Dimeric Aluminum Chloride Complexes of *N*-Alkoxyalkyl-*β*-ketoimines: Activation with Propylene Oxide To Form Efficient Lactide Polymerization Catalysts

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Received December 17, 2003

The ter- and tetradentate *N*-alkoxyalkyl-*β*-ketoimines $CH_3C(O)CH_2C(NCH_2CHROH)CH_3$ {**L**$_{1-3}$} react with diethylaluminum chloride to afford the dimeric chloride bridged complexes [{**L**$_{1-3}$}AlCl]$_2$ (**1a**−**c**), which are activated by addition of propylene oxide or cyclohexene oxide to afford efficient initiators for the ring-opening polymerization of (D,L)-lactide. The active species is believed to be a chloroalkoxide formed by nucleophilic ring opening of a coordinated PO by migration of the chloride coordinated to the adjacent aluminum center. The resulting polymers have a high molecular weight, close to that calculated for the monomer:initiator ratio of 100, and a narrow molecular weight distribution. While the corresponding aluminum methyl dimer [{**L**$_1$}AlMe]$_2$ (**2a**), formed by reaction of **L**$_1$ (R = H) with $AlMe_3$, is a poor inititaor for the polymeriation of (D,L)-lactide, addition of 2-chloroethanol affords a catalyst with an activity comparable to that of **1a**/PO. The molecular weight and molecular weight distribution of the resulting polylactide is similar to that obtained with **1a**/PO and consistent with formation of a similar chloroalkoxide initiator.

Introduction

Neutral and cationic Lewis acid complexes of aluminum are rapidly evolving as versatile promoters for the polymerization of ethylene,[1] alkene oxides,[2] (D,L)-lactide,[3] and cyclic lactones.[4] In the case of ethylene polymerization, the catalysts of choice appear to be three- and four-coordinate aluminum alkyl cations, stabilized by bulky bi- and terdentate ligands such as *N*,*N*-amidinates,[1a] *N*,*N*,*N*-pyridyliminoamides,[1b] and pendent arm Schiff bases;[1c] in some instances polymerization occurred under extremely mild conditions. While aluminum procatalysts of the type [{**L**}$AlMe_2$] are generally synthesized by elimination of methane during the reaction between an appropriate monoprotic ligand and $AlMe_3$, those based on *N*,*N*,*N*-pyridyliminoamides rely on migration of a methyl group to one of the imine carbon atoms of a coordinated 2,6-bis(imino)pyridine. Similar transformations have also since been identified in the reaction of Schiff base ligands with $AlMe_3$.[5] In contrast, recent advances in the aluminum-catalyzed ring-opening polymerization of lactide have established that neutral five-coordinate complexes of N_2O_2-donor Schiff bases are highly efficient initiators for chain-end controlled and enantiomorphic site-controlled stereoselective ring-opening polymerization of *meso*- and *rac*-lactide.[6] In a recent study, Gibson and co-workers reasoned that the polymerization activity of aluminum-based initiators could be increased by enhancing the electrophilicity of the aluminum center and showed that introduction of electron-withdrawing substituents onto the Schiff base ligand backbone generates initiators that polymerize (D,L)- and (L)-lactide at ambient temperature.[7]

We have recently begun to explore an alternative strategy to enhance the activity of aluminum-based

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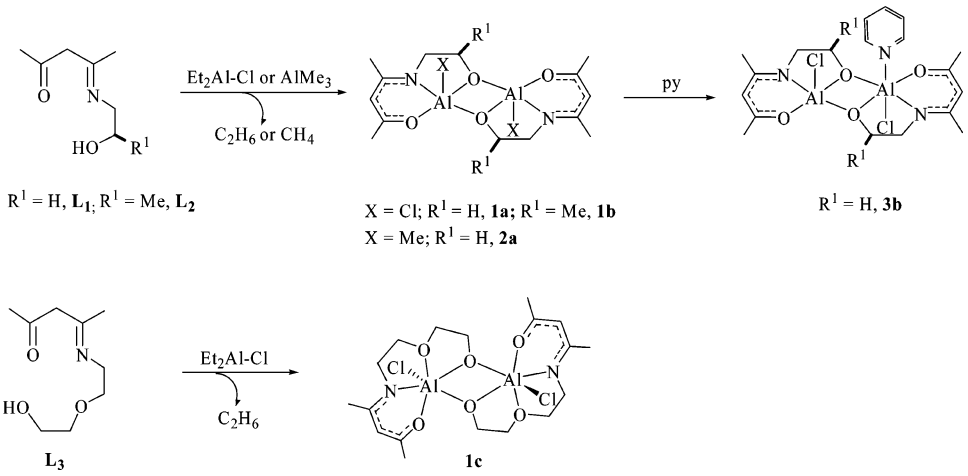
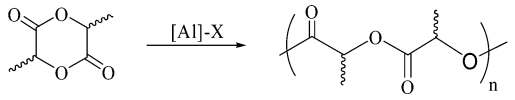
10.1021/om0343770 CCC: $27.50
Publication on Web 03/23/2004

Scheme 1



initiators that involves the use of diprotic *N*-alkoxyalkyl-*β*-ketoimines $\mathbf{L_{1-3}}$[8] to stabilize well-defined neutral four-coordinate complexes of the type [{$\mathbf{L_{1-3}}$}AlX] (X = halide, OR, Me), reasoning that these four-coordinate complexes would be substantially more electrophilic than their five-coordinate counterparts. Herein we report that these *N*-alkoxyalkyl-*β*-ketoimines react with diethylaluminum chloride to form 5-coordinate dimeric chloride complexes that are inactive as initiators for alkene oxide and lactide polymerization but form efficient initiators for the ring-opening polymerization of D,L-lactide upon addition of propylene oxide (PO) or cyclohexene oxide (CHO) (eq 1).



eq 1

Results and Discussion

The Schiff bases $\mathbf{L_{1-2}}$, prepared by condensation of 2,4-pentanedione with the corresponding amine, react with diethylaluminum chloride in THF at low temperature to afford the dimeric aluminum chloride complexes [($\mathbf{L_{1-2}}$)AlCl]$_2$ (**1a**,**b**) via elimination of ethane as shown in Scheme 1. Similarly, addition of $\mathbf{L_1}$ to a tetrahydrofuran solution of trimethylaluminum cooled to −30 °C results in elimination of methane to afford the corresponding aluminum methyl dimer **2a**. In the room temperature ^{1}H NMR spectrum of **1a** the presence of two singlets at δ 1.99 and 2.04 associated with the methyl groups of the ketoiminate fragment and two broad ill-defined signals at δ 4.04 and 3.60 for the methylene protons of the alkoxyethyl group are consistent with a structure of C_s symmetry. However, a variable-temperature ^{1}H NMR study (Figure 1) revealed that the room temperature spectrum of **1a** is simplified by a dynamic process and upon cooling the alkoxyethyl signals broaden further and eventually resolve into four sets of multiplets, which correspond to the diastereotopic methylene protons expected based on the solid-state structure (vide infra). The ^{1}H NMR spectrum of **1b** is considerably more complex but shows similar line-broadening behavior. The dynamic process responsible

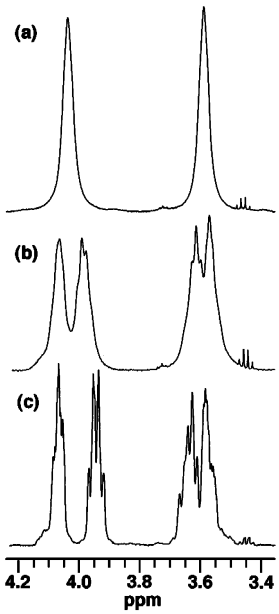
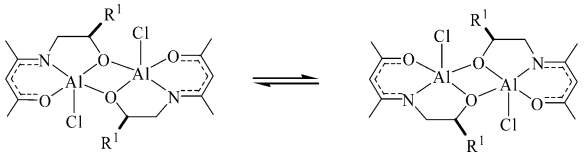


Figure 1. Variable-temperature ^{1}H NMR spectra of [{MeC(O)CHC(NCH$_2$CH$_2$O)CMe}AlCl]$_2$ (**1a**) recorded in $CDCl_3$ at (a) 328, (b) 273, and (c) 218 K.

for the time-averaged C_s symmetry of **1a** most likely involves chloride exchange/migration or a monomer ↔ dimer equilibrium (eq 2). At this stage we favor the



eq 2

former explanation since **1b** reacts with pyridine to give the monoadduct [($\mathbf{L_2}$)$_2$Al$_2$Cl$_2$(py)] (**3b**), with no evidence for cleavage of the alkoxide bridge and formation of the monomeric pyridine adduct [($\mathbf{L_2}$)AlCl(py)], which suggests that the Al_2O_2 ring is strongly bonded and unlikely to undergo the Al−O bond cleavage required for a monomer−dimer equilibrium. In addition, since the reaction between **1a** and pyridine, to give adduct **3a**, does not involve chloride dissociation it is eminently reasonable to assume that if exchange occurs via chloride migration it will do so in an intramolecular manner, most probably via a chloride-bridged interme-

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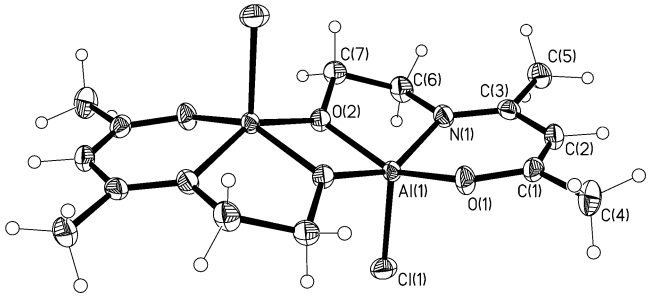

Figure 2. Molecular structure of [{MeC(O)CHC(NCH$_2$-CH$_2$O)Me}AlCl]$_2$ (**1a**). Hydrogen atoms have been omitted for clarity. Ellipsoids are at the 40% probability level. Selected bond lengths (Å) and angles (deg): Al(1)−Cl(1) 2.1728(7); Al(1)−O(1) 1.7943(13); Al(1)−O(2A) 1.8354(12); Al(1)−O(2) 1.8553(12); Al(1)−N(1) 1.9368(15); C(1)−O(1) 1.311(2); C(1)−C(2) 1.365(3); C(2)−C(3) 1.423(3); C(3)−N(1) 1.312(2); Cl(1)−Al(1)−O(2) 105.63(5); O(2)−Al(1)−O(2A) 76.29(6); Cl(1)−Al(1)−N(1) 105.47(5); Cl(1)−Al(1)−O(1) 105.34(5); Cl(1)−Al(1)−O(2) 105.63(5); Cl(1)−Al(1)−O(2A) 103.17(5); Al(1)−O(2)−Al(1A) 103.71(6).

diate. The ^{27}Al NMR chemical shifts of δ 48 and 50 for **1a** and **1b**, respectively, are consistent with five-coordinate solution-state aluminum complexes, which generally appear at 50−100 ppm.[9a]

In contrast to the room temperature ^{1}H NMR spectrum of **1a**, that of **2a** contains four well-separated multiplets which correspond to the diastereotopic methylene protons and there is no sign of line broadening even at elevated temperatures, a clear indication that **2a** does not undergo the same dynamic exchange as **1a**. The ^{1}H NMR spectrum of **2a** also contains a high-field signal at δ −0.53, which is characteristic of an Al-Me group, and the ^{27}Al NMR spectrum contains a broad signal ($\nu_{1/2}$ = 1800 Hz) centered at δ 70 ppm, in the range expected for a five-coordinate aluminum center.[9] The fact that **2a** does not undergo dynamic exchange itself supports the migration mechanism described above since this process would require that the migrating group either bridge two aluminum centers or dissociate, both of which are much less likely to occur for methyl than for chloride. Moreover, if exchange involved a monomer ↔ dimer equilibrium it would still be expected to operate for **2a** since this process only involves Al−O bond cleavage.

The molecular structure of **1a** has been confirmed by single-crystal X-ray crystallography, the result of which is shown in Figure 2, together with a selection of bond lengths and angles. The structure reveals that $\mathbf{L_1}$ acts as a *O,N,O* terdentate ligand, forming six- and five-membered chelate rings and a μ_2-O bridge between the two metal centers. The geometry at aluminum is distorted square pyramidal with the chlorides occupying apical sites in an anti arrangement. The Al(1)−Cl(1) bond length of 2.1728(7) Å is identical to that of 2.176(9) Å in [{Salpen(^{t}Bu)}AlCl][9a] and longer than that of 2.081(1) Å in a tetrahedral bis(phenoxide) aluminum chloride dimer reported by Chisholm.[10] The two aluminum atoms are asymmetrically bridged by the μ-OR group [Al(1)−O(2) = 1.8553(12) Å; Al(1)−O(2A) = 1.8354(12) Å], which is a feature characteristic of many oxygen-bridged aluminum compounds including [Al$_3$(μ_3-O)(μ-OEt)$_2$(py)$_4$Cl$_5$],[11] [AlMe$_2$(μ-OCH(Me)C(O)OEt)$_2$]$_2$, and [AlCl$_2$(μ-OCH$_2$CH$_2$NMe$_2$)]$_2$.[12,13] As expected both Al(1)−O(2) and Al(1)−O(2A) are significantly longer than the terminal Al(1)−O(1) bond of length 1.7943(13) Å, and such differences are common place.[14] The bond length pattern in the six-membered aluminum−ketoiminate ring suggests significant localization of bonding electron density, consistent with $\mathbf{L_1}$ coordinating as an enolate, with N(1) bonded through the sp^2 lone pair of the imine and O(2) as a conventional alkoxide. The difference of 0.058 Å in the C(1)−C(2) and C(2)−C(3) bond lengths is substantially larger than the corresponding difference of 0.005 Å in the bis(iminate) complex [Zr{CH$_3$C(NPh)CH(O)CH$_3$}$_2$Cl$_2$][15] and is clear evidence of the localized bonding.

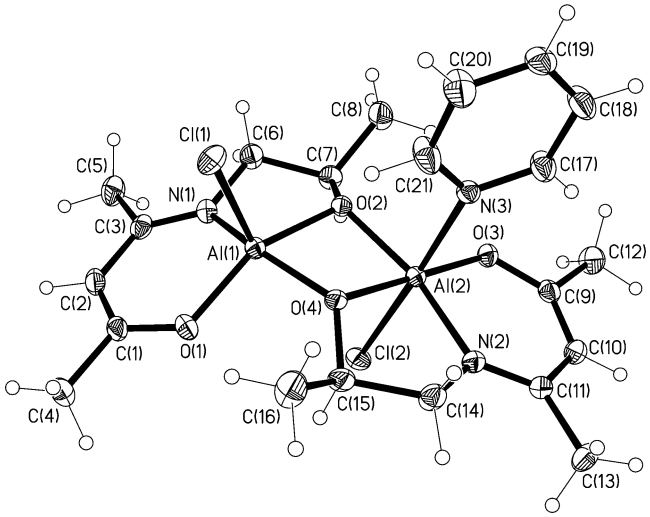

Figure 3. Molecular structure of [{MeC(O)CHC{NCH$_2$-CH(Me)O}Me}$_2$Al$_2$Cl$_2$(py)] (**3b**). Hydrogen atoms have been omitted for clarity. Ellipsoids are at the 40% probability level. Selected bond lengths (Å) and angles (deg): Al(1)−Cl(1) 2.1988(5); Al(1)−O(1) 1.8058(11); Al(1)−O(2) 1.8751(10); Al(1)−N(1) 1.9448(13); Al(1)−O(4) 1.8470(10); Al(2)−Cl(2) 2.3936(5); Al(2)−O(2) 1.8613(10); Al(2)−O(3) 1.8132(10); Al(2)−O(4) 1.8823(10); Al(2)−N(2) 1.9459(12); Al(2)−N(3) 2.1373(12); C(1)−C(2) 1.360(2); C(2)−C(3) 1.434(2); C(9)−C(10) 1.368(2); C(10)−C(11) 1.432(2); O(4)−Al(1)−N(1) 153.59(5); O(1)−Al(1)−O(2) 149.99(5); Cl(2)−Al(2)−N(3) 177.51(4); O(2)−Al(2)−N(2) 162.39(5); O(4)−Al(2)−O(3) 179.35(5).

The molecular structure of **3b** has also been determined to examine the influence of the pyridine on the coordination geometry and metal−ligand bonding. A perspective view of the molecular structure of **3b** is shown in Figure 3, together with a selection of relevant bond lengths and angles. The structure confirms that a single molecule of pyridine coordinates to Al(2), which adopts a distorted octahedral geometry, while Al(1) is

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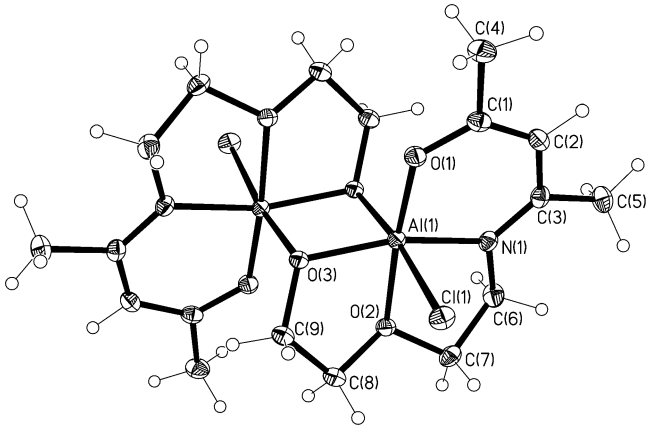

Figure 4. Molecular structure of $[\{CH_3COCHC(CH_3)NCH_2CH_2OCH_2CH_2O\}AlCl]_2$ (**1c**). Hydrogen atoms have been omitted for clarity. Ellipsoids are at the 40% probability level. Selected bond lengths (Å) and angles (deg): Al(1)−Cl(1) 2.3652(6); Al(1)−O(1) 1.8210(12); Al(1)−O(2) 1.9823(12); Al(1)−O(3) 1.8655(12); Al(1)−O(3A) 1.9466(12); Al(1)−N(1) 1.9508(14); C(1)−O(1) 1.303(2); C(1)−C(2) 1.370(2); C(2)−C(3) 1.432(2); C(3)−N(1) 1.303(2); Cl(1)−Al(1)−O(3A) 173.37(4); O(1)−Al(1)−O(2) 175.28(5); O(3)−Al(1)−N(1) 158.81(6).

best described as a square-based pyramid with the chloride occupying the apical site. The ^{27}Al NMR spectrum of **3b** contains two broad overlapping resonances, one at δ 56 associated with the five-coordinate aluminum and the other at a much lower frequency, δ 16, in the region expected for a six-coordinate aluminum center.[9] Coordination of pyridine results in a significant folding of the dimer about the two bridging oxygen atoms, with a hinge angle of 159.1°, presumably to reduce contacts between Cl(1) and the pyridine ligand. The Al(2)−N(3) bond length of 2.1373(12) Å is markedly shorter than that of 2.254(2) Å in $[AlMe_2\{3,5\text{-}Bu^t_2\text{-}2\text{-}(O)C_6H_2CH{=}N\text{-}2\text{-}CH_2C_5H_4N\}]$[5] and much closer to that of 2.096(1) Å for pyridine trans to chloride in $[AlCl_3(py)_3]$[16] and 2.132(4) Å in $[Al_3(\mu_3\text{-}O)(\mu\text{-}OEt)_2(py)_4Cl_5]$.[11] The Al(1)−Cl(1) bond length of 2.1988(5) Å is 0.2 Å shorter than that of 2.3936(5) Å for Al(2)−Cl(2) trans to pyridine, which is not surprising given the trans influence of pyridine and the difference in Lewis acidity and coordination numbers of the two aluminum centers. The six-membered chelate rings are close to planar with Al(1) and Al(2) lying 0.395 and 0.759 Å, respectively, out of the plane defined by the remaining five atoms.

Since *N*-alkoxyalkyl-*β*-ketoimines $\mathbf{L_{1-2}}$ readily form dimeric aluminum complexes we reasoned that the potentially tetradentate ketomine $\mathbf{L_3}$ would stabilize a five-coordinate monomeric initiator of the type [{$\mathbf{L_3}$}-Al-Cl]. However, treatment of $\mathbf{L_3}$ with diethylaluminum chloride in THF at low temperature affords the dimeric complex **1c**, the structure of which has been confirmed by a single-crystal X-ray analysis (Figure 4). The geometry at aluminum is distorted octahedral with the oxygen atom of the bridging alkoxyalkyl group trans to chloride on one aluminum and the nitrogen atom of the ketoiminate fragment on the other aluminum. The ^{27}Al NMR chemical shift of δ 11 is within the range commonly encountered for six-coordinate aluminum complexes. The Al(1)−Cl(1) bond length of 2.3652(6) Å is significantly longer than the corresponding distance of 2.1728(7) Å in **1a**, consistent with the trans influence of alkoxide and the higher coordination number of aluminum. The Al(1)−O(1) and Al(1)−O(2) bond lengths of 1.8210(12) and 1.9823(12) Å are markedly different [Δ(Al−O) = 0.1613 Å], but within the range of 1.837(8) to 1.982(9) Å found by Healy and Barron for six-coordinate aluminum.[17]

Table 1. Results of (D,L)-Lactide Polymerization in Toluene at 70 °C with 1a−c and 2a

initiator (2 mol %)	time (h)	convn (%)[a]	M_n[b]	PDI[b]
1a	168	5		
1b	168	2		
1c	168	11		
1a/PO	18	6	11 259	1.27
1b/PO	18	97	12 533	1.19
1c/PO	18	97	14 450	1.17
1a/CHO	18	97	15 869	1.15
1b/CHO	18	98	12 588	1.13
1c/CHO	18	94	11 669	1.19
2a	168	58	9 081	1.18
2a/2-chloroethanol	18	97	13 937	1.18

[a] Obtained by integration of the monomer vs polymer resonances in the ^{1}H NMR spectra. [b] Obtained by gel permeation chromatography analysis (2 PLgel 5 μm Mixed-C column, flow rate 1.00 mL min^{-1}) versus polystyrene standard.

The Lewis acid complexes **1a−c** are poor initiators for the polymerization of (D,L)-lactide in toluene at 70 °C and give low conversions even after 7 days (Table 1). The low activity of these compounds is not surprising and is most likely due to a combination of the poor donor property of lactide and an unfavorable initiation step that must involve transformation of Al-Cl to AlOCH(Me)C(O)OCHMeC(O)Cl. As [Al]-Cl species that are poor lactide polymerization initiators have been shown to be active for the polymerization of epoxides,[21] we investigated the reaction of propylene oxide (PO) with **1a−c** and discovered that addition of 1 equiv of PO activates these complexes for the ring-opening polymerization of (D,L)-lactide. Thus, a toluene solution of **1a−c,** activated by addition of a stoichiometric quantity of PO, catalyzes the ring-opening polymerization of (D,L)-lactide at 70 °C and under these conditions a 1 mol % solution of **1a−c** requires 18 h to reach completion. The resultant polymer has a molecular weight close to that calculated from the monomer:initiator ratio, assuming each dimer generates a single active species ([**1a−c**]/lactide = 100, calculated M_n = 14 400) and exhibits a narrow molecular weight distribution. This narrow molecular weight distribution and the near-linear correlation between M_n and percent conversion is indicative of a living polymerization as well as a single type of active site. The ^{1}H and ^{13}C NMR spectra of polymer derived from **1a−c** show an atactic polymer with stereosequences associated with the eight possible tetrads of polylactide.[18] Similarly, cyclohexene oxide (CHO) also activates **1a−c** for the ring-opening polymerization of (D,L)-lactide, which suggests a common mechanism of activation. In this regard, Bertrand has noted that neutral and cationic aluminum chloride complexes of terdentate nitrogen donors are inert toward (D,L)-lactide but can

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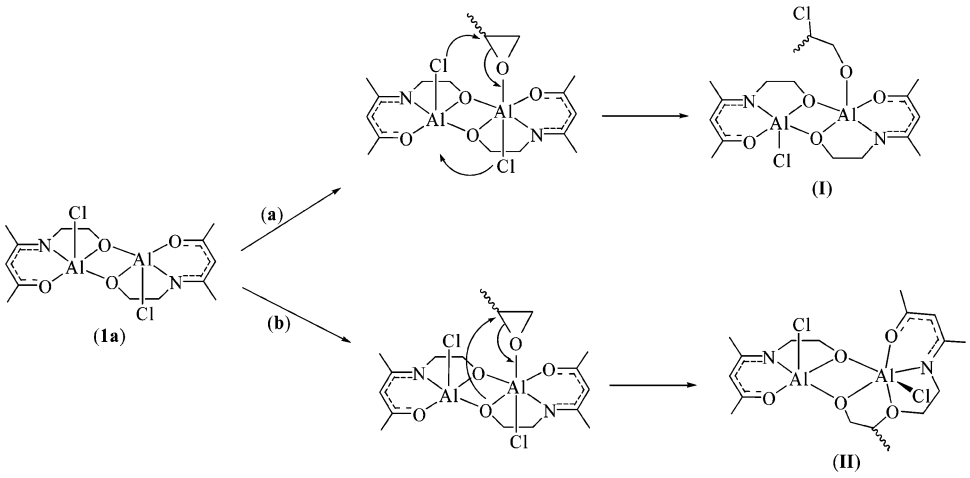
Scheme 2



be activated for ring-opening polymerization by addition of PO.[19] Earlier, Shen reported the use of PO to activate rare earth chlorides for the random copolymerization of ϵ-caprolactone with D,L-lactide and demonstrated that the initiator is most likely a rare earth alkoxide formed by ring-opening insertion of PO into the M−Cl bond and that propagation proceeds via a coordination−insertion mechanism with acyl-oxygen bond cleavage of caprolactone and lactide.[20]

Examination of the ^{1}H NMR spectra of these polymers reveals that after initiation with PO there is no further incorporation of PO into the polymer, which is perhaps not surprising since **1a**−**c** do not catalyze the polymerization of PO. Moreover, polymerizations performed in the presence of an excess of PO gave polylactide with a similar molecular weight and polydispersity to that formed by activation of **1a**−**c** with 1 equiv of PO. In contrast, Chisholm has recently demonstrated that while dimeric aluminum chloride complexes of the type $[(O{-}O)AlCl]_2$ (where O−O is a bulky biphenoxide or bisphenoxide) are inactive for the ROP of lactides (L or *rac*), addition of PO results in the formation of block oligomers/polymers of the form $(PPO)_n(PLA)_m$.[21]

To investigate the role of the PO as an activator a ^{1}H NMR study was carried out in which 1 equiv of propylene oxide was added to a toluene solution of **1a** at room temperature. After 0.5 h the resulting spectrum showed no sign of **1a** and contained a new set of resonances consistent with addition of PO to **1a** to form the propagating species. At this stage we tentatively suggest that PO reacts with **1a**−**c** via ring-opening insertion into the [Al]−Cl bond to give the corresponding chloroalkoxide species **I** (Scheme 2 pathway a) rather than insertion into the bridging alkoxide to form **II** (Scheme 2 pathway b), which would contain a tetradentate *O*,*N*,*O*,*O* ligand analogous to that of $\mathbf{L_3}$ in **1c** (Scheme 1). Such a process most likely occurs via coordination of PO followed by a concerted intramolecular nucleophilic ring-opening migration by the chloride on the adjacent five-coordinate aluminum with concomitant migration of the chloride trans to the newly formed chloroalkoxide onto the resulting four-coordinate aluminum, as shown for a single molecule of PO in Scheme 2. Although an alternative pathway involving intermolecular nucleophilic addition of chloride to a coordinated PO of a cationic intermediate cannot be excluded,[3c] we favor the former pathway since **1b** reacts with pyridine to form the 1:1 complex **3b**, which can be considered as a model for the proposed PO adduct in Scheme 2. Moreover, if we assume that activation of **1a**,**b** with PO involved insertion into the μ-OR bridge to give **II**, one might expect its analogue **1c** to be highly active for the ROP of D,L-lactide. However, only very poor conversions were obtained with **1c** in the absence of PO, which lends further support to formation of a chloroalkoxide initiator. Interestingly, even though **1c** is a poor initiator, it too is activated by addition of PO/CHO to form a highly efficient initiator for the ROP of (D,L)-lactide, generating a polymer with similar molecular weight and polydispersity to that obtained with **1a**,**b** (Table 1).

In a comparative study we found that the corresponding [Al]-Me precursor **2a** is a poor initiator for the polymerization of (D,L)-lactide and requires 168 h to reach 58% conversion (Table 1) whereas catalysts generated by alcoholysis of **2a** with chloroethanol are considerably more active and reach levels of conversion comparable to those obtained with **1a**−**c**/PO after only 18 h. The molecular weight and molecular weight distribution of the resulting polymer is similar to that obtained with catalysts formed by activation of **1a**−**c** with PO, consistent with formation of the proposed chloroalkoxide initiator **I**.

In summary, *N*-alkoxyalkyl-β-ketomines react with diethylaluminum chloride to form dimeric aluminum chloride complexes which are activated by addition of PO and CHO to generate highly active initiators for the ring-opening polymerization of (D,L)-lactide. Further studies are underway to isolate and characterize the initiator species and to synthesize enantiopure aluminum complexes of *N*-alkoxyalkyl-β-ketomines for the stereoselective ring-opening polymerization of *meso*- and *rac*-lactide.

Experimental Section

General Procedures. All manipulations involving air-sensitive materials were carried out in an inert-atmosphere glovebox or with standard Schlenk line techniques under an

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atmosphere of nitrogen or argon in oven-dried glassware. Diethyl ether and hexane were distilled from sodium, tetrahydrofuran from potassium, dichloromethane from calcium hydride, and methanol from magnesium. Unless otherwise stated, commercially purchased materials were used without further purification. Diethylaluminum chloride was purchased from Aldrich and used as received. Deuteriochloroform was predried with calcium hydride and vacuum transferred and stored over 4 Å molecular sieves. ^{1}H, ^{13}C{^{1}H}, and ^{27}Al NMR spectra were recorded on a JEOL LAMBDA 500 and on Bruker AC 200 and AMX 300 spectrometers. ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to Me_4Si as an external standard and those of ^{27}Al are relative to external $Al(NO_3)_3$. Mass spectra were measured on a VG Autospec or a VG Platfrom II spectrometer. GPC analyses versus polystyrene standards were carried out with a 2 PLgel 5 mm Mixed-C column (300 × 7.5 mm^2 dimension) with a flow rate of 1.0 mL min^{-1}.

Synthesis of 4-(2-Hydroxyethylimino)pentane-2-one (L_1). A methanol solution of 2-aminoethanol (6.1 g 0.1 mol) was added dropwise to a stirred solution of pentane-2,4-dione (10.0 g, 0.1 mol) in methanol (100 mL). Sodium sulfate was added to remove the water generated during the condensation reaction and the mixture was stirred for 12 h. The resulting yellow solution was diluted by addition of dichloromethane (50 mL) and filtered, and the solvent was removed under reduce pressure. The residue was crystallized by cooling a saturated ethanol solution at −30 °C to give analytically pure $\mathbf{L_1}$ in 74% yield (10.6 g). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 10.8 (br, 1H, NH), 4.90 (s, 1H, CH), 3.69 (t, J = 6 Hz, 2H, OCH_2), 3.34 (dd, J = 7.5, 6.0 Hz, 2H, NCH_2), 1.91 (s, 3H, CH_3), 1.90 (s, 3H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 125,65 MHz, δ): 194.8 (s, CO), 164.1 (CN), 95.6 (CH), 61.4 (OCH_2), 45.5 (*NCH*$_2$), 28.6 (*C*H$_3$), 19.2 (*CH*$_3$). MS (EI): m/z 143 [M]$^+$. Anal. Calcd for $C_7H_{13}NO_2$: C, 58.70; H, 9.16; N, 9.79. Found: C, 58.83; H, 9.46; N, 9.88.

Synthesis of 4-(2-hydroxy-1-methyl-ethylimino)-pentane-2-one (L_2). *N*-Alkoxyalkyl-β-ketoimine $\mathbf{L_2}$ was prepared from *rac*-1-amino-propan-2-ol and pentane-2,4-dione according to the procedure described above for $\mathbf{L_1}$ and isolated as X-ray quality crystals in 68% yield by slow diffision of hexane into a dichloromethane solution at room temperature. ^{1}H NMR (500.1 MHz, $CDCl_3$, 200 MHz): δ 10.9 (br, 1H, N*H*), 4.93 (s, 1H, C*H*), 3.89 (m, 1H, OC*H*Me), 3,18 (m, 2H, NC*H*2), 1.95 (s, 3H, CH_3), 1.88 (s, 3H, CH_3). MS (EI): m/z 157 [M]$^+$. Anal. Calcd for $C_8H_{15}NO_2$: C, 61.12; H, 9.62; N, 9.91. Found: C, 60.93; H, 9.69; N, 10.04.

Synthesis of 4-{2-(2-Hydroxyethoxy)ethylimino}pentane-2-one (L_3). *N*-Alkoxyalkyl-β-ketoimine $\mathbf{L_3}$ was prepared from 2-(2-aminoethoxy)ethanol and pentane-2,4-dione according to the procedure described above for $\mathbf{L_1}$ and isolated as an analytically pure yellow oil in 95% yield. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 10.91 (br, 1H, N*H*), 4.89 (s, 1H, C*H*), 3.66 (m, 2H, CH_2OH), 3.50 (m, 4H, CH_2OCH_2), 3.32 (m, 2H, NCH_2), 1.88 (s, 3H, CH_3), 1.85 (s, 3H, CH_3). MS (EI): m/z 187 [M]$^+$. Anal. Calcd for $C_9H_{17}NO_3$: C, 57.73; H, 9.15; N, 7.48. Found: C, 57.76; H, 9.21; N, 7.42.

Synthesis of [{MeC(O)CHC(NCH$_2$CH$_2$O)Me}AlCl]$_2$ (1a). A 1.0 M solution of diethylaluminum chloride in hexane (4.0 mL, 4.0 mmol) was added dropwise to a cooled THF (50 mL) solution of **1a** (0.57 g, 4.0 mmol) at −78 °C. The reaction mixture was allowed to warm to room temperature, during which time the solution became turbid and evolution of ethane was observed. The resulting solution was stirred for 4 h, concentrated, and filtered to give an off-white solid that was crystallized by slow diffusion of hexane into a dichloromethane solution at room temperature, to afford **1a** as colorless crystals in 74% yield (0.6 g). Mp 190 °C dec. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ δ 5.23 (s, 1H, C*H*), 4.04 (br, 2H, OCH_2), 3.60 (br, 2H, NCH_2), 2.04 (s, 3H, CH_3), 1.99 (s, 3H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 125.65 MHz): δ 179.70 (*C*O), 174.62 (*C*N), 101.61 (*C*H), 59.33 (OCH_2), 47.46 (NCH_2), 26.21 (*C*H$_3$), 22.95 (*C*H$_3$). ^{27}Al NMR ($CDCl_3$, 130.336 MHz): δ 48 ($\nu_{1/2}$ = 3000 Hz). MS (EI): m/z 406 [M]$^+$, 371 [M − Cl]$^+$. Anal. Calcd for $C_{14}H_{22}Al_2Cl_2N_2O_4$: C, 41.32; H, 5.45; N, 6.89. Found: C, 40.96; H, 5.42; N, 6.70.

Synthesis of [{MeC(O)CHC(NCH$_2$CHMeO)Me}AlCl]$_2$ (1b). Compound **1b** was prepared according to the procedure described above for **1a** and isolated as a colorless solid in 54% yield by slow diffusion of hexane into a dichloromethane solution at room temperature. Mp 235 °C dec. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 5.22 (s, 1H, C*H*), 5.20 (s, 1H, C*H*), 4.24 (br, 1H, OC*H*Me), 4.17 (m, ^3J = 10.5 Hz, ^3J = 5.2 Hz, 1H, OC*H*Me), 3.61 (br, 1H, NCH_aH$_b$), 3.57 (dd, ^2J = 13.2 Hz, ^3J = 5.2 Hz, 1H, NCH_aH$_b$), 3.22 (br, 1H, NCH$_a$$H_b$), 3.31 (dd, ^3J = 13.2 Hz, ^3J = 10.5 Hz, 1H, NCH$_a$$H_b$), 2.02 (s, 3H, C$H_3$), 2.01 (s, 3H, C$H_3$), 1.99 (s, 3H, C$H_3$), 1.98 (s, 3H, C$H_3$), 1.45 (d, ^3J = 6.4 Hz, 3H, OCH(CH_3)), 1.41 (d, ^3J = 6.1 Hz, 3H, OCH(CH_3)). ^{13}C{^{1}H} NMR (125.65 MHz, $CDCl_3$): δ 179.4 (*C*O), 178.3 (*C*O), 173.9 (*C*N), 172.7 (*C*N), 101.6 (*C*H), 101.3 (*C*H), 68.5 (OCHMe), 67.9 (OCHMe), 54.5 (NCH_2), 54.1 (NCH_2), 26.1 (*C*H$_3$), 22.9 (*C*H$_3$), 21.9 (*C*H$_3$), 21.8 (*C*H$_3$). ^{27}Al NMR ($CDCl_3$, 130.336 MHz): δ 40 ($\nu_{1/2}$ = 3000 Hz). MS (EI): m/z 434 [M]$^+$, 399 [M − Cl]$^+$. Anal. Calcd for $C_{16}H_{26}Al_2Cl_2N_2O_4$: C, 44.18; H, 5.98; N, 6.44. Found: C, 43.69; H, 6.02; N, 6.51.

Synthesis of [{CH$_3$COCHC(CH$_3$)NCH$_2$CH$_2$OCH$_2$CH$_2$O}AlCl]$_2$ (1c). A 1.0 M solution of diethylaluminum chloride in hexane (7.6 mL, 7.6 mmol) was added dropwise to a cooled THF (30 mL) solution of $\mathbf{L_3}$ (1.4 g, 7.6 mmol) at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight, after which time the solution was filtered and the resulting yellow solid crystallized by slow evaporation of a dichloromethane at room temperature, to give **1c** as yellow crystals in 76% yield (1.44 g). Mp 170 °C dec. ^{1}H NMR (500.1 MHz, CD_2Cl_2): δ 5.08 (br, s, 1H, C*H*), 3.98 (br, s, 2H, CH_2OAl), 3.84 (br, 2H, OCH_2CH$_2$O), 3.65 (br, 2H, NCH$_2$CH_2O), 3.40 (br, 1H, NC*H*$_2$), 1.98 (s, 3H, CH_3), 1.92 (s, 3H, CH_3). ^{27}Al NMR ($CDCl_3$, 130.336 MHz): δ 11 ($\nu_{1/2}$ = 4100 Hz). MS (EI): m/z 494 [M]$^+$. Anal. Calcd for $C_{18}H_{30}Al_2Cl_2N_2O_6$: C, 43.64; H, 6.06; N, 5.66. Found: C, 43.41; H, 6.18; N, 5.46.

Synthesis of [{MeC(O)CHC(NCH$_2$CH$_2$O)Me}AlMe]$_2$ (2a). Addition of a tetrahydrofuran solution of **1a** to a solution of trimethylaluminum (0.5 mL, 5.2 mmol) in tetrahydrofuran (10 mL) cooled to −30 °C resulted in immediate evolution of methane and formation of a pale yellow coloration. After gas evolution had ceased the reaction mixture was allowed to warm to room temperature and stirred for a further 2.5 h, after which time the solution was concentrated under reduced pressure. The resulting precipitate was isolated by filtration and dried under vacuum to give spectroscopically pure **2a** in 63% yield (0.6 g). X-ray quality crystals were obtained by slow diffusion of hexane into the mother liquid at room temperature overnight. Mp 195 °C. ^{1}H NMR (500.1 MHz, C_7D_8): δ 4.86 (s, 1H, CH), 4.01 (ddd, ^2J = 9.5 Hz, ^3J = 6.7 Hz, ^3J = 4.6 Hz, 1H, OCH_aH$_b$), 3.84 (ddd, ^2J = 9.5 Hz, ^3J = 7.8 Hz, ^3J = 6.1 Hz, 1H, OCH_aH$_b$), 3.06 (ddd, ^2J = 13.3 Hz, ^3J = 7.8 Hz, ^3J = 6.7 Hz, 1H, NCH$_a$$H_b$), 2.94 (ddd, ^2J = 13.3 Hz, ^3J = 6.1 Hz, ^3J = 4.3 Hz, 1H, NCH$_a$$H_b$), 1.93 (s, 3H, C$H_3$), 1.34 (s, 3H, C$H_3$), −0.54 (s, 3H, Al−C$H_3$). ^{13}C{^{1}H} NMR (125.65 MHz, C_7D_8): δ 178.2 (*C*O), 171.90 (*C*N), 99.54 (*C*H), 58.8 (OCH_2), 48.0 (NCH_2), 25.7 (*C*H$_3$), 21.9 (*C*H$_3$). ^{27}Al NMR ($CDCl_3$, 130.336 MHz): δ 70 ($\nu_{1/2}$ = 1800 Hz). MS (EI): m/z 366 [M]$^+$, 365 [M − H]$^+$, 351 [M − CH$_3$]$^+$. Anal. Calcd for $C_{16}H_{28}Al_2N_2O_4$: C, 54.55; H, 7.65; N, 7.95. Found: C, 54.80; H, 7.91; N, 8.12.

Synthesis of [{MeC(O)CHC{NCH$_2$CH(Me)O}Me}$_2$Al$_2$Cl$_2$(py)] (3b). A solution of **1b** (0.16 g, 0.36 mmol) in pyridine (5.0 mL) was concentrated, filtered, layered with *n*-hexane, and left to stand overnight to give X-ray quality crystals of **3b** in 77% yield (0.14 g). ^{1}H NMR (500.1 MHz, CD_2Cl_2): δ 8.57 (br m, J = 4.2 Hz, 4H, C_5H_5N), 7.63 (m, J = 7.6 Hz, 1.8 Hz, 2H, C_5H_5N), 7.23 (m, J = 7.6, 4.5 Hz, 4H, C_5H_5N), 5.15 (s, 1H,

C*H*), 5.09 (s, 1H, C*H*), 4.43 (br, 1H, OC*H*Me), 4.22 (br, 1H OC*H*Me), 3.51 (dd, $J = 13.1$, 5.1 Hz, 2H, NCH_aCH_b), 3.15 (br, 1H, NCH_aH_b), 2.95 (br 1H, NCH_aH_b), 1.95 (s, 3H, CH_3), 1.91 (br s, 9H, 3 × $C(O)CH_3$), 1.38 (d, $J = 6.1$ Hz, 3H, $OCHCH_3$), 1.25 (d, $J = 5.2$ Hz, 3H, $OCHCH_3$). ^{27}Al NMR ($CDCl_3$, 130.336 MHz): δ 56 (broad overlapping), 16 (broad overlapping). Anal. Calcd for $C_{21}H_{31}Al_2Cl_2N_3O_4$: C, 49.03; H, 6.07; N, 8.17. Found: C, 49.53; H, 5.77; N, 8.44.

General Procedure for Polymerization of D,L-Lactide with Aluminum Chloride Precursors 1a−c. The aluminum initiator (0.14 mmol) and D,L-lactide (1.0 g, 6.9 mmol) were loaded into a Schlenk flask in the drybox. Toluene (15 mL) was added and the resulting mixture was stirred at 70 °C for 168 h, after which the solvent was removed under reduced pressure to yield either a viscous oil (high M_n PLA) or a glassy solid (lower M_n PLA). Percentage conversion was determined by integration of monomer vs polymer methane resonances in the ^{1}H NMR spectrum of the crude product. The polymer was dissolved in dichloromethane (40 mL) and hydrolyzed with a 1.0 M solution of acetic acid (5 mL, 5.0 mmol). The organic phase was separated, washed with water (4 × 20 mL), dried over sodium sulfate, and filtered. The resulting solution was concentrated and the polymer precipitated by addition of methanol. The PLA sample was dried under vacuum and submitted for GPC analysis.

General Procedure for Polymerization of D,L-Lactide with Aluminum Chloride Precursors 1a−c Activated by Addition of Alkene Oxide. The aluminum initiator (0.14 mmol), D,L-lactide (1.0 g, 6.9 mmol), and either propylene oxide or cyclohexene oxide (0.14 mmol) were loaded into a flame-dried Schlenk flask. Toluene (15 mL) was added and the resulting mixture was stirred at 70 °C for 18 h, after which the solvent was removed and the polymer purified according to the procedure described above.

Crystal Structure Determination of Compounds 1a, 1c, and 3b. Crystals of **1a** suitable for single-crystal X-ray crystallography were grown by slow diffusion of a dichloromethane solution layered with hexane at room temperature, those of **1c** by slow evaporation of a dichloromethane solution, and those of **3b** by slow diffusion of hexane into a concentrated pyridine solution at room temperature. Data were collected on a Bruker SMART CCD diffractometer, using SMART and SAINT software (Bruker AXS Inc., Madison, WI, 2001) with Mo Kα radiation ($\lambda = 0.71073$ Å) at 160 K. The structures were solved by using direct methods and refined with the SHELXTL program package (G. M. Sheldrick, Bruker AXS Inc., Madison, WI, 2001) and all non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included at idealized positions and a riding model was used for subsequent refinement.

Acknowledgment. We gratefully acknowledge the University of Newcastle upon Tyne and the Queen's University of Belfast (CenTACat) for funding.

Supporting Information Available: Details of structure determination, non-hydrogen atomic positional parameters, full listings of bond distances and angles, anisotropic displacement parameters, and hydrogen atom parameters for compounds **1a**, **1c**, and **3b**, including a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org. Observed and calculated structure factor tables are available from the authors upon request.

OM0343770