Aluminium complexes bearing functionalized trisamido ligands and their reactivity in the polymerization of ε-caprolactone and *rac*-lactide†

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The addition of 1 and 2 equivalents of $AlMe_3$ to *cis*,*cis*-$C_6H_9(NHCH_2C_6H_4$-*o*-R$)_3$ (R = PPh_2 (**3**) and SPh (**4**)) gives complexes [*cis*,*cis*-$C_6H_9(NCH_2C_6H_4$-*o*-R-κ*N*$)_2(NHCH_2C_6H_4$-*o*-R-κ*N*)]AlMe (R = PPh_2 (**7**) and SPh (**8**)) and [*cis*,*cis*-$C_6H_9(NCH_2C_6H_4$-*o*-R$)_3$-$\kappa^5\mu^2N$]Al_2Me_3 (R = PPh_2 (**5**) and SPh (**6**)), respectively. The bimetallic complexes are active in the polymerization of ε-caprolactone and *rac*-lactide whereas the monometallic complexes are not, although no cooperative behaviour is observed between the two aluminium atoms of **5** and **6**. The polycaprolactone samples, which were characterized using ^{1}H NMR, MALDI-TOF, and SEC, show the presence of residual ligands **3** or **4** bound to the polymer and the *in situ* NMR studies confirm that the insertion occurs in an Al–N bond.

Introduction

The worldwide consumption of plastics has risen steadily since the revolutionary discovery of alkene polymerization by Ziegler and Natta.[1] While a significant percentage of the polymers currently produced are recycled, there is still a large amount finding their way into the ecosystem, having a negative impact on the environment.[2] An ecological alternative to saturated polyolefins are biodegradable polymers such as polylactides and polycaprolactones.[3] In addition to biodegradability, these materials are biocompatible and are widely used for medical applications.[3] However, in order to obtain polymers with good mechanical properties, the microstructure of the polymeric chains, including their molecular weight and polydispersity, needs to be controlled; something that can be done using catalysis. As such, interest over the past decade for the catalytic ring-opening polymerization (ROP) of lactones and lactides has spurred several review articles.[4]

Numerous metals have been known to catalyze the formation of polylactones and polylactides with the most notable catalysts being electrophilic metal ions, such as magnesium,[5] calcium,[5c,6] titanium,[7] iron,[8] zinc,[5a-c,9] tin,[10] and aluminium.[11] Aluminium is one of the most efficient catalysts for ε-caprolactone and lactide polymerization and is generally stabilized using N or O supported ligands. Whereas single site catalysts are numerous, examples where more than one metal site is required for efficient catalysis are scarce.[12-14] Examples of such collaborative work are found in dizinc-monoalkoxide complexes that are believed to behave similarly to metalloenzymes[13] (Fig. 1A) and in a macrocyclic Schiff base bisaluminium complex where a cooperative effect between the two aluminium centers has been observed (R = H, Fig. 1B).[14] In the latter example, one aluminium atom serves as the Lewis acid, and an alkyl functionality bound to the second metal atom attacks the carbonyl group of the incoming ester during catalysis. It was also proposed that adjacent aluminium centers linked in a fashion similar to aluminoxane (R = $AlMe_2$, Fig. 1B), hindered the polymerization process, and that cooperation came instead between aluminium atoms on both extremities of the macrocycle. A specific arrangement of the metallic centers is thus crucial for cooperative behaviour.

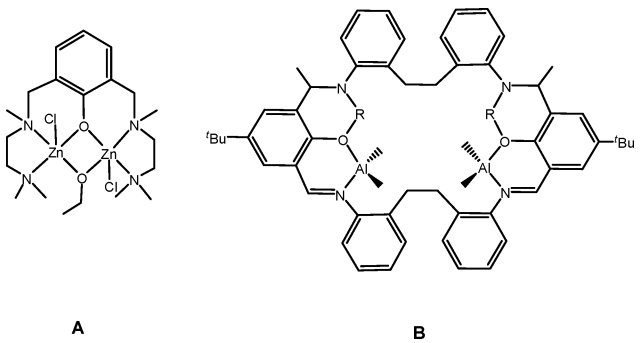

Fig. 1 Two examples of bimetallic catalysts for ring-opening polymerization of cyclic esters.

Our research group has been investigating the coordination chemistry of ambiphilic aluminium complexes having both Lewis acidic and basic moieties.[15] Derivatives of *cis*,*cis*-triaminocyclohexane with pendant soft donor groups were chosen as ligands for the synthesis of ambiphilic ligands. Hard electrophilic metals such as Al^{3+} prefer to bind covalently to amido moieties,[16] generating a Lewis acidic coordination site, whereas soft ligands are free to coordinate low oxidation state transition metals, such as platinum(0).[17] In our systematic study of the reactivity of the functionalized triaminocyclohexane ligands, we wish to report that the hexadentate ligands *cis*,*cis*-$C_6H_9(NHCH_2C_6H_4$-*o*-R$)_3$ (R = PPh_2, SPh) can bind one or two equivalents of $AlMe_3$ depending on the stoichiometry of the reaction. The bimetallic complexes formed are also active in ring-opening polymerization of cyclic esters, such as ε-caprolactone and lactides.

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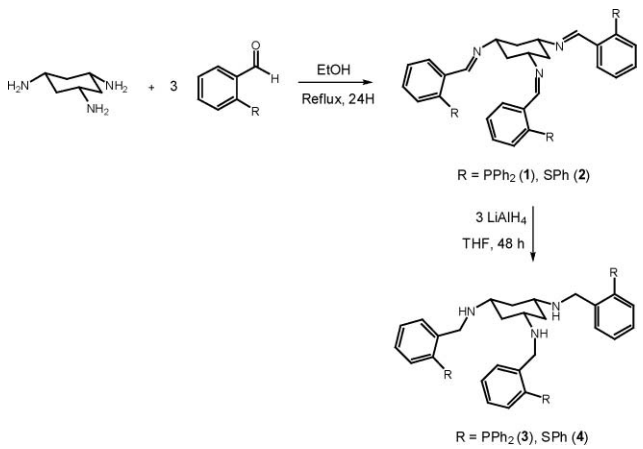
Results and discussion

Ligand synthesis

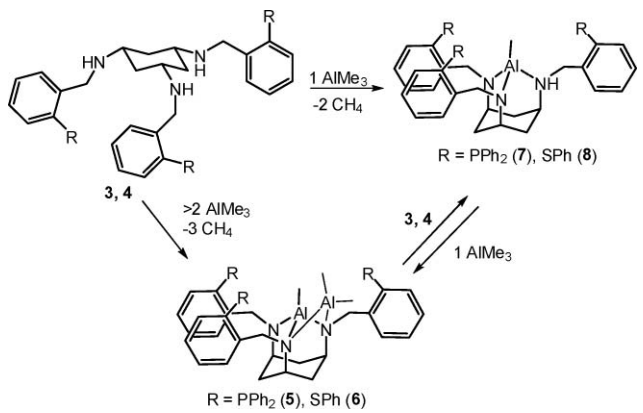
The general procedure for the synthesis of the aminophosphine/thiol ligands is summarized in Scheme 1. Reaction of three equivalents of the corresponding 2R-benzaldehyde with one equivalent of *cis*,*cis*-1,3,5-triaminocyclohexane afforded the Schiff bases *cis*,*cis*-$C_6H_9(N{=}CHC_6H_4\text{-}o\text{-}R)_3$ (**1**, **2**) (R = PPh_2, SPh) in approximately 70% yield. The reduction of **1** and **2** using excess $LiAlH_4$ gave the hexadentate ligands *cis*,*cis*-$C_6H_9(NHCH_2C_6H_4\text{-}o\text{-}R)_3$ (**3**, **4**) (R = PPh_2, SPh) in excellent yields. It should be noted that thiol analogues **2** and **4** show similar spectroscopic features to what was observed for **1** and **3**, which have been previously reported.[17]



Scheme 1 Synthesis of the aminophosphine/thiol ligands.

Synthesis of the aluminium complexes

The protonolysis of an aluminium alkane precursor is a well-known strategy for the synthesis of aluminium amido complexes.[18] As expected, **3** and **4** were completely converted to amido complexes **5** and **6** (Scheme 2) upon addition of more than 2 equivalents of trimethylaluminium (or 1 equivalent of hexamethyldialuminium). Although the release of methane was observed as a singlet at 0.15 ppm by ^{1}H NMR spectroscopy in both reactions, the presence of three singlets at –0.12, –0.22, and –0.52 ppm for **5** and at –0.15, –0.26, and –0.32 ppm for **6** did show that three methyl groups remained bound to the aluminium atoms. Another significant spectroscopic feature was the splitting of the single resonance for the methylene protons on the functional arms into three resonances integrating for two protons each. The resonances for the protons on the cyclohexyl ring also indicated a loss of symmetry; the signals that were observed as singlets in **3** and **4** were split into two series of resonances in a 1 : 2 ratio. Finally, two resonances were observed by $^{31}P\{^1H\}$NMR spectroscopy at –14.1 and –14.9 ppm for **5**, integrating at a 1 : 2 ratio. These observations, and literature precedent by the groups of Johnson[18b] and Chen,[19] are in agreement with the structure depicted in Scheme 2, where the functional arms of the cyclohexyl ring are in an axial position and a plane of symmetry is passing through the Al_2Me_3 core. Coordination to the aluminium atoms induces a flip in the cyclohexane framework, with the functionalized arms now in axial position, something that was previously observed for some *cis*,*cis*-triamidocyclohexane complexes of early transition metals.[16] While the formation of **5** was clean by NMR spectroscopy, in the case of **6**, a small excess of trimethylaluminium remained coordinated by the sulfide moieties and could not be removed under reduced pressure, as observed by the presence of broad signals in the ^{1}H NMR spectrum. Adding triethylamine proved efficient to generate **6** cleanly by forming the $Et_3N{\cdot}AlMe_3$ adduct (^{1}H NMR $\delta = 2.19$, 0.68 and –0.40) which could be removed by subsequent washings with pentane. For comparison, Chen and *al.* reported that upon the addition of 2 equivalents of $AlMe_3$ to the more flexible ligand $MeSi[SiMe_2NH(4\text{-}MeC_6H_4)]_3$, only two of the amido moieties, instead of three as observed for **5** and **6**, were binding the metal centers, generating a complex with a Al_2N_2 core.[19]



Scheme 2 Synthesis of aluminium amido complexes.

It was possible to obtain crystals of complex **6** by slow evaporation of a pentane solution, thus confirming its connectivity. The complex crystallizes in a $P\bar{1}$ space group with two independent molecules ($Z = 4$). The main difference between the molecules is the conformation of one of the functionalized arms. Indeed, the Al(1)–N(3)–C(36)–C(37) torsion angle is –135.2(1)° whereas the equivalent torsion angle on the other molecule (Al(11)–N(13)–C(136)–C(137)) is 147.9(2)°. However, in both molecules the thiophenyl moieties are in the same quadrant relative to the metallic core. An ORTEP representation of one of the molecules is shown in Fig. 2 and a simplified depiction of the conformers is shown in Fig. 3.

As observed for the solid state structure of **3**,[17] the higher symmetry observed in solution for the dialuminium complex is not present in the solid state structure of **6**, suggesting a fast rotation of the functional arms in solution. In this complex, the ligand is bound to an Al–Me fragment by three nitrogen atoms while an $AlMe_2$ fragment shares two nitrogen atoms with the other metal center. Both aluminium centers are in distorted tetrahedral environments, with the N–Al–N angles of the N_2Al_2 four-membered ring being small (78.90 to 79.66°). The nitrogen atoms N(1), N(2), N(11), and N(12) are in tetrahedral environments. On the other hand, N(3) and N(13), which are only bound to one Al atom, are in a sp^2 planar environment, as shown by the sum of the angles of 359°. The Al–N bond lengths are similar, ranging from 1.963(2) Å to 2.000(2) Å, with the exception of the Al(1)–N(3) and Al(11)–N(13) distances that are significantly shorter (1.7806(17) and 1.7960(17) Å, respectively). To our knowledge, three other structurally characterized complexes bound to tripodal

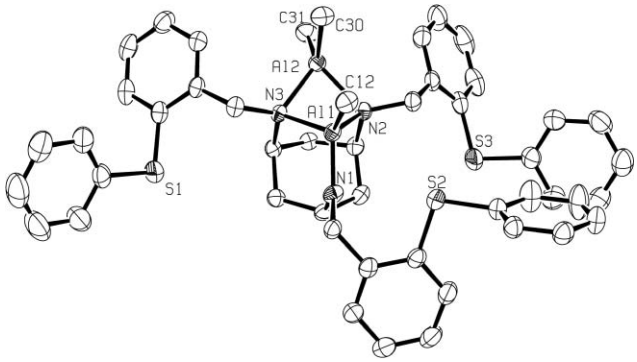


Fig. 2 ORTEP diagram of **6**. Thermal ellipsoids are presented at 50% probability. The hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): **Molecule 1:** Al(1)–N(1) 2.0000(16); Al(1)–N(2) 1.9727(16); Al(1)–N(3) 1.7806(17); Al(2)–N(1) 1.9783(16); Al(2)–N(2) 1.9890(17); Al(1)–C(7) 1.948(2); Al(2)–C(8) 1.971(2); Al(2)–C(9) 1.970(2); N(3)–Al(1)–C(7) 114.64(9); N(3)–Al(1)–N(2) 109.07(7); N(3)–Al(1)–N(1) 107.00(7); N(2)–Al(1)–N(1) 79.45(6); N(1)–Al(2)–N(2) 79.59(6); C(36)–N(3)–C(3) 115.38(16); C(36)–N(3)–Al(1) 131.90(13); C(3)–N(3)–Al(1) 111.59(12). **Molecule 2:** Al(11)–N(11) 1.9625(17); Al(11)–N(12) 1.9824(17); Al(11)–N(13) 1.7960(17); Al(12)–N(11) 1.9976(18); Al(12)–N(12) 1.9793(17); Al(11)–C(107) 1.949(2); Al(12)–C(108) 1.971(2); Al(12)–C(109) 1.971(2); N(13)–Al(11)–C(107) 112.87(9); N(13)–Al(11)–N(12) 108.74(8); N(13)–Al(11)–N(11) 108.09(8); N(12)–Al(11)–N(11) 79.66(7); N(11)–Al(12)–N(12) 78.90(7); C(136)–N(13)–C(105) 113.10(16); C(136)–N(13)–Al(11) 124.94(13); C(105)–N(13)–Al(11) 110.80(12).

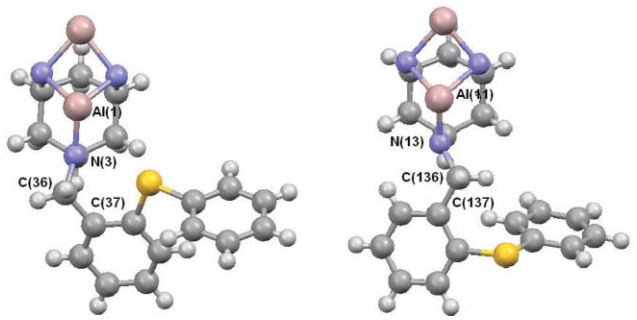


Fig. 3 Depiction of the different orientations of the functionalized arm in crystal of **6**.

ligands have been reported having similar $N_3Al_2R_3$ cores.[18b,19] In all examples, the terminal amido ligands have a short N–Al bond length compared to the bridging amido. Complexes $P[CH_2N\text{-}3,5\text{-}(CF_3)_2C_6H_3]_3Al_2Me_3$ and $Me_3Al.P(CH_2NPh)_3Al_2Me_3$, reported by Johnson,[18b] and complex $MeSi[SiMe_2N(4\text{-}MeC_6H_4)]_3AlH(AlH_2)$, reported by Chen,[19] have terminal amido N–Al bonds of 1.829(3), 1.825(2), and 1.842(4) Å, respectively, and bridging amido N–Al bond lengths between 1.958 and 1.997 Å. The short bond length and the sp^2 hybridization could be induced by additional π-donation of the nitrogen lone pair to the aluminium atom, which would increase the N–Al bond strength while reducing the nucleophilicity of the amido group. It should be noted that no significant interaction between the sulfide and aluminium is observed. The similarity in the $^{31}P\{^1H\}$ NMR chemical shifts of the dialuminium complex (–14.1 and –14.9 ppm) to that of free ligand **3** (–15.0 ppm), also suggests the absence of an Al–P interaction in complex **5**.

When one equivalent of $AlMe_3$ was added to either **3** or **4** in C_6D_6, new products were observed exhibiting only one Al–Me resonance in the ^1H NMR spectrum at –0.87 ppm and –0.82 ppm, for **7** and **8**, respectively. The ^1H NMR spectra of the two latter aluminium compounds were also much more complex, with all hydrogen atoms on the organic framework integrating for one each, indicating a total absence of symmetry in solution. It can be proposed that the tripodal ligand is bound to the methylaluminium fragment with the metal in a pseudo-tetrahedral fashion. For this to happen, one of the nitrogen atom forms a dative interaction with a secondary amine. Using HMQC and COSY experiments, it was possible to locate the amine protons at 3.56 and 3.62 ppm, for **7** and **8** respectively, since they were the only ones not correlated to a carbon atom. Due to this nitrogen atom being chiral and sp^3-hybridized, all of the diastereotopic fragments become magnetically unequivalent, as proposed by Chen *et al.*[19] The isolation of these compounds in the solid state proved impossible, since they did not precipitate from solution and remained as oils with small amount of uncharacterized impurities. Reaction of the bimetallic complexes with one equivalent of their respective free ligand readily afforded the corresponding monometallic complexes and the addition of one equivalent of $AlMe_3$ to **7** and **8** affords **5** and **6**, respectively.

Polymerization of ε-caprolactone

The ring opening polymerization (ROP) of ε-caprolactone (CL) was performed using complexes **5**, **6**, and **8** as catalysts in a toluene solution. Since the isolation and the purification of **7** proved not feasible, no catalytic run was done with it. The yields were calculated according to the mass of the polymer that precipitated after quenching the solution with a CH_2Cl_2 and CH_3OH mixture, and the M_n and M_w values were calculated using steric exclusion chromatography (SEC) for the high molecular weight domain (ESI, Fig. S1,† before 20 min). The results are summarized in Table 1.

Complex **6** was shown to afford better yields of polycaprolactone at room temperature, or at 50 °C, than **5**, as can be observed in entries 1 to 6. It is believed that the larger steric hindrance of PPh_2 compared to SPh may play an important role in reducing the polymer yield and the activity of the catalyst. The reaction with both catalysts was slow at room temperature, since the polymer isolated yields were very low after one hour, but the reaction proceeded more efficiently with **6** at 50 °C. At higher monomer to catalyst ratios, the TOFs ranged between 6.2 and 7.1 min^{-1} (entries 11 and 12). One limiting factor in the polymerization was the jellification of the reaction mixture at high concentration and temperature (entry 6), which occurred after 15 min. However, running the experiment in a more dilute solution (0.8 M) instead of a 2.4 M solution with 150 equivalents of CL, in order to prevent jellification, gave lower yields of isolated polymer (entries 6 and 9). The use of benzyl alcohol ($PhCH_2OH$) as activator for the polymerization of cyclic esters has been reported.[19,20] However, as shown in entry 7, the presence of the alcohol greatly reduced both the yield and the M_n of the polymer. The reaction between one equivalent of benzyl alcohol and catalyst **6** in benzene-d_6 did show by ^1H NMR the presence of free ligand **4**, thus indicating the catalyst's degradation in presence of $PhCH_2OH$.

Table 1 Polymerization of ε-caprolactone using **5**, **6**, and **8** as catalysts

Entry	Catalyst	[Cat] : [CL]	Vol/ml	Time/h	Temp./°C	Yield (%)	M_n[d]	M_w[d]	M_{RMN}[e]	PDI[d]	Small : High[f]
1	5	1 : 150	1	1	RT	7	10900	14100	1510	1.3	85 : 15
2	5	1 : 150	1	6	RT	65	18000	47100	810	2.62	NA
3	5	1 : 150	1	1	50	78	25400	47100	4190	1.85	62 : 38
4	6	1 : 150	1	1	RT	17	NA	NA	1100	NA	26 : 74
5	6	1 : 150	1	6	RT	99	14600	45500	7180	3.12	8 : 92
6	6	1 : 150	1	1	50	98	19300	47900	10800	2.48	3 : 97
7	6	1 : 150[b]	1	6	RT	64	8700	16300	7550	1.87	20 : 80
8	6	1 : 76[c]	3	1	50	35	12500	25500	5030	2.03	4 : 96
9	6	1 : 150[c]	3	1	50	68	23800	48200	7680	2.03	11 : 89
10	6	1 : 300[c]	3	1	50	88	52000	110800	24500	2.13	2 : 98
11	6	1 : 400[c]	3	1	50	94	82000	135200	26100	1.65	4 : 96
12	6	1 : 600[c]	3	1	50	71	69500	145200	36100	2.09	7 : 93
13	6	1 : 76	1	1	50	79	13700	26600	5100	1.94	15 : 85
14	8[a]	1 : 76	1	1	50	78	46400	108500	31800	2.34	6 : 94
15	8[a]	1 : 76	1	1	RT	6	NA	NA	NA	NA	NA
16	8[a]	1 : 76	1	6	RT	54	11600	33700	NA	2.91	5 : 95

The experiments were carried out using a 2.4 mM solution of catalyst in toluene. The volume includes the volume of the ε-caprolactone.[a] The catalyst was prepared *in situ* and monitored by ^{1}H NMR prior its transfer into the Schlenk vessel. [b] In presence of one equivalent of benzyl alcohol. [c] 0.8 mmol solution of catalyst. [d] According to the higher molecular weight fractions of the chromatogram. [e] In $CDCl_3$, using the $HOCH_2R$ end group of both polymers terminated by the R-C(O)OMe and R-C(O)-X (X = **3** or **4**). [f] Using SEC, where "small" and "high" represent the relative integrations of the fractions after and before 20 min, respectively.

The effect of the caprolactone concentration on the yield and M_n and M_w was assessed (entries 8 to 12). Experiments were done using catalyst **6** with 76 to 600 equivalents of CL at 50 °C for one hour. Between 76 and 400 equivalents of CL, M_n values increased linearly with CL concentration. The yields also increased. At 600 equivalents, the trend no longer held and the M_n value and yield were lower than expected. This could be due to saturation of the system, since jellification of the reaction mixture occurred too rapidly and slowed down the reaction.[21]

The activity of monoaluminic catalyst **8** was also compared against its bimetallic counterpart (entries 14–16). **8** was not isolable in the solid state and was thus prepared *in situ* in an NMR tube prior to catalysis attempts. It was found that **8** afforded comparable yields at 50 °C and higher M_n values compared to catalyst **6** (entries 13 and 14). However at room temperature, the reaction was slow to start and low yields were obtained along with lower M_n values (entries 15 and 16).

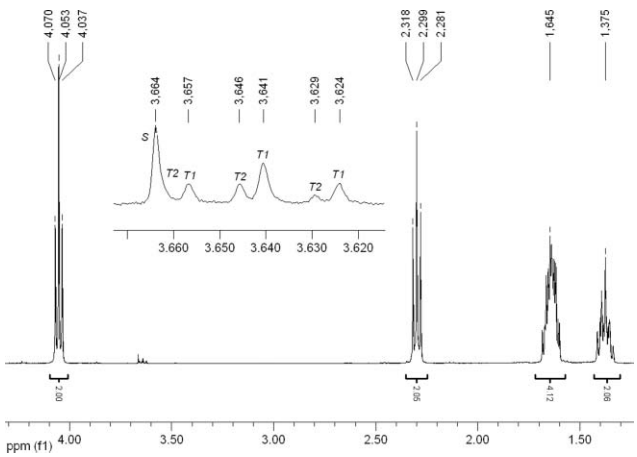


Fig. 4 Typical ^{1}H NMR spectrum of polycaprolactone (entry 9) with a blow up of the resonances of the terminal groups. T1 and T2 are for the two triplets and S for the singlet.

^{1}H NMR spectroscopy analysis of polycaprolactone

The end group analysis using NMR spectroscopy is a powerful method to obtain the molecular weight of polycaprolactones in solution.[22] The ^{1}H NMR spectra of the polycaprolactones isolated in the catalytic experiments were typical of the reported values, with δ = 4.05 (t), 2.30 (t), 1.64 (m), and 1.37 (m). However, the end group resonances were untypical for polycaprolactones synthesized using aluminium catalysts that are quenched with methanol. Indeed, two triplets, at 3.641 and 3.646 ppm (J_{H-H} = 5.1 Hz), and a singlet at 3.664 ppm, were observed by ^{1}H NMR spectroscopy (Fig. 4). In all samples, the upfield triplet and the singlet were integrated in a 2 : 3 ratio, as would be expected for a polycaprolactone having -CH_2OH (triplet) and -C(O)OCH_3 (singlet) as end groups.[22a] However, no other end group could be assigned to the triplet corresponding to the -CH_2OH (triplet) at 3.646 ppm. After careful examination, the ^{1}H NMR spectra of polycaprolactones having a low molecular weight did show some broad and ill defined resonances at 7.3–7.1, 4.3–4.1, and 2.6–1.1 ppm; these chemical shifts are typical for ligands **3** and **4**. The ^{31}P{^{1}H} NMR spectrum of the polymer obtained in entry 3 using catalyst **5** did exhibit three minor overlapping resonances for ligand **3** at –15.6 and –15.9 ppm, along with major resonances between 32.2 and 31.5 ppm. These resonances are typical for the phosphine oxide analogue of **3**. Therefore, quenching the reaction with methanol allows to get rid of the aluminium from the catalyst, but not of the ligand that remains bound by an amide linkage to the polymeric chain. Indeed, the NC(O)R stretching frequency was observed at 1651 cm^{-1} by FTIR spectroscopy. Such amide linkage could be formed by a ROP initiated by an insertion within an aluminium–amido bond (*vide infra*).

The molecular weight of the polymers was calculated by integrating both methylene triplets at 3.641 and 3.646 ppm for a total of 2 protons. It can be observed that the M_n obtained by ^{1}H NMR spectroscopy is systematically lower than the M_n observed

using SEC. However, it should be noted that the difference between the M_n by NMR and SEC is much more acute with polymers having a lower M_n. With these samples, the presence of **3** or **4**, or its oxidized analogue, as an end group will artificially increase the molecular weight observed by SEC (**3** has a molecular weight of 952 g mol^{-1}), whereas the ^{1}H NMR integrations will give a much more reliable number of repetition units of the polycaprolactone.

MALDI-TOF analysis

One general characteristic of this catalytic system is that polydispersity indexes (PDI) are rather high at 50 °C. The SEC traces clearly show the presence of two domains with different molecular weights (ESI, Fig. S1†). A MALDI-TOF experiment on the isolated product of entry 3 was carried out (Fig. 5) to have a more reliable idea of the structure of the lower molecular weight fraction. It was possible to observe a repetition pattern starting at $m/z = 1114$ with a repetition unit of 114.3, which corresponds to the molecular weight of CL (molecular weight = 114.06, ESI, Fig. S2†). The first value of 1114 corresponds to a unit of CL (m/z = 114) bound to ligand **3** where the phosphines are oxidized (m/z = 999) with an additional proton (H^+), as previously assumed by NMR spectroscopy.

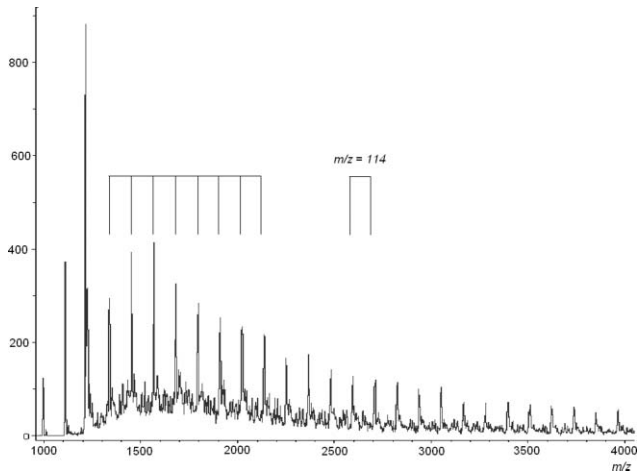


Fig. 5 MALDI-TOF spectrum of entry 3.

In the mass spectrum of the fractions having a $m/z < 1000$, some signals could be observed that could be attributed to repeating units of CL (for example, m/z = 596.3, 710.4, and 824.3), but no end group could be clearly assigned. However, the presence of the oxidized analogue of **3** was clearly observed at m/z = 1000.4 as the main signal (expected value for **3** + H^+ = 1000.4), suggesting that not all of the ligands are incorporated in the polymeric chains.

In situ study of the polymerization of ε-caprolactone

NMR scale reactions were done to gain a better understanding of the polymerization mechanism. Upon addition of 1 equivalent of CL to a solution of **6** in C_6D_6, immediate changes in the ^{1}H NMR spectrum were visible for the aluminium complex suggesting the complete conversion to a new species (Fig. 6). The methylene protons were split into 6 doublets ranging from 3.92 to 5.27 ppm, implying that the **6** no longer possessed a mirror plane in solution, as stated above, and that the hydrogen atoms were now diastereotopic. Two of the Al–Me signals were shifted upfield at –0.58 and –0.68 ppm, respectively, and signals attributed to bound CL emerged at 3.42, 2.07, 1.12, and 0.94 ppm. The fact that the three Al–Me signals were still clearly visible in the upfield region of the spectrum indicated that the ring opening insertion of CL did not occur in the Al–Me bond. These observations are in agreement with results reported by Milione *et al.* when using a cationic heteroscorpionate complex.[23] Furthermore, the signals that shifted upfield (at –0.58 and –0.68 ppm) are reminiscent of the aluminium complex $Me_2Al(\mu\text{-}OCH_2CH_2NMe_2)Al(tBu)_3$ having a

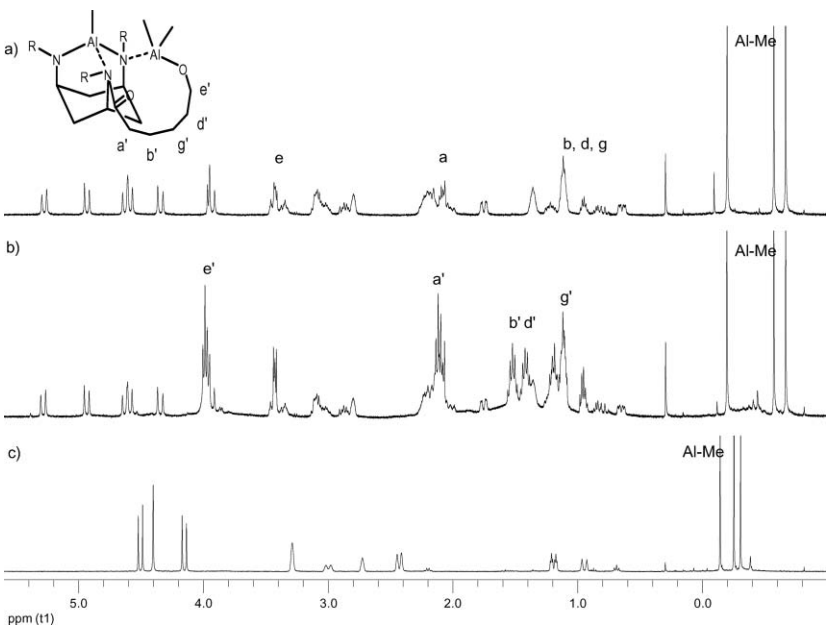


Fig. 6 ^{1}H NMR spectra of catalyst **6** in the presence of 1 equivalent of CL in benzene-d_6 after (a) 5 min at room temperature, (b) 18 h at 60 °C after the addition of a second equiv. of CL, and (c) before the addition of CL.

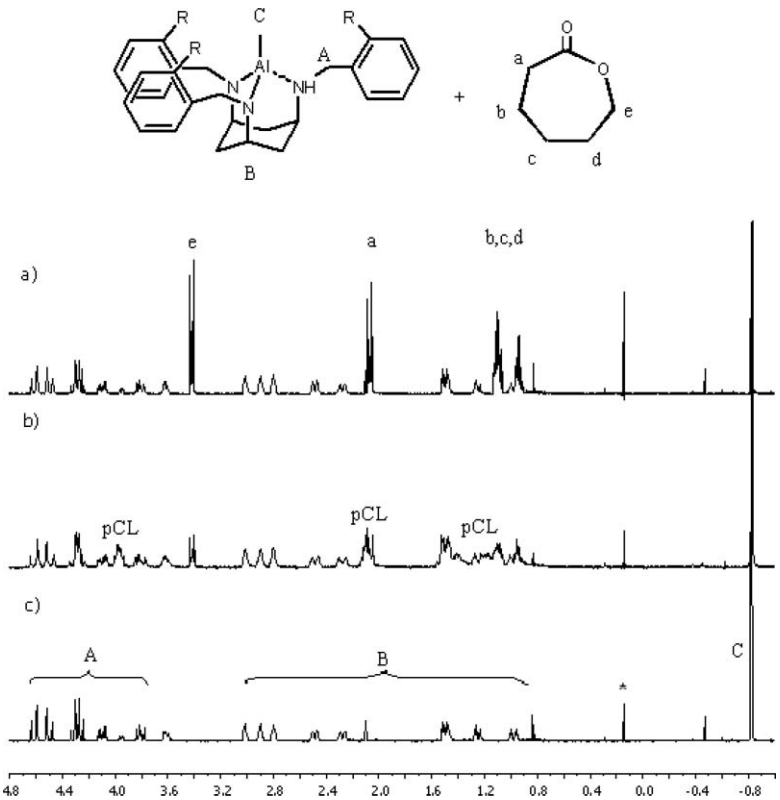


Fig. 7 ^{1}H NMR spectra of catalyst **8** in the presence of 1 equiv. of CL in benzene-d_6 after (a) 5 min at room temperature, (b) 18 h at 60 °C, and (c) before the addition of CL.

R_2N-$AlMe_2$-OCH_2 core, where the $AlMe_2$ fragment exhibits a ^{1}H NMR chemical shift of –0.56 ppm.[24] We therefore propose that the insertion occurs into one of the two amido-aluminium bonds of the N_2AlMe_2 four-member cycle, rather than in the N_3AlMe central core, to form the species depicted in Fig. 6. The presence of the ligand bound to the isolated polymeric chain and the low reactivity of **8**, as seen in the next paragraph, support this hypothesis.

After addition of one equivalent of CL to **8** in C_6D_6 almost no reaction was detected by ^{1}H NMR after one hour at room temperature (Fig. 7). When heated at 60 °C for one hour, the signals attributed to CL decreased and a new multiplet at 3.98 ppm became more pronounced. After an additional 17 h at 60 °C, the signals attributed to CL have decreased further but conversion was still incomplete. However, the most important pieces of information were that a large amount of **8** was still present in solution, that the aluminium complex did not seem to be affected by the presence of CL, and that no new signals were attributed to an active catalyst. Whereas the exact nature of the active catalyst with precatalyst **8** could not be confirmed, it can be speculated that some species in low concentration was formed after heating the solution. Since the ligand was also observed in the polymer obtained by **8**, as deduced from the series of triplet at 3.64 ppm in the isolated polymer of entry 14, two possible pathways can be imagined. First, it is possible that the CL inserts in one of the N–Al bond at a very slow rate, thus allowing polymerization by few activated species. Also, it might be possible for some residual aluminium species to form an analogue of **6**, which would be the active species.

Polymerization of *rac*-lactide

Complex **6** proved to be active for *rac*-lactide ROP. A first attempt at room temperature with 75 equivalents of *rac*-lactide afforded less than 5% yield after 5 days. A second attempt at 100 °C lead to 96% yield after 4 days. SEC analyses gave a M_n of 32000 with a PDI of 1.56.

The tacticity of the polymer was determined by $^{13}C\{^{1}H\}$ and homodecoupled ^{1}H NMR experiments. The resonances at 69.0 and 69.2 ppm, integrating for 4 : 1 and representing the methyne carbon in the $^{13}C\{^{1}H\}$, were attributed to the tetrads *iii*, *iis*, *sii* and *isi* (ESI, Fig. S3†). These are the stereosequences expected in the polymerization of *rac*-lactide by an achiral catalyst.[25] However, three weaker resonances present in the spectrum at 69.1, 69.3 and 69.4 ppm corresponding to the *iss* tetrads, which cannot be normally present in polymers coming from *rac*-lactide, were observed. This result implies that some transesterification or racemization reaction occurred, which have been known to induce inversion of the stereocenters.[25] The methyne region of the homodecoupled ^{1}H NMR spectrum corroborates the results obtained from the $^{13}C\{^{1}H\}$ spectrum. These preliminary results show that the activity of catalyst **6** is slightly inferior to other aluminium catalysts that are active in *rac*-lactide ROP.[4a-b,26]

Conclusion

The coordination chemistry of an aminothiol and a previously reported aminophosphine ligand with aluminium was explored. With both ligands, the reaction with two equivalents of $AlMe_3$

leads to the formation of bimetallic methylalane species. The reaction of one equivalent afforded monometallic complexes with one secondary amine bound to aluminium.

The reactivity of these complexes towards ε-caprolactone ROP was assessed and it was found that the bimetallic complexes **5** and **6** were active catalysts. Precatalyst **8** did exhibit some catalytic activity, but probing the reaction using ^{1}H NMR spectroscopy did show that the complex did not react significantly with ε-caprolactone and that the activity was probably a consequence of a minor species not observed resulting from the degradation of **8**. No activator, such as benzyl alcohol, is needed for the reaction to proceed, as the site of the CL insertion on the bimetallic complexes was found to be at the N-$AlMe_2$ moiety, as could be demonstrated by the presence of the residual ligand bound to the isolated polymer. In the presence of the sulfide containing catalyst **6**, the polymers obtained consist mainly of high molecular weight polymers, however, catalyst **5**, with bulky PPh_2 groups on the functionalized arms, produced mainly oligomers. The synthesis of analogues of **5** and **6** with other functional groups and the formation of the bimetallic species are currently under way to test their catalytic activity and probe and cooperative behaviour between early and late metal systems.

Experimental

cis,*cis*-1,3,5-Triaminocyclohexane·3HBr[27] and 2-(phenylthio)-benzaldehyde were prepared according to literature procedures.[28] Syntheses for *cis*,*cis*-1,3,5-triaminocyclohexane and compounds **1** and **3** were previously reported.[17] Trimethylaluminium was purchased from Sigma-Aldrich and used as received. ε-caprolactone was heated at 80 °C with CaH_2 and distilled at 0.07 mmHg at 80 °C. Dry and deoxygenated solvents were used throughout all syntheses. Toluene and pentane were distilled on sodium/benzophenone and collected under nitrogen. The reactions were carried out using usual Schlenk and glovebox methodologies. ^{1}H (400.0 MHz), ^{31}P{H} (161.9 MHz) and ^{13}C{^{1}H} (100.568 MHz) solution NMR spectra were recorded on a Varian Inova NMR AS400 spectrometer or on a Bruker NMR AC-300 spectrometer (^{1}H (300.0 MHz), ^{31}P{H} (121.42 MHz) and ^{13}C{^{1}H} (75.42 MHz). *J* values are given in Hz. The elemental analyses were carried out by GCL & Chemisar Laboratories.

cis,*cis*-$C_6H_9(N{=}CHC_6H_4(SPh))_3$ (2)

cis,*cis*-1,3,5-Triaminocyclohexane (120 mg, 0.90 mmol) and 2-(phenylthio)benzaldehyde (600 mg, 2.8 mmol) were dissolved in 30 ml of anhydrous ethanol and molecular sieves (4 Å) were added. The solution was heated under reflux for 24 h and then cooled at −35 °C. A white precipitate appeared which was filtered affording a white crystalline powder (460 mg, 68% yield). δ_H (400 MHz; C_6D_6) 8.98 (s, 3H, N=C*H*), 8.31 (br d, $^3J_{H-H}$ = 7.7, 3H, C_6H_4), 7.30 (br d, $^3J_{H-H}$ = 7.7, 3H, C_6H_4), 7.17 (m, 6H, *o*-S*Ph*), 7.03–6.80 (m, 15H, *m*,*p*-S*Ph* and C_6H_4), 3.15 (tt, $^3J_{H-H}$ = 11.4, $^3J_{H-H}$ = 3.5, 3H, C*H*N=CHC$_6$H$_4$), 2.22 (dd, $^3J_{H-H}$ = 11.8 and $^3J_{H-H}$ = 11.8, 3H, ax. CH_2) and 1.65 (td, $^3J_{H-H}$ = 11.8 and $^3J_{H-H}$ = 3.5, 3H, equ. CH_2); δ_C (100.57 MHz; C_6D_6) 157.3 (s, N=*C*H), 138.0 (s, C_6H_4), 137.4 (s, C_6H_4), 135.2 (s, *i*-S*Ph*), 134.3 (s, C_6H_4), 131.0 (s, *p*-S*Ph*), 129.6 (s, *m*-S*Ph*), 129.0 (s, C_6H_4), 128.5 (s, C_6H_4), 128.0 (s, *o*-S*Ph*), 128.7 (s, C_6H_4), 66.7 (s, *C*H$_2$) and 41.6 (s, *C*HN=CHC$_6$H$_4$). Elemental analysis calc. for $C_{45}H_{39}N_3S_3$: C, 75.27; H, 5.47; N, 5.85. Found: C, 75.01; H, 5.56; N, 5.72%.

cis,*cis*-$C_6H_9(NHCH_2C_6H_4SPh)_3$ (4)

To a solution of **2** in 40 ml of THF (600 mg, 0.84 mmol), a suspension of $LiAlH_4$ (96 mg, 2.5 mmol) in 10 ml of THF was added. The suspension was stirred at room temperature for 48 h. The reaction was then filtered to remove excess $LiAlH_4$ and quenched with water. The mixture was extracted with 3 × 20 ml water. The organic fraction was dried with $MgSO_4$ and filtered. The volatiles were removed under vacuum to yield **4** as yellow oil (530 mg, 91% yield). δ_H (400 MHz; C_6D_6) 7.52 (d, $^3J_{H-H}$ = 7.0, 3H, C_6H_4(S*Ph*)), 7.37 (d, $^3J_{H-H}$ = 7.7, 3H, C_6H_4(S*Ph*)), 7.20 (m, 6H, C_6H_4(S*Ph*)), 7.09 (t, $^3J_{H-H}$ = 7.5, 3H, C_6H_4(S*Ph*)), 6.92 (m, 12H, C_6H_4(S*Ph*)), 3.95 (s, 6H, CHNHCH_2C$_6$H$_4$), 2.23 (tt, $^3J_{H-H}$ = 11.2 and $^3J_{H-H}$ = 3.4, 3H, C*H*NHCH$_2$C$_6$H$_4$), 2.00 (dt, $^2J_{H-H}$ = 11.6 and $^3J_{H-H}$ = 3.4, 3H, equ. CH_2), 0.87 (br s, 3H, CHN*H*CH$_2$C$_6$H$_4$) and 0.79 (q, $^2J_{H-H}$ = 11.6 and $^3J_{H-H}$ = 11.6, 3H, ax. CH_2); δ_C (100.57 MHz; C_6D_6) 143.6 (s, C_6H_4(S*Ph*)), 137.6 (s, C_6H_4(S*Ph*)), 134.1 (s, C_6H_4(S*Ph*)), 133.8 (s, C_6H_4(S*Ph*)), 130.0 (s, C_6H_4(S*Ph*)), 129.8 (s, C_6H_4(S*Ph*)), 129.5 (s, C_6H_4(S*Ph*)), 127.9 (s, C_6H_4(S*Ph*)), 126.5 (s, C_6H_4(S*Ph*)), 53.9 (s, *C*HNHCH$_2$C$_6$H$_4$), 49.5 (s, CHNH*C*H$_2$C$_6$H$_4$) and 41.0 (s, *C*H$_2$). One aromatic signal is hidden beneath the solvent peak. Elemental analysis calc. for $C_{45}H_{45}N_3S_3$: C, 74.75; H, 6.26; N, 5.80. Found: C, 74.36; H, 6.52; N, 5.77%.

[*cis*,*cis*-$C_6H_9(NCH_2C_6H_4$-*o*-$PPh_2)_3$-$\kappa^5\mu^2N$]Al_2Me_3 (5)

In a glove box filled with nitrogen, **3** (300 mg, 0.32 mmol) and trimethylaluminium (45 mg, 0.63 mmol) were mixed in 10 ml of toluene. The Schlenk flask was sealed with a glass stopper and the solution heated at 80 °C for 72 h after which the volatiles were removed under vacuum. The crude product was dried under vacuum at 40 °C for 2 h to assure the removal of all excess $AlMe_3$. In the glove box, the crude product was washed with several portions of pentane to afford a white flaky powder (163 mg, 53% yield). δ_H (400 MHz; C_6D_6) 8.09 (dd, $^3J_{H-H}$ = 7.1 and $^3J_{H-P}$ = 4.8, 1H), 7.63 (dd, $^3J_{H-H}$ = 7.7 and $^3J_{H-P}$ = 4.6, 2H), 7.38 (m, 15H), 7.18–6.99 (m, 21H), 6.93 (dt, $^3J_{H-H}$ = 7.6 and $^3J_{H-P}$ = 1.1, 3H), 4.64 (dd, $^4J_{H-P}$ = 4.5 and $^2J_{H-H}$ = 14.2, 2H), 4.52 (d, $^4J_{H-P}$ = 2.8, 2H), 4.25 (d, $^2J_{H-H}$ = 14.2, 2H), 3.50 (s, 2H), 3.18 (d, $^2J_{H-H}$ = 15.2, 1H), 2.79 (s, 1H), 2.48 (d, $^2J_{H-H}$ = 13.8, 2H), 1.15 (td, $^3J_{H-H}$ = 3.6 and $^2J_{H-H}$ = 13.8, 2H), 1.04 (d, $^2J_{H-H}$ = 15.2, 1H), −0.12 (s, Al–Me, 3H), −0.22 (s, Al–Me, 3H) and −0.52 (s, Al–Me, 3H); δ_P (121.422 MHz; C_6D_6) −14.1 and −14.9; δ_C (100.57 MHz; C_6D_6) 149.3 (d, $^1J_{C-P}$ = 20.9), 144.0 (d, $^1J_{C-P}$ = 24.8), 138.0 (m), 137.3 (d, $^3J_{C-P}$ = 10.5), 137.2 (d, $^3J_{C-P}$ = 10.5), 136.0 (d, $^3J_{C-P}$ = 14.4), 134.3 (m), 133.1 (s), 129.7–129.1 (m), 126.6 (s), 54.7 (d, $^5J_{C-P}$ = 2.2), 51.5 (d, $^3J_{C-P}$ = 24.0), 50.9 (s), 49.6 (d, $^3J_{C-P}$ = 22.8), 35.7 (d, $^5J_{C-P}$ = 5.2), 35.3 (s), −0.6 (s, Al–C), −5.2 (s, Al–C) and −11.5 (s, Al–C). Elemental analysis calc. for $C_{66}H_{66}Al_2N_3P_3$: C, 75.56; H, 6.30; N, 4.01. Found: C, 75.90; H, 6.58; N, 4.00%.

[*cis*,*cis*-$C_6H_9(NCH_2C_6H_4$-*o*-$SPh)_3$-$\kappa^5\mu^2N$]Al_2Me_3 (6)

In a Schlenk flask with a Teflon stopper, **4** (420 mg, 0.58 mmol) was dissolved in 10 ml toluene. 83 mg (1.2 mmol) of $AlMe_3$ were added and the solution heated at 100 °C for 24 h. The solution was

evaporated and dried under vacuum for 2 h. The resulting yellow oil was then dissolved in 10 ml toluene and 64 mg (0.63 mmol) of triethylamine was added. The reaction was stirred at ambient temperature for 15 min after which the volatile materials were removed. The crude product was washed with 5 portions of 2 ml of pentane. Crystals were grown from slow evaporation of a pentane solution (238 mg, 50% yield). δ_H (400 MHz; C_6D_6) 7.68 (dd, $^3J_{H-H} = 7.6$ and $^3J_{H-H} = 1.2$, 1H), 7.55 (dd, $^3J_{H-H} = 7.7$ and $^3J_{H-H} = 1.4$, 2H), 7.37 (dd, $^3J_{H-H} = 7.8$ and $^3J_{H-H} = 1.2$, 1H), 7.31 (m, 4H), 7.19–7.14 (m, 4H), 7.05 (td, $^3J_{H-H} = 7.6$ and $^3J_{H-H} = 1.4$, 2H), 6.95 (m, 8H), 6.91–6.84 (m, 6H), 4.50 (d, $^2J_{H-H} = 13.9$, 2H), 4.40 (s, 2H), 4.15 (d, $^2J_{H-H} = 13.9$, 2H), 3.28 (s, 2H), 3.00 (dt, $^2J_{H-H} = 15.2$ and $^3J_{H-H} = 2.5$, 1H), 2.72 (s, 1H), 2.43 (d, $^2J_{H-H} = 14.0$, 2H), 1.19 (dt, $^2J_{H-H} = 14.0$ and $^3J_{H-H} = 3.7$, 2H), 0.94 (dt, $^2J_{H-H} = 15.2$ and $^3J_{H-H} = 1.9$ Hz, 1H), –0.15 (s, Al–Me, 3H), –0.26 (s, Al–Me, 3H) and –0.32 (s, Al–Me, 3H); δ_C (100.57 MHz; C_6D_6) 145.8 (s), 141.2 (s), 137.6 (s), 137.2 (s), 135.5 (s), 134.8 (s), 134.3 (s), 133.0 (s), 131.3 (s), 130.7 (s), 129.8 (s), 129.5 (s), 129.5 (s), 129.4 (s), 128.8 (s), 128.8 (s), 127.5 (s), 127.2 (s), 126.7 (s), 126.5 (s), 54.5 (s), 52.0 (s), 50.5 (s), 49.3 (s), 35.4 (s), 35.1 (s), –0.8 (s, Al*Me*), –5.0 (s, Al*Me*) and –11.3 (s, Al*Me*). Elemental analysis calc. for $C_{48}H_{51}Al_2N_3S_3$: C, 70.23; H, 6.22; N, 5.12. Found: C, 69.80; H, 6.59; N, 5.50%.

[*cis*,*cis*-$C_6H_9(NCH_2C_6H_4$-*o*-PPh_2-κ*N*)$_2$($NHCH_2C_6H_4$-*o*-PPh_2-κ*N*)]AlMe (7)

In a glove box filled with nitrogen, **3** (140 mg, 0.15 mmol) and $AlMe_3$ (11 mg, 0.15 mmol) were dissolved in 2 ml of toluene. The solution was heated at 100 °C for 48 h. The volatiles were removed under vacuum to afford a white powder (NMR yield > 98%). Small impurities prevented from doing an elemental analysis. δ_H (400 MHz; C_6D_6) 8.18 (dd, $^3J_{H-H} = 7.2$ and $^3J_{H-P} = 4.5$, 1H), 8.12 (dd, $^3J_{H-H} = 7.7$ and $^3J_{H-P} = 4.4$, 1H), 7.47–6.88 (m, 40H), 4.80 (dd, $^2J_{H-H} = 15.3$ and $^4J_{H-P} = 3.3$, 1H), 4.57 (d, $^2J_{H-H} = 15.3$, 1H), 4.42 (dd, $^2J_{H-H} = 15.2$ and $^4J_{H-P} = 1.7$, 1H), 4.31 (dd, $^2J_{H-H} = 15.3$ and $^4J_{H-P} = 2.9$, 1H), 4.27 (dd, $^2J_{H-H} = 11.3$ and $^3J_{H-H} = 4.7$, 1H), 3.92 (dd, $^2J_{H-H} = 14.1$ and $^3J_{H-H} = 9.8$, 1H), 3.56 (dd, $^3J_{H-H} = 14.9$ and $^3J_{H-H} = 7.1$, 1H, N–H), 3.05 (br, 1H), 2.92 (br, 1H), 2.86 (br, 1H), 2.45 (d, $^3J_{H-H} = 12.4$, 1H), 2.33 (d, $^3J_{H-H} = 14.1$, 1H), 1.48 (tt, $^3J_{H-H} = 12.2$ and $^3J_{H-H} = 3.6$, 1H), 1.45 (d, $^3J_{H-H} = 15.0$, 1H), 1.24 (dt, $^3J_{H-H} = 13.8$ and $^3J_{H-H} = 3.1$, 1H), 0.97 (dt, $^3J_{H-H} = 14.3$ and $^3J_{H-H} = 3.0$, 1H) and –0.87 (s, 3H, Al*Me*); δ_P (121.422 MHz; C_6D_6) –13.8 and –17.0; δ_C (100.57 MHz; C_6D_6) 150.0 (d, $^1J_{C-P} = 20.9$), 149.8 (d, $^1J_{C-P} = 20.9$), 139.7 (d, $^1J_{C-P} = 25.0$), 138.7 (d, $^2J_{C-P} = 12.5$), 138.6 (d, $^2J_{C-P} = 11.8$), 138.3 (d, $^1J_{C-P} = 11.7$), 138.3 (d, $^1J_{C-P} = 12.0$), 137.2 (d, $^2J_{C-P} = 13.9$), 135.1 (s), 134.4 (s), 133.3 (s), 133.3 (s), 132.3 (d, $^3J_{C-P} = 5.8$), 129.9 (s), 129.4 (s), 129.1 (s), 128.8 (s), 126.6 (s), 53.4 (s), 53.3 (s), 53.2 (d, $^3J_{C-P} = 25.0$), 53.0 (s), 52.3 (d, $^3J_{C-P} = 23.0$), 49.7 (d, $^3J_{C-P} = 16.0$), 38.1 (s), 36.6 (s), 29.1 (s) and –15.8 (s, Al*Me*). Some aromatic signals are hidden beneath the solvent peak.

[*cis*,*cis*-$C_6H_9(NCH_2C_6H_4$-*o*-SPh-κ*N*)$_2$($NHCH_2C_6H_4$-*o*-SPh-κ*N*)]AlMe (8)

In a glove box filled with nitrogen, compound **4** (140 mg, 0.15 mmol) and $AlMe_3$ (11 mg, 0.15 mmol) were dissolved in 2 ml of toluene. The solution was heated at 100 °C for 48 h. The volatiles were removed under vacuum to afford an off-white powder (NMR yield > 98%). Small impurities prevented from doing an elemental analysis. δ_H (400 MHz; C_6D_6) 8.00 (d, $^3J_{H-H} = 7.3$, 1H), 7.85 (d, $^3J_{H-H} = 7.0$, 1H), 7.39–7.45 (m, 25H), 4.62 (d, $^2J_{H-H} = 15.2$, 1H), 4.50 (d, $^2J_{H-H} = 15.3$, 1H), 4.32 (d, $^2J_{H-H} = 14.8$, 1H), 4.26 (d, $^2J_{H-H} = 15.1$, 1H), 4.10 (dd, $^2J_{H-H} = 14.0$ and $^3J_{H-H} = 5.2$, 1H), 3.81 (dd, $^2J_{H-H} = 14.1$ and $^3J_{H-H} = 9.5$, 1H), 3.62 (dd, $^3J_{H-H} = 8.0$ and $^3J_{H-H} = 6.3$, 1H, N–H), 3.01 (br, 1H), 2.90 (br, 1H), 2.80 (br, 1H), 2.49 (d, $^3J_{H-H} = 12.7$, 1H), 2.28 (d, $^3J_{H-H} = 14.5$, 1H), 1.48 (tt, $^3J_{H-H} = 12.2$ and $^3J_{H-H} = 3.6$ Hz, 1H), 1.45 (d, $^3J_{H-H} = 15.0$, 1H), 1.24 (dt, $^3J_{H-H} = 13.8$ and $^3J_{H-H} = 3.1$, 1H), 0.97 (dt, $^3J_{H-H} = 14.3$ and $^3J_{H-H} = 3.0$, 1H), –0.82 (s, 3H, Al*Me*); δ_C (100.57 MHz; C_6D_6) 147.0 (s), 146.6 (s), 143.6 (s), 138.2 (s), 137.9 (s), 136.5 (s), 136.0 (s), 134.6 (s), 134.1 (s), 133.3 (s), 133.0 (s), 132.8 (s), 130.6 (s), 130.1 (s), 129.6 (s), 129.3 (s), 129.1 (s), 128.7 (s), 127.2 (s), 127.1 (s), 126.4 (s), 126.2 (s), 53.8 (s), 53.7 (s), 53.4 (s), 53.3 (s), 53.2 (s), 53.0 (s), 49.7 (s), 49.4 (s), 41.6 (s), 37.9 (s), 37.3 (s), 29.4 (s), –15.7 (s). Some aromatic signals are hidden beneath the solvent peak.

Table 2 Crystallographic information for **6**

	6
Formula	$C_{48}H_{51}Al_2N_3S_3$
Fw	820.06
Size/mm	0.09 × 0.05 × 0.02
Cryst syst	Triclinic
Space group	$P\bar{1}$
a/Å	13.1455(11)
b/Å	16.7733(14)
c/Å	20.6807(17)
α/°	100.937(1)
β/°	99.373(1)
γ/°	94.655(1)
V/Å^3	4387.7(6)
Z	4
Wavelength/Å	0.71073
D_c/g cm^{-3}	1.241
F_{000}	1736
T/K	200(2)
No. of unique/total reflns	15420/44407
GOF	1.013
R_{int}	0.0301
Final R indices [$I > 2\sigma(I)$]	0.0391

Crystallographic structural determination†

Crystallographic data are reported in Table 2. Single crystals were coated with Paratone-N oil, mounted using a glass fibre and frozen in the cold nitrogen stream of the goniometer. The data were collected on a Bruker SMART APEX II diffractometer. The data were reduced (SAINT)[29] and corrected for absorption (SADABS).[30] The structure was solved and refined using SHELXS-97 and SHELXL-97.[31] All non-H atoms were refined anisotropically. The hydrogen atoms were placed at idealized positions. Neutral atom scattering factors were taken from the International Tables for X-Ray Crystallography.[32] All calculations and drawings were performed using the SHELXTL package.[33]

Polymerization procedures. The reaction mixtures were prepared in a glove box. In a Schlenk tube with a magnetic stir bar, a solution of the catalyst in toluene was added to the monomer in toluene in order to obtain a 2.4 mM solution, unless stated otherwise. The solutions were stirred for a specific period of time

at room temperature or at 50 °C. The reaction was quenched by adding 1 mL of dichloromethane and pouring the solution in cold methanol. The precipitate was filtered and dried under vacuum. A fine suspension of the polymer in methanol could also be centrifuged at 7000 rpm at 4 °C for 30 min.

Polymerization of *rac*-lactide was performed in a similar fashion in 5 ml of toluene and heated at 100 °C for four days. The reaction was quenched by pouring the solution into slightly acidic cold methanol at pH 5. No significant reactivity was observed with $AlMe_3$ and CL. The precipitate was filtered and dried under vacuum.

SEC experiments. The SEC measurements were performed in chloroform on a Waters apparatus with 515 HPLC pumps and a Waters Associates 441 detector and two Jordi columns. M_n and M_w were calculated using polystyrene standards by integrating the domain corresponding to the larger polymers.

MALDI-TOF experiments. The experiments were carried out at the Mass Spectrometry service at the Durham University Chemistry department. The sample was prepared by first solubilizing a small portion (~1 mg) in acetonitrile (1 mL). A ten fold dilution of this was made in a solution MALDI matrix (saturated α-cyano-4-hydroxy cinnamic acid prepared in 0.1% trifluoroacetic acid : acetonitrile (2 : 1)). 1 μL of this was spotted onto a ground steel target prior to running on the MALDI ToF instrument (Autoflex MALDI ToF/ToF, Bruker, Coventry, UK).

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References

1 (*a*) C. S. Bajgur and S. Sivaram, *Curr. Science*, 2000, **78**, 1325–1335; (*b*) H. Hagen, J. Boersma and G. van Koten, *Chem. Soc. Rev.*, 2002, **31**, 357–364 and references therein.

2 (*a*) C. J. Moore, S. L. Moore, M. K. Leecaster and S. B. Weisberg, *Mar. Pollut. Bull.*, 2001, **42**, 1297–1300; (*b*) R. C. Thompson, Y. Olsen, R. P. Mitchell, A. Davis, S. J. Rowland, A. W. G. John, D. McGonigle and A. E. Russell, *Science*, 2004, **304**, 838.

3 (*a*) Y. Ikada and H. Tsuji, *Macromol. Rapid Commun.*, 2000, **21**, 117–132; (*b*) S. Mecking, *Angew. Chem., Int. Ed.*, 2004, **43**, 1078–1085.

4 (*a*) O. Dechy-Cabaret, B. Martin-Vaca and D. Bourissou, *Chem. Rev.*, 2004, **104**, 6147–6176; (*b*) J. Wu, T.-L. Yu, C.-T. Chen and C.-C. Lin, *Coord. Chem. Rev.*, 2006, **250**, 602–626; (*c*) C. K. Williams, *Chem. Soc. Rev.*, 2007, **36**, 1573–1580; (*d*) C. A. Wheaton, P. G. Hayes and B. J. Ireland, *Dalton Trans.*, 2009, 4832–4846.

5 Some leading references: (*a*) B. M. Chamberlain, M. Cheng, D. R. Moore, T. M. Ovitt, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2001, **123**, 3229–3238; (*b*) M. H. Chisholm, J. C. Gallucci and K. Phomphrai, *Inorg. Chem.*, 2005, **44**, 8004–8010; (*c*) V. Poirier, T. Roisnel, J.-F. Carpentier and Y. Sarazin, *Dalton Trans.*, 2009, 9820–9827; (*d*) L. F. Sanchez-Barba, A. Garces, M. Fajardo, C. Alonso-Moreno, J. Fernandez-Baeza, A. Otero, A. Antinolo, J. Tejeda, A. Lara-Sanchez and M. I. Lopez-Solera, *Organometallics*, 2007, **26**, 6403–6411; (*e*) M.-Y. Shen, Y.-L. Peng, W.-C. Hung and C.-C. Lin, *Dalton Trans.*, 2009, 9906–9913.

6 Some leading references: (*a*) M. H. Chisholm, J. C. Gallucci and K. Phomphrai, *Inorg. Chem.*, 2004, **43**, 6717–6725; (*b*) L. Piao, M. Deng, X. Chen, L. Jiang and X. Jing, *Polymer*, 2003, **44**, 2331–2336; (*c*) S.-M. Ho, C.-S. Hsiao, A. Datta, C.-H. Hung, L.-C. Chang, T.-Y. Lee and J.-H. Huang, *Inorg. Chem.*, 2009, **48**, 8004–8011.

7 Some leading references: (*a*) R. R. Gowda, D. Chakraborty and V. Ramkumar, *Eur. J. Inorg. Chem.*, 2009, 2981–2993; (*b*) L. Postigo, J. Sanchez-Nieves, P. Royo and M. E. G. Mosquera, *Dalton Trans.*, 2009, 3756–3765; (*c*) F. Gornshtein, M. Kapon, M. Botoshansky and M. S. Eisen, *Organometallics*, 2007, **26**, 497–507.

8 Some leading references: (*a*) M.-Z. Chen, H.-M. Sun, W.-F. Li, Z.-G. Wang, Q. Shen and Y. Zhang, *J. Organomet. Chem.*, 2006, **691**, 2489–2494; (*b*) V. C. Gibson, E. L. Marshall, D. Navarro-Llobet, A. J. P. White and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 2002, 4321–4322; (*c*) B. J. O'Keefe, L. E. Breyfogle, M. A. Hillmyer and W. B. Tolman, *J. Am. Chem. Soc.*, 2002, **124**, 4384–4393.

9 Some leading references: (*a*) M. Cheng, A. B. Attygalle, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 1999, **121**, 11583–11584; (*b*) C. Zhang and Z.-X. Wang, *J. Organomet. Chem.*, 2008, **693**, 3151–3158; (*c*) C. A. Wheaton, B. J. Ireland and P. G. Hayes, *Organometallics*, 2009, **28**, 1282–1285; (*d*) Z. Zheng, G. Zhao, R. Fablet, M. Bouyahyi, C. M. Thomas, T. Roisnel, O. Casagrande Jr. and J.-F. Carpentier, *New J. Chem.*, 2008, **32**, 2279–2291.

10 Some leading references: (*a*) N. Nimitsiriwat, V. C. Gibson, E. L. Marshall and M. R. J. Elsegood, *Inorg. Chem.*, 2008, **47**, 5417–5424; (*b*) A. P. Dove, V. C. Gibson, E. L. Marshall, H. S. Rzepa, A. J. P. White and D. J. Williams, *J. Am. Chem. Soc.*, 2006, **128**, 9834–9843; (*c*) A. Kowalski, J. Libiszowski, K. Majerska, A. Duda and S. Penczek, *Polymer*, 2007, **48**, 3952–3960; (*d*) G. Jiang, I. A. Jones, C. D. Rudd and G. S. Walker, *J. Appl. Polym. Sci.*, 2009, **114**, 658–662; (*e*) P. Degée, P. Dubois, R. Jerôme, S. Jacobsen and H.-G. Fritz, *Macromol. Symp.*, 1999, **144**, 289–302.

11 Some leading references: (*a*) M. H. Chisholm, J. C. Gallucci, K. T. Quisenberry and Z. Zhou, *Inorg. Chem.*, 2008, **47**, 2613–2624; (*b*) H. Du, A. H. Velders, P. J. Dijkstra, J. Sun, Z. Zhong, X. Chen and J. Feijen, *Chem.–Eur. J.*, 2009, **15**, 9836–9845; (*c*) A. Arbaoui, C. Redshaw and D. L. Hughes, *Chem. Commun.*, 2008, 4717–4719; (*d*) M. Haddad, M. Laghzaoui, R. Welter and S. Dagorne, *Organometallics*, 2009, **28**, 4584–4592; (*e*) S. Milione, F. Grisi, R. Centore and A. Tuzi, *Organometallics*, 2006, **25**, 266–274.

12 (*a*) S. Range, D. F.-J. Piesik and S. Harder, *Eur. J. Inorg. Chem.*, 2008, 3442–3451; (*b*) D. F.-J. Piesik, R. Stadler, S. Range and S. Harder, *Eur. J. Inorg. Chem.*, 2009, 3569–3576; (*c*) Z. Zhang, X. Xu, S. Sun, Y. Yao, Y. Zhang and Q. Shen, *Chem. Commun.*, 2009, 7414–7416.

13 C. K. Williams, R. B. Brooks, M. A. Hillmayer and W. B. Tolman, *Chem. Commun.*, 2002, 3132–3133.

14 A. Arbaoui, C. Redshaw and D. L. Huges, *Chem. Commun.*, 2008, 4717–4719.

15 (*a*) F.-G. Fontaine and D. Zargarian, *J. Am. Chem. Soc.*, 2004, **126**, 8786–8794; (*b*) M.-H. Thibault, J. Boudreau, S. Mathiotte, F. Drouin, A. Michaud, O. Sigouin and F.-G. Fontaine, *Organometallics*, 2007, **26**, 3807–3815; (*c*) F.-G. Fontaine, J. Boudreau and M.-H. Thibault, *Eur. J. Inorg. Chem.*, 2008, 5439–5454.

16 Some leading references: (*a*) J. E. Bollinger, J. T. Mague, W. A. Banks, A. J. Kastin and D. M. Roundhill, *Inorg. Chem.*, 1995, **34**, 2143–2152; (*b*) L. Turculet and T. D. Tilley, *Organometallics*, 2004, **23**, 1542–1553; (*c*) Y. Kajita, H. Arii, Y. Saito, S. Nagatomo, T. Kitagawa, Y. Fanahashi, T. Ozawa and H. Masuda, *Inorg. Chem.*, 2007, **46**, 3322–3335.

17 M.-H. Thibault, B. E. G. Lucier, R. W. Schurko and F.-G. Fontaine, *Dalton Trans.*, 2009, 7701–7716.

18 (*a*) W. Yao, Y. Mu, A. Gao and L. Ye, *Dalton Trans.*, 2008, 3199–3206; (*b*) H. Han and S. A. Johnson, *Organometallics*, 2006, **25**, 5594–5602; (*c*) M. Garcia-Castro, A. Martin, M. Mena and C. Yélamos, *Organometallics*, 2007, **26**, 408–416.

19 H. Zhu and E. Y.-X. Chen, *Organometallics*, 2007, **26**, 5395–5405.

20 (*a*) T. Biela, A. Kowalski, J. Libiszowski, A. Duda and S. Penczek, *Macromol. Symp.*, 2006, **240**, 47–55; (*b*) N. Wasa, S. Katao, J. Liu, M. Fujiki, Y. Furukawa and K. Nomura, *Organometallics*, 2009, **28**, 2179–2187; (*c*) C. Zhang and Z. X. Wang, *Appl. Organomet. Chem.*, 2009, **23**, 9–18.

21 One of the referee suggested that the jellification of the solution was certainly due to transesterification reactions. Although it was not possible to confirm it, it is a likely reason for such change in the viscosity of the solution.

22 (*a*) A. Duda, Z. Florjanczyk, A. Hofman, S. Slomkowski and S. Penczek, *Macromolecules*, 1990, **23**, 1640–1646; (*b*) G. Deshayes,

F. A. G. Mercier, P. Degée, I. Verbruggen, M. Biesemans, R. Willem and P. Dubois, *Chem.–Eur. J.*, 2003, **9**, 4346–4352.
23 S. Milione, F. Grisi, R. Centore and A. Tuzi, *Organometallics*, 2006, **25**, 266–274.
24 C. N. McMahon, S. G. Bott and A. R. Barron, *J. Chem. Soc., Dalton Trans.*, 1998, 3301–3304.
25 K. A. M. Thakur, R. T. Kean, E. S. Hall, J. J. Kolstad, T. A. Lindgren, A. M. Doscotch, J. I. Siepmann and E. J. Munson, *Macromolecules*, 1997, **30**, 2422–2428.
26 (*a*) M. Bouyahyi, E. Grunova, N. Marquet, E. Kirillov, C. M. Thomas, T. Roisnel and J.-F. Carpentier, *Organometallics*, 2008, **27**, 5815–5825; (*b*) Z. Tang and V. C. Gibson, *Eur. Polym. J.*, 2007, **43**, 150–155.
27 L. Cronin, S. P. Foxon, P. J. Lusby and P. H. Walton, *JBIC, J. Biol. Inorg. Chem.*, 2001, **6**, 367–377.
28 S. Laue, L. Greiner, J. Wötlinger and A. Liese, *Adv. Synth. Catal.*, 2001, **343**, 711–720.
29 *SAINT* Version 7.07a; Bruker AXS Inc.: Madison, WI, 2003. G. M. Sheldrick.
30 *SADABS* Version 2004/1; Bruker AXS Inc.: Madison, WI, 2004.
31 G. M. Sheldrick, *SHELXS-97 and SHELXL-97. Programs for the refinement of crystal structures*University of Gottingen: Germany, 1997.
32 *International Tables for Crystallography, Vol C.*, A. J. C. Wilson, Ed. Kluwer Academic Publishers: Dordecht, 1992, pp 219–222 and pp. 500–502.
33 *SHELXTL*. Version, 6.12; Bruker AXS: Madison, WI, 2001.