), 7.01 (dt, ³ J_{HH} = 7.5 Hz, ⁴ J_{HH} = 1.5 Hz, 2H), 7.01 (dt, ³ J_{HH} = 7.5 Hz, ⁴ J_{HH} = 1.5 Hz, 2H), 7.01 (dt, ³ J_{HH} = 7.5 Hz, ⁴ J_{HH} = 1.5 Hz, 2H), 7.01 (dt, ³ J_{HH} = 7.5 Hz, ⁴ J_{HH} = 1.5 Hz, 2H), 7.01 (dt, ³ J_{HH} = 7.5 Hz, ⁴ J_{HH} = 1.5 Hz, 2H), 7.01 (dt, ³ J_{HH} = 7.5 Hz, ⁴ J_{HH} = 1.5 Hz, 2H), 7.01 (dt, ³ J_{HH} = 7.5 Hz, ⁴ J_{HH} = 1.5 Hz, 2H), 7.01 (dt, ³ J_{HH} = 7.5 Hz, ⁴ J_{HH} = 1.5 Hz, 2H), 7.01 (dt, ³ J_{HH} = 7.5 Hz, ⁴ J_{HH} = 1.5 Hz, 2H), 7.01 (dt, ³ J_{HH} = 7.5 Hz, ⁴ J_{HH} = 1.5 Hz, 2H). {¹H}¹³C NMR (75 MHz, C_6D_6): δ 24.1 (C_5H_9), 33.5 (C_5H_9), 54.4 (N-CH), 112.3 (CH), 116.7 (CH), 118.3 (CH), 124.4 (CH), 140.0 (C_{ipso}), 144.4 (C_{ipso}). Anal. Calcd for $C_{22}H_{28}N_2O$: C, 78.53; H, 8.39. Found: C, 78.36; H, 8.18.

 $[\eta^2 - N, N - \{(C_5H_9)N - o - C_6H_4\}_2 O\} AlH(\mu - H)Li(THF)]_2$ (2a). In a glovebox, LiAlH₄ (113.5 mg, 2.99 mmol) was added in several portions via a spatula to a precooled (-35 °C) THF solution (15 mL) of the diamino proligand 1a (1.00 g, 2.98 mmol). The resulting grey suspension was then allowed to warm to room temperature; upon warming, bubbling occurred (H₂ formation). The reaction mixture was stirred at room temperature for 20 h, filtered through a glass frit and the obtained colorless solution evaporated to dryness in vacuo to afford a colorless solid as the crude product. The latter residue was recrystallized from a 5/1 pentane/CH₂Cl₂ solvent mixture cooled at -35 °C to yield analytically pure 2a (660 mg, 50% yield). ¹H NMR (300 MHz, CD₂Cl₂): δ 1.40–1.89 (m, 40H, C₅H₉ and H_β-THF), 3.53–3.60 (m, 12H, N-CH and H_{α}-THF), 6.48 (t, ${}^{3}J_{HH} = 7.5$ Hz, 4H), 6.75 (d, ${}^{3}J_{\rm HH} = 8.1$ Hz, 4H), 6.84 (d, ${}^{3}J_{\rm HH} = 7.8$ Hz, 4H), 7.00 (t, ${}^{3}J_{\rm HH} =$ 7.6 Hz, 4H). {¹H}¹³C NMR (75 MHz, CD₂Cl₂): δ 24.2 (CH₂), 25.2 (THF), 34.0 (CH₂), 60.6 (N-CH), 68.4 (THF), 114.4 (CH), 116.4 (CH), 118.9 (CH), 125.6 (CH), 147.4 (Cipso), 148.5 (Cipso). IR (cm⁻¹): 1789 (br s, Al–H). Anal. Calcd for $C_{52}H_{72}Al_2Li_2N_4O_4$: C, 70.57; H, 8.20. Found: C, 70.23; H, 8.38.

 $[η^2-N, N-{(CyN-o-C_6H_4)_2O}AIH(μ-H)Li(THF)]_2$ (2b). The diamido Al hydrido complex 2b was synthesized following an identical procedure to that used for 2a and involved the reaction of LiAlH₄ (133.0 mg, 3.50 mmol) with ligand 1b (1.15 g, 3.20 mmol). Complex 2b was isolated as an analytically colorless crystalline powder after a toluene wash of the crude product (630 mg, 42% yield). ¹H NMR (300 MHz, CD₂Cl₂): δ 1.12–1.26 (br m, 12H, Cy), 1.68–1.76 (m, 36H, Cy and H_β-THF), 2.95 (br s, 4H, N–CH), 3.51 (br s, 8H, H_α-THF), 6.45 (t, ³J_{HH} = 7.5 Hz, 4H), 6.72 (d, ³J_{HH} = 8.1 Hz, 4H), 6.83 (d, ³J_{HH} = 7.8 Hz, 4H), 6.97

(t, ${}^{3}J_{HH} = 7.6$ Hz, 4H). { ${}^{1}H$ } ${}^{13}C$ NMR (75 MHz, CD₂Cl₂): δ 25.2 (CH₂), 26.1 (CH₂), 26.5 (CH₂), 34.2 (CH₂), 58.9 (N–CH), 68.3 (THF), 113.8 (CH), 114.6 (CH), 119.2 (CH), 125.9 (CH), 146.5 (C_{*ipso*}), 147.9 (C_{*ipso*}). ⁷Li NMR (155.5 MHz, CD₂Cl₂): δ –0.14 (s). IR (cm⁻¹): 1751 (br s, Al–H). Anal. Calcd for C₂₈H₄₀AlLiN₂O₂: C, 71.47; H, 8.57. Found: C, 71.15; H, 8.32.

{(CyN-o-C₆H₄)₂O}Al(H)(THF) (3b) NMR-scale reaction. A J-Young NMR tube containing a CD₂Cl₂ solution of pure 2b was left for 24 h at RT. Subsequent ¹H NMR analysis revealed the complete conversion of the Al salt species 2b into the neutral monohydrido aluminium complex 3b, along with formation of CHD₂Cl (δ 2.99, q, ² J_{HD} = 1.6 Hz). Preparative scale. In a glove box, a CH₂Cl₂ of complex 2b (200 mg, 0.425 mmol) was stirred at room temperature overnight to yield, after drying in vacuo, a pale light suspension (formation of LiCl), which was filtered through a glass frit to afford a colorless foam as the crude product. Recrystallization of the latter residue from a 9/1 pentane/CH2Cl2 solvent mixture stored at -5 °C afforded pure 3b (277 mg, 63% yield). ¹H NMR (300 MHz, CD₂Cl₂): δ 1.14–1.33 (m, 8H, Cy), 1.59-1.82 (m, 16H, Cy and H_{β}-THF), 2.78 (br s, 1H, Al–H), 3.09 (br s, 2H, N–CH), 3.73 (br s, 4H, H_{α} -THF), 6.44 (t, ${}^{3}J_{HH} = 7.6$ Hz, 2H), 6.70 (d, ${}^{3}J_{HH} = 8.1$ Hz, 2H), 6.79 (d, ${}^{3}J_{HH} = 7.8$ Hz, 2H), 6.96 (t, ${}^{3}J_{\rm HH} = 7.7$ Hz, 2H). { ${}^{1}H$ } ${}^{13}C$ NMR (75 MHz, CD₂Cl₂): δ 24.8 (CH₂), 25.9 (CH₂), 26.3 (CH₂), 36.3 (CH₂), 55.9 (N-CH), 69.9 (THF), 110.7 (CH), 111.1 (CH), 116.2 (CH), 125.8 (CH), 144.1 (Cipso), 145.6 (Cipso). IR (cm-1): 1842 (br s, Al-). Anal. Calcd for C₂₈H₃₉AlN₂O₂: C, 72.70; H, 8.50. Found: C, 72.93; H, 8.77.

 $n^2 - N$. $N-\{(C_5H_9)N-o-C_6H_4\}_2O\}Al(H)(\mu-OCH_2Ph)Li(THF)_2$ (4a). The mono-alkoxide species 4a was synthesized using an identical procedure to that for 5a (vide infra) but using one equivalent of benzaldehvde. Compound 5a was isolated as a colorless solid after recrystallization of the crude product at -35 °C from a 1/5 THF/pentane solvent mixture (352 mg, 47%) yield). ¹H NMR (300 MHz, CD₂Cl₂): δ 1.41–.55 (m, 4H, C₅H₉), 1.61–1.82 (m, 20H, C_5H_9 and H_β -THF), 3.50 (m, 8H, H_α -THF), 3.91 (m, 2H, N–CH), 4.65 (s, 2H, PhCH₂), 6.37 (t, ${}^{3}J_{HH} = 7.5$ Hz, 2H), 6.81 (d, ${}^{3}J_{HH} = 8.1$ Hz, 2H), 7.01–7.09 (m, 4H), 7.27–7.35 (m, 5H). { 1 H} 13 C NMR (75 MHz, CD₂Cl₂): δ 24.4 (CH₂), 25.6 (CH₂), 31.8 (CH₂), 60.0 (N-CH), 65.9 (PhCH₂), 68.5 (THF), 113.9 (CH), 116.7 (CH), 117.5 (CH), 125.1 (CH), 126.3 (CH), 126.9 (CH), 128.4 (CH), 144.4 (Cipso), 147.52 (Cipso), 148.1 (Cipso). IR (cm⁻¹): 1805 (br s, Al–H). Anal. Calcd for $C_{37}H_{50}AlLiN_2O_4$: C, 71.79; H, 8.12. Found: C, 72.21; H, 7.98.

η²-*N*, *N*-{(CyN-*o*-C₆H₄)₂O}Al(H)(*μ*-OCH₂Ph)Li(THF)₂ (4b). The mono-alkoxide species 4b was synthesized using an identical procedure to that for 5b (*vide infra*) but using one equivalent of benzaldehyde. Compound 5b was isolated as a colorless solid after recrystallization of the crude product at -35 °C from a 1/5 THF/pentane solvent mixture (274 mg, 45% yield). ¹H NMR (300 MHz, CD₂Cl₂): δ 1.10–1.33 (m, 8H, Cy), 1.66–1.73 (m, 8H, H_β-THF), 1.71–1.82 (m, 8H, Cy), 1.95–2.09 (m, 4H, Cy), 3.06 (m, 2H, N–CH), 3.49 (m, 8H, H_α-THF), 4.70 (s, 2H, PhCH₂), 6.38 (t, ³*J*_{HH} = 7.5 Hz, 2H), 6.91–7.06 (m, 6H), 7.14–7.34 (m, 5H). {¹H}¹³C NMR (75 MHz, CD₂Cl₂): δ 25.2 (CH₂), 26.3 (CH₂), 27.2 (CH₂), 33.7 (CH₂), 34.3 (CH₂), 58.7 (N–CH), 64.2 (PhCH₂), 67.9 (THF), 111.5 (CH), 113.3 (CH), 119.0 (CH), 125.1. (CH), 125.8 (CH), 126.8 (CH), 127.0 (CH), 145.1 (C_{ipso}), 147.4 (C_{ipso}), 148.8 (C_{ipso}).

IR (cm⁻¹): 1811 (br s, Al–H). Anal. Calcd for $C_{39}H_{54}AlLiN_2O_4$: C, 72.20; H, 8.39. Found: C, 72.56; H, 8.17.

 η^2 -N, N-{((C₅H₉)N-o-C₆H₄)₂O}Al(μ -OCH₂Ph)₂Li(THF)₂ (5a). In a glovebox, two equivalents of benzaldehvde (245 uL, 2.42 mmol) were added via a syringe to a precooled (-35 °C) THF solution (10 mL) of the Al hydrido species 2a. The initial colorless solution turned immediately vellow upon addition of PhCHO; it was then allowed to warm to room temperature and stirred overnight at this temperature. The resulting yellow solution was then evaporated to dryness to afford a yellow residue as the crude product, which was recrystallized at -35 °C from a 1/5 THF/pentane solvent mixture to afford compound 5a as a pale yellow powder in pure form (400.0 mg, 50% yield). ¹H NMR (300 MHz, CD₂Cl₂): δ 1.49–1.53 (m, 4H, C₅H₉), 1.68–1.88 (m, 20H, C_5H_9 and H_8 -THF), 3.50 (m, 8H, H_{α} -THF), 3.87 (m, 2H, N–CH), 4.76 (s, 4H, PhCH₂), 6.47 (t, ${}^{3}J_{HH} = 7.5$ Hz, 2H), 6.88 (d,, ${}^{3}J_{HH} = 8.1$ Hz, 2H), 6.97–7.03 (m, 4H), 7.20–7.30 (m, 10H). {¹H}¹³C NMR (75 MHz, CD₂Cl₂): δ 24.5 (CH₂), 25.3 (THF), 31.0 (CH₂), 59.7 (N-CH), 65.4 (PhCH₂), 67.9 (THF), 112.9 (CH), 116.4 (CH), 118.0 (CH), 124.9 (CH), 126.2 (CH), 126.7 (CH), 127.9 (CH), 144.9 (Cinso), 147.5 (Cinso), 147.8 (Cinso). Anal. Calcd for C44H56AlLiN2O5: C, 72.71; H, 7.77. Found: C, 73.05; H, 7.92.

 η^2 -N,N-{(CyN-o-C₆H₄)₂O}Al(μ -OCH₂Ph)₂Li(THF)₂ (5b). The dialkoxide Al complex 4b was synthesized following an identical procedure to that used for 5a and was isolated as an analytically pale yellow powder from a 1/5 THF/pentane solvent mixture cooled at -35 °C (630 mg, 42% yield). ¹H NMR (300 MHz, CD₂Cl₂): δ 1.08–1.29 (m, 8H, Cy), 1.55–1.62 (m, 8H, H₈-THF), 1.71–1.78 (m, 8H, Cy), 1.91–2.04 (m, 4H, Cy), 3.09 (m, 2H, N-CH), 3.25 (m, 8H, H_a-THF), 4.83 (s, 4H, PhCH₂), 6.44 (t, ${}^{3}J_{HH} = 7.5$ Hz, 2H), 6.87–6.96 (m, 6H), 7.17–7.28 (m, 10H). ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): δ 25.0 (CH₂), 25.3 (CH₂), 25.9 (CH₂), 33.3 (CH₂), 58.8 (N-CH), 65.4 (PhCH₂), 67.9 (THF), 112.9 (CH), 115.6 (CH), 118.4 (CH), 124.2 (CH), 126.3 (CH), 126.8 (CH), 126.0 (CH), 144.9 (C_{ipso}), 146.9 (C_{ipso}), 148.5 (C_{ipso}). Anal. Calcd for C₄₆H₆₀AlLiN₂O₅: C, 73.19; H, 8.01. Found: C, 73.56; H, 8.21.

 $\{(CyN-o-C_6H_4)_2O\}Al(OCH_2Ph)(THF)$ (6b). NMR-scale reaction. In a J-Young NMR tube, the Al hydrido complex 3b (30.0 mg, 0.053 mmol) was charged and dissolved in CD₂Cl₂ (0.75 mL) and one equivalent of benzaldehyde (5.4 µL, 0.053 mmol) was immediately added via a microsyringe to the latter solution. The NMR tube was tightly capped, vigorously shaken and a ¹H NMR spectrum was immediately recorded showing the quantitative formation of the Al alkoxide 6b. Preparative scale. In a glove box, one equivalent of benzaldehyde (35.7 µL, 0.352 mmol) was added via a microsyringe to a precooled CH₂Cl₂ solution (-35 °C, 10 mL) of complex 3b (200 mg, 0.352 mmol). The resulting mixture was left under stirring at room temperature overnight and subsequently evaporated to dryness to afford a colorless solid as the crude product. Recrystallization of the latter residue in Et₂O stored at -35 °C afforded pure **6b** as a colorless powder (112 mg, 56% yield). ¹H NMR (300 MHz, CD₂Cl₂): δ 1.16–1.34 (m, 4H, Cy), 1.64–1.89 (m, 20H, Cy and H_B-THF), 2.99 (br m, 2H, N–CH), 3.41 (m, 4H, H_α-THF), 4.52 (s, 2H, PhCH₂), 6.45 (t, ${}^{3}J_{HH} = 7.6$ Hz, 2H), 6.76 (d, ${}^{3}J_{HH} = 7.6$ Hz, 2H), 6.92 (d, ${}^{3}J_{HH} = 7.6$ Hz, 2H), 6.93–7.03 (m, 4H), 7.12–7.28 (m, 3H). {¹H}¹³C NMR (75 MHz, CD₂Cl₂): δ 24.8 (CH₂), 25.9 (CH₂), 26.3 (CH₂), 33.4 (CH₂), 34.6 (CH₂), 58.7 (N–CH), 63.9 (PhCH₂), 67.9 (THF), 113.1 (CH), 114.5 (CH), 118.7 (CH), 125.5 (CH), 126.0 (CH), 126.5 (CH), 127.7 (CH), 143.8 (C_{1pso}), 146.4 (C_{1pso}), 147.9 (C_{1pso}). Anal. Calcd for C₃₃H₄₅AlN₂O₃: C, 73.92; H, 7.98. Found: C, 73.65; H, 8.11.

Typical procedure for lactide polymerisation by 5a-b. In a glovebox, the desired Al alkoxide ROP initiator (0.012 mmol) was charged in a vial equipped with a TeflonTM-tight screw-cap and a CH₂Cl₂ solution (1.8 mL) of rac-lactide (230 equiv., 400.0 mg) was added via a syringe all at once. The resulting colorless solution was vigorously stirred at room temperature for the appropriate time, during which several aliquots were taken and analyzed by ¹H NMR spectroscopy to monitor the conversion. When the appropriate conversion was reached, the vial was removed from the glovebox and the reaction mixture was quenched with MeOH along with a few drops of acetic acid provoking the precipitation of PLA. The resulting polymer was washed several times with MeOH, dried in vacuo until constant weight and subsequently analyzed by ¹H NMR, SEC and, in some cases, by MALDI-TOF spectrometry. In the case of the ROP of (S)-lactide by the Al complexes 5a-b, the isolated PLA was also analyzed by ¹³C NMR spectroscopy which confirmed it to be (S)-PLA, thus showing that no epimerization takes place during the ROP process.

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