

Ligand Variations in New Sulfonamide-Supported Group 4 Ring-Opening **Polymerization Catalysts**

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Received May 24, 2010

The synthesis, structures, and ring-opening polymerization (ROP) capability of a wide range of sulfonamide-supported group 4 amide, alkyl, and alkoxide complexes, varying in sulfonamide N-substituent, metal, coordination number, and geometry, are reported. Reaction of Ti(NMe₂)₄ N-substituent, metal, coordination number, and geometry, are reported. Reaction of Ti(NMe₂)₄ or Ti(NMe₂)₂(OⁱPr)₂ with MeOCH₂CH₂N(CH₂CH₂NHSO₂Me)₂ (**12**, H₂N₂^{Ms}N^{OMe}) or PhCH₂N-(CH₂CH₂NHSO₂R)₂ (R = Tol (**10**, H₂N₂^{Ts}N^{Ph}) or Me (**11**, H₂N₂^{Ms}N^{Ph})) afforded Ti(N₂^{Ms}N^{OMe})-(NMe₂)₂ (**18**), Ti(N₂^{Ts}N^{Ph})(NMe₂)₂ (**19**), Ti(N₂^{Ms}N^{Ph})(NMe₂)₂ (**20**), Ti(N₂^{Ms}N^{OMe})(OⁱPr)₂ (**21**), Ti(N₂^{Ts}N^{Ph})(OⁱPr)₂ (**22**), Ti(N₂^{Ms}N^{Ph})(OⁱPr)₂ (**23**), and Ti(N₂^{Ts}N^{Ph})(OⁱPr)(NMe₂) (**24**). Reaction of N(CH₂CH₂NHSO₂R)₃ (R = Tol (**13**, H₃N₃^{Ts}N), Me (**14**, H₃N₃^{Ms}N), or Ar^F (**15**, H₃N₃^{ArF}N, Ar^F = 3,5-C₆H₃(CF₃)₂)) with Zr(CH₂SiMe₃)₄ formed Zr(N₃^{ArF}N)(CH₂SiMe₃) (R = Ts (**30**), Ms (**31**), or Ar^F (**32**)). Reaction of **15** with Zr(NMe₂) gave Zr(N₄^{ArF}N)(NMe₃) (22). Complement **10**, 21, 24, 20, 22). (32)). Reaction of 15 with Zr(NMe₂)₄ gave Zr(N₃^{ArF}N)(NMe₂) (33). Complexes 19, 21, 24, 30, 32, and 33 were crystallographically characterized. Monomeric six- or five-coordinate structures were found for the titanium complexes 19, 21, and 24, whereas the zirconium alkyls 30 and 32 were dimeric in the solid state with terminal and bridging $\kappa^2(N,O)$ -bound sulfonamides. Complexes 18–24 and 30–33, the previously reported $Ti(CyN_2^{R})(O^{i}Pr)_2$ (25 or 26; $CyN_2^{R} = 1,2-C_6H_{10}(NSO_2Tol)_2$ or $1,2-C_6H_{10}$ -(NSO₂Mes)₂), and *in situ* generated isopropoxide initiators derived from **30–32** were investigated for the ROP of ε -caprolactone (ε -CL). The four-coordinate 25 was the most active, forming poly(ε -CL) with a relatively narrow PDI and well-controlled $M_{\rm p}$. Compounds 22, 23, 25, and 26 and isopropoxides generated *in situ* from 30-32 were all active for the ROP of *rac*-lactide. Of these, the initiators based on Zr(N₃^RN)(CH₂SiMe₃) (30-32) with ⁱPrOH co-initiator gave good activities and excellent PDIs (1.08–1.11) and agreement between measured and predicted $M_{\rm p}$.

Introduction

Over the past decade the most extensively studied biocompatible and biodegradeable polyesters have been those derived from ε -caprolactone and lactide. These materials have attracted much attention as replacements for oilbased plastics and have found extensive applications in the areas of medicine, packaging, film, and thermoplastics.¹⁻⁷ Industrially these polyesters are synthesized by ring-opening polymerization (ROP) of the cyclic esters lactide (LA) or *ɛ*-caprolactone (CL) catalyzed by Lewis acidic metal complexes.8 ROP initiators have also been

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extensively studied in academia and are often based on a Lewis acidic metal, feature one or more alkoxide initiating groups, and are supported by a polydentate ancillary ligand (set), which influences the catalyst nuclearity and controls the coordination-insertion chain growth mechanism. Research into ROP initiators has been extensively reviewed recently.^{9–12} Many metals have been studied in this context, in particular magnesium,^{13–17} zinc,^{13,15,17–21} calcium,^{16,17,22,23} aluminum,^{21,24–27} yttrium,^{28–30} the lanthanides,^{31–34} tin,³⁵

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^{123, 3229.}



Figure 1. Group 4 ROP initiators employing polydentate N,O-donor ligands.^{46,53,62–65}

the group 4 elements,^{21,36-45} germanium,⁴⁶ indium,⁴⁷ and iron.48,49



Among the many supporting ligands that have been used, polydentate alkoxides and phenolates have been among the

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Figure 2. Recently reported group 4 and aluminum ROP initiators supported by tetradentate bis(sulfonamide)amine ligands.68,69

most widely exploited across the periodic table. This progress has been summarized in recent reviews.9-11,16,50-52 Within group 4, Davidson, Aida, Okuda, and Harada have used titanium complexes of bi- and tridentate bis(phenolate) ligands for the ROP of ε -CL and L-LA.^{53–56} Davidson found that polymerization of ε -CL with five-coordinate 1 (Figure 1) gave polyesters with narrow PDIs (polydispersity indices, $M_{\rm w}/M_{\rm n}$) and well-defined molecular weights, $M_{\rm n}$.⁵³ The polymerization was much more effective than with the analogous six-coordinate complex 2 with a tetradentate bis-(phenolate)amine, which showed no activity under the same

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Figure 3. Protio versions of the ligands used in this study $(Ar^F = 3,5-C_6H_3(CF_3)_2)$.⁶⁹⁻⁷²

conditions.⁵⁷ Indeed, of all those studied, the only tetradentate bis(phenolate)amine complex found to be active gave a very poorly controlled polymerization, forming poly(*e*-CL)s with very broad PDIs and poorly controlled M_n values.⁵ Other four- or five-coordinate titanium complexes of bi- or tridentate bis(phenolate) ligands with either CH₂ or chalcogen bridges were studied for the ROP of ε -CL by Aida, Okuda, and Harada.^{54-56,58} Good yields, narrow PDIs, and close agreement between measured and predicted $M_{\rm n}$ were achieved with these initiators. Recently, Kol and Coates described group 4 salophan complexes, which demonstrate remarkable activity, with titanium complexes found to be more active than zirconium. This is in contrast to all other studies of the activities of the group 4 metals for a given ligand.43,57,59 Arnold and Dagorne employed five-coordinate titanium complexes of alkoxide or phenolate donors containing a linked N-heterocyclic carbene. Good conversions of lactide to poly(LA) with narrow PDIs are observed, indicative of living behavior.^{60,61}

Very effective group 4 initiators supported by C_3 -symmetric alkyl or aryl oxides have been developed by Verkade, Davidson, and Kol.^{37,59,63,65,66} Verkade was the first to employ titanatranes of various structures (e.g., 3, Figure 1) for the ROP of rac-LA.^{37,63,64,66} Polymerizations conducted under melt conditions (130 °C, 2 h) gave poly(LA) with a range of PDIs and poorly controlled $M_{\rm n}$. In contrast, the same systems in toluene at 70 °C yielded an extremely well controlled polymerization of L- and rac-LA for 3.37,62-64,66,67 Kol subsequently compared six-coordinate titanium and zirconium complexes of tetradentate bis(phenolate)amines to five-coordinate ones of the type 4 (Figure 1) with C_3 symmetric tris(phenolate)amine ligands.⁵⁹ For both titanium and zirconium, the five-coordinate tripodal ligand complexes were more active for the ROP of L-LA. There

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was also a marked dependence of performance on the phenolate R' ring substituents. Davidson has also evaluated group 4 complexes of the type 4 for the ROP of rac-LA.⁵⁷ Activity generally increased down the triad, and the titanium complex (4: $R = {}^{i}Pr$, $R' = {}^{t}Bu$) gave a ROP activity and control that were similar to those observed previously by Verkade and Kol. In contrast, the zirconium and hafnium analogues effected the extremely well controlled ROP of rac-LA (as judged by narrow PDIs and predictable M_n), giving excellent degrees of heterotactic enrichment ($P_r = 0.98$) and high conversions after 30 min under melt conditions. Solution polymerizations gave similar results, although the conversions were low (50% after 48 h at room temperature).65

We very recently reported a series of new aluminum, titanium, and zirconium isopropoxide complexes $(L)M(O^{I}Pr)_{n}$ (n = 1 or)2, M = Al, Ti, Zr) supported by dianionic bis(sulfonamide)amine ligands, L (Figure 2 shows selected examples).^{68,69} These thermally robust complexes allowed for the well-controlled ROP of *e*-CL and *rac*-LA by a coordinationinsertion mechanism initiated by the respective M-OⁱPr groups. These were the first detailed studies of any sulfonamide-supported ROP initiators. The rates of ROP were significantly faster for the zirconium complexes 6 and 8 than for their titanium congeners (5 and 7). For 6 and 8, both the ROP activity and control were comparable to zirconium complexes of the extensively exploited tetradentate bis-(phenolate)amine ligands. Similar results were found for the aluminum-based initiators, leading us to propose that, in these regards at least, the bis(sulfonamide)amine ligands are able to act as "phenolate mimics".

In these earlier studies for group 4 we focused only on tetradentate bis(sulfonamide)amine ligands with tosyl N-substituents (i.e., -NSO₂Tol donors). Encouraged by the performance of complexes 5-8 and given the current intense interest in the ROP of cyclic esters, we decided to further develop this new class of initiator using several different approaches. In light of the success of bi- and tridentate phenolate ligands (vide supra), it was of interest to target four- and five-coordinate bis(sulfonamide) initiators since they might give more accessible metal centers and faster ROP. Five-coordinate complexes bearing C3-symmetric tris(sulfonamide)amine ligands (analogous to the tris(phenolate)amines) were also clearly of interest. We also reasoned that introducing sulfonamide ligands with sterically less encumbering groups such as mesyl (-SO₂Me) instead of tosyl (-SO₂Tol) could improve the activity of the resulting initiators. Therefore, the synthesis of tri- and tetradentate sulfonamide complexes bearing -NSO₂Me donors was also undertaken. For the new tetradentate ligands, methoxy pendant donors were targeted (cf. 5 and 6) rather

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than pyridyl ones (cf. 7 and 8) because it had been found previously that this gave more active initiators.⁶⁸

Results and Discussion

Synthesis of Protio-ligand Precursors. Figure 3 shows the protio versions of the ligands used in this study, along with their general abbreviations. $H_2N_2^{Ts}N^{Ph}$ (10), ⁶⁹ $H_2N_2^{Ms}N^{Ph}$ $(11)_{,69}^{,69}$ H₃N₃^{Ts}N $(13)_{,70}^{,70}$ H₂CyN₂^{Ts} $(16)_{,71}^{,71}$ and H₂CyN₂^{SO₂Mes} $(17)^{72}$ were prepared according to the literature methods. The new tetradentate protio-ligand $H_2N_2^{Ms}N^{OMe}$ (12) with -NSO₂Me donors was synthesized in good yield by reaction of MeOCH₂CH₂NH₂ with N-mesyl aziridine (eq 1). The other new protio-ligands, N(CH₂CH₂NHSO₂Me)₃ (14, $H_3N_3^{Ms}N)$ and $N(CH_2CH_2NHSO_2Ar^F)_3$ (15, $H_3N_3^{ArF}N)$, were prepared by reaction of tris(2-aminoethyl)amine with SO_2ClR (R = Me or Ar^F) in a biphasic solution of diethyl ether and water (eq 2). For 15 this proceeded satisfactorily in high vield. However, the reaction with SO₂ClMe gave only poor yields (ca. 20%) of 14 due to its high solubility in water, even at high pH. So as to make comparisons with their metal complexes (*vide infra*) and the previously reported **16**,^{73,74} $H_2N_2^{Ts}N^{OMe}$,⁶⁸ and $H_2N_2^{Ts}N^{py}$,⁷⁵ the X-ray structures of **14** and 17 were determined. Further details, a discussion of the

Scheme 1. Synthesis of the New Five- and Six-Coordinate Bis(sulfonamide)amine Complexes





Titanium Complexes of Tri- and Tetradentate Bis(sulfonamide)amine Ligands. Protonolysis reactions of $Ti(NMe_2)_4$ with $H_2N_2^{Ms}N^{OMe}$ (12) $H_2N_2^{Ts}N^{Ph}$ (10), or $H_2N_2^{Ms}N^{Ph}$ (11) gave the corresponding six- and five-coordinate bis-(dimethylamide) complexes $Ti(N_2^{Ms}N^{OMe})(NMe_2)_2$ (18), $Ti-(N_2^{Ts}N^{Ph})(NMe_2)_2$ (19), and $Ti(N_2^{Ms}N^{Ph})(NMe_2)_2$ (20), respectively, in moderate to good yield after recrystallization (Scheme 1). When the reactions were followed in CD₂Cl₂ on the NMR tube scale, the conversions were quantitative and the expected HNMe₂ side product was observed. The lower isolated yields of the mesyl sulfonamide complexes (45% and 39% for 18 and 20, respectively) compared to the tosyl one (60%, 19) are a consequence of their high solubility.

Metal alkoxide complexes (L)M–OR are often superior initiators compared to their amide counterparts (L)M– NR₂.^{11,54,55,68} In our previous work,⁶⁸ we also found that Ti(N₂^{Ts}N^X)(OⁱPr)₂ (X = OMe (5) or py (7)) were more effective in ROP than the corresponding amides, Ti(N₂^{Ts}N^X)-(NMe₂)₂. To explore further these structure–activity relationships, we therefore prepared the bis(isopropoxide) compounds Ti(N₂^{Ms}N^{OMe})(OⁱPr)₂ (21), Ti(N₂^{Ts}N^{Ph})(OⁱPr)₂ (22), and Ti(N₂^{Ms}N^{Ph})(OⁱPr)₂ (23) from Ti(NMe₂)₂(OⁱPr)₂ and the respective protio-ligand (Scheme 1). NMR tube scale investigations showed quantitative formation of 21, 22, or 23 and no evidence for the bis(dimethylamide) complexes 18, 19, and 20. On the preparative scale, 21–23 were obtained in 44–56% yield after 2 h reaction time. Regrettably, attempts to prepare zirconium analogues of 21–23 from Zr(OⁱPr)₄.ⁱPrOH

Scheme 2. Syntheses of Ti(N₂^{Ts}N^{Ph})(OⁱPr)(NMe₂) (24)



using analogous methods to those successfully applied for **6** and **8** (Figure 2) gave ill-defined mixtures. The corresponding reactions with $Zr(NMe_2)_4$ were also unsuccessful. Therefore further work with the $N_2^{Ms}N^{OMe}$ and $N_2^{R}N^{Ph}$ ligands focused exclusively on titanium systems.

As discussed later, both the bis(dimethylamide) compound 19 and its bis(isopropoxide) analogue 22 were good initiators for the ROP of ε -CL, but gave poly(ε -CL)s of quite different molecular weights. To explore these differences further, we prepared the mixed amide-alkoxide complex Ti- $(N_2^{Ts}N^{Ph})(\hat{O}^iPr)(NMe_2)$ (24). As shown in Scheme 2, NMR tube scale experiments in C_6D_6 found that 24 could be quantitatively formed via a redistribution reaction between 19 and 22. However, this reaction is rather slow, requiring heating for 4 days at 80 °C in benzene solution to achieve completion. A more convenient route was the reaction of $H_2N_2^{Ts}N^{Ph}$ (10) with 3 equiv of Ti(NMe₂)₂(OⁱPr)₂, which formed 24 after 16 h at room temperature in CH₂Cl₂. Separation of 24 from excess Ti(NMe₂)₂(O¹Pr)₂ and the Ti-(NMe₂)(O¹Pr)₃ side product was straightforward, giving 24 in 74% yield.

Finally, so as to compare the ROP performance of four-, five-, and six-coordinate titanium bis(sulfonamide) initiators, the previously reported complexes $Ti(CyN_2^{Ts})(O^iPr)_2$ (25) and $Ti(CyN_2^{SO_2Mes})(O^iPr)_2$ (26) were also synthesized $(CyN_2^{R} = 1,2-C_6H_{10}(NSO_2Tol)_2 \text{ or } 1,2-C_6H_{10}(NSO_2Mes)_2)$. These contain a (*rac*)-*trans*-cyclohexyl diamine backbone and were prepared according to literature methods.⁷⁶



R = Tol (25) or Mes (26)

The solid-state structures of **19**, **21**, and **24** have been determined (see below) and confirm those shown in Schemes 1 and 2. In solution, all seven compounds **18–24** show dynamic behavior. For **18–23** this involves exchange of the equatorial and axial Ti–X groups (X = NMe₂ (**18**, **19**, and **20**) or OⁱPr (**21**, **22**, and **23**)) and in all cases pairwise exchange of the two sets of R'CH₂N(CH₂CH₂NSO₂R)₂ ligand methylene protons (R = Ms or Ts; $\overline{R'}$ = Ph or CH₂OMe). For example, at 90 °C in toluene-*d*₈ the ¹H

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Figure 4. Displacement ellipsoid plot of $Ti(N_2^{Ms}N^{OMe})(O^iPr)_2$ (21). Ellipsoids are drawn at the 20% probability level, and H atoms are omitted for clarity.

NMR spectra of **19** and **20** show equivalent environments for the two pairs of ligand CH_2CH_2 protons along with a single resonance for the axial and equatorial NMe₂ groups. Cooling to 248 or 213 K, respectively, gives four CH_2CH_2 proton environments and separate signals for the axial and equatorial NMe₂ ligands. These fluxional processes are likely to be of the type illustrated in eq 3 for **19** and **20**, as discussed elsewhere for diamide-amine-supported titanium complexes.⁷⁷



The solid-state structure of Ti($N_2^{Ms}N^{OMe}$)(OⁱPr)₂ (**21**) is shown in Figure 4, and selected distances and angles are listed in Table 1. Compound **21** has a pseudo-octahedral titanium and overall C_s molecular symmetry. Its geometry is analogous to those of the tosyl analogues Ti($N_2^{Ts}N^{OMe}$)-(OⁱPr)₂ (**5**) and Zr($N_2^{Ts}N^{OMe}$)(OⁱPr)₂ (**6**),⁶⁸ and the principal metric parameters in **21** are similar to those of **5**. For example, the Ti- N_{SO_2R} (av 2.099(4) in **21** vs 2.089(2) Å in **5**) and Ti-OⁱPr (av 1.770(3) in **21** vs 1.773(2) Å in **5**) distances are equivalent within error, while the distances to the dative donors, namely, Ti-OMe and Ti- N_{amine} in **21** (2.271(4) and 2.248(4) Å) are somewhat shorter than in **5** (2.327(2) and 2.277(2) Å).

The molecular structures of $Ti(N_2^{Ts}N^{Ph})(NMe_2)_2$ (19) and $Ti(N_2^{Ts}N^{Ph})(O^{i}Pr)(NMe_2)$ (24) are shown in Figure 5, and selected distances and angles are listed in Tables 2 and 3. The geometry around Ti(1) in 19 is best described as distorted

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Table 1. Selected Bond Distances (Å) and Angles (deg) for Ti(N2^{Ms}N^{OMe})(OⁱPr)₂ (21)

	< <u>-</u>		
Ti(1)-N(1)	2.103(5)	Ti(1) - N(2)	2.248(4)
Ti(1) - N(3)	2.096(5)	Ti(1) - O(1)	1.778(4)
Ti(1)-O(2)	1.762(4)	Ti(1) - O(3)	2.271(4)
N(1) - Ti(1) - N(2)	75.4(2)	N(1) - Ti(1) - N(3)	151.1(2)
N(2) - Ti(1) - N(3)	76.2(2)	N(1)-Ti(1)-O(1)	94.2(2)
N(2) - Ti(1) - O(1)	94.5(2)	N(3) - Ti(1) - O(1)	93.2(2)
N(1) - Ti(1) - O(2)	102.0(2)	N(2) - Ti(1) - O(2)	163.0(2)
N(3) - Ti(1) - O(2)	103.6(2)	O(1) - Ti(1) - O(2)	102.6(2)
N(1) - Ti(1) - O(3)	84.9(2)	N(2) - Ti(1) - O(3)	74.3(2)
N(3)-Ti(1)-O(3)	82.4(2)	O(1) - Ti(1) - O(3)	168.6(2)
O(2) - Ti(1) - O(3)	88.7(2)		



Figure 5. Displacement ellipsoid plots of $Ti(N_2^{Ts}N^{Ph})(NMe_2)_2$ (19, top) and $Ti(N_2^{Ts}N^{Ph})(O^{i}Pr)(NMe_2)$ (24, bottom). Ellipsoids are drawn at the 20% probability level, and H atoms are omitted for clarity.

trigonal bipyramidal with N(1) and N(4) occupying the apical positions. The N(1)–Ti(1)–N(4) angle of 156.4(1)° is somewhat less than that for an ideal trigonal bipyramid (TBP), while N(2)–Ti(1)–N(3) (131.0(1)°) is greater than the expected 120° between equatorial groups. These deviations from an ideal TBP increase in **24** with N(1)–Ti(1)–N-(4) decreasing to 139.5(1)° and N(2)–Ti(1)–N(3) increasing to 144.9(1)°. Indeed, **24** could also be described as a square-based pyramid (SBP) with O(1) occupying the axial site since the four angles O(1)–Ti(1)–N(x) (x = 1, 2, 3, 4) lie in the narrow range 102.8(1)–114.6(1)°. We note that Nagashima recently described Ti{O(CH₂CH₂NTs)₂}(NMe₂)₂ (**27**), containing a tridentate bis(sulfonamide)ether ligand analogous

Table 2. Selected Bond Distances (Å) and Angles (deg) for Ti(N₂^{Ts}N^{Ph})(NMe₂)₂ (19)

	1.(1.)	(1) (1) (1) (1)	
Ti(1) - N(1)	2.278(2)	Ti(1) - N(2)	2.081(2)
Ti(1) - N(3)	2.041(2)	Ti(1) - N(4)	1.889(2)
Ti(1) - N(5)	1.878(2)		
N(1) - Ti(1) - N(2)	73.4(1)	N(1) - Ti(1) - N(3)	76.4(1)
N(2) - Ti(1) - N(3)	131.0(1)	N(1) - Ti(1) - N(4)	156.4(1)
N(2) - Ti(1) - N(4)	93.1(1)	N(3) - Ti(1) - N(4)	100.0(1)
N(1) - Ti(1) - N(5)	99.4(1)	N(2) - Ti(1) - N(5)	115.2(1)
N(3) - Ti(1) - N(5)	107.1(1)	N(4) - Ti(1) - N(5)	103.9(1)

Table 3. Selected Bond Distances (Å) and Angles (deg) for $Ti(N_2^{Ts}N^{Ph})(O^iPr)(NMe_2)$ (24)

		/ =/ ()	
Ti(1) - N(1)	2.267(2)	Ti(1) - N(2)	2.086(2)
Ti(1) - N(3)	2.073(2)	Ti(1) - N(4)	1.855(2)
Ti(1)-O(5)	1.766(2)		
N(1) - Ti(1) - N(2)	74.1(1)	N(1) - Ti(1) - N(3)	73.9(1)
N(2) - Ti(1) - N(3)	144.9(1)	N(1) - Ti(1) - N(4)	139.5 (1)
N(2) - Ti(1) - N(4)	98.57(8)	N(3) - Ti(1) - N(4)	96.37(9)
N(1) - Ti(1) - O(5)	114.6(1)	N(2) - Ti(1) - O(5)	103.4(1)
N(3) - Ti(1) - O(5)	102.8(1)	N(4) - Ti(1) - O(5)	105.8(1)

to $N_2^{Ts}N^{Ph}$ (but with O in place of NCH₂Ph).⁷⁸ In this compound the NMe₂ groups occupy the equatorial sites of a distorted TBP (N_{Ts} -Ti- N_{Ts} =143.5(1)°), in contrast to **19**, in which one NMe₂ is equatorial and one is axial.



The Ti-N_{Ts} distances in **19** and **24** (av 2.070, range 2.041(2)-2.086(2) Å) are shorter than in their six-coordinate counterparts Ti(N₂^{Ts}N^X)(NMe₂)₂ (X = py (**28**) or OMe (**29**), av Ti-N_{Ts} = 2.105 Å), as expected, and comparable to those in **27**. Likewise, the average Ti-NMe₂ distance of 1.884(2) Å in the bis(dimethylamide) **19** is shorter than those in Ti-(N₂^{Ts}N^X)(NMe₂)₂ (av 1.927, range 1.898(6)-1.981(7) Å).⁶⁸ It is interesting to note the decrease in Ti-NMe₂ distance from 1.884(2) Å (av) in **19** to 1.855(2) Å in **24**, which has only one NMe₂ ligand. This shortening is attributed to improved σ and π (2p_{π}-3d_{π}) bonding between titanium and the remaining NMe₂ ligand in **24** since alkoxides are not as good donors as amides in both of these regards.^{79–82} The implications of these structural changes for the ROP characteristics of **19**, **24**, and their homologues are discussed later.

Zirconium Complexes of *C***₃-Symmetric Tris(sulfonamide)-amine Ligands.** We turn now to the synthesis of complexes with tetradentate *tri*anionic sulfonamide-amine ligands. Certain titanium and aluminum complexes of this class of ligand have been reported previously, but not with the ligands used herein and not in the context of polymerization catalysis.⁸³ Tris(amido)amine ("tren") ligands in general have been widely used in transition metal chemistry, but again not in

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Scheme 3. Synthesis of the New Tris(sulfonamide)amine Complexes 30-33



the context of ROP catalysis.^{80,81,84,85} We initially attempted the direct synthesis of alkoxide complexes from the protioligands $H_3N^{Ts}N(13)$, $H_3N^{Ms}N(14)$, and $H_3N_3^{ArF}N(15)$ and either Ti(OⁱPr)₄ or Zr(OⁱPr)₄.ⁱPrOH by analogy with the successful synthesis of $M(N_2^{Ts}N^{OMe})(O^iPr)_2$ and $M(N_2^{Ts}N^{py})$ -(OⁱPr)₂ (5–8, Figure 2).⁶⁸ Unfortunately, no reaction was observed between these metal isopropoxides and 13–15, even under forcing solution conditions or in the melt. Reactions were therefore carried out with Ti(NMe_2)_4, Zr(NMe_2)_4, and Zr(CH_2SiMe_3)_4 in the hope that the so-formed metalamide or -alkyl products could in turn be converted to the more desirable metal-isopropoxides. Reaction of 13–15 with Ti(NMe_2)_4 (by analogy with the successful syntheses of 18-20 and certain literature precedents⁸³) led to complicated mixtures from which no single product could be isolated. However, the reactions with Zr(CH₂SiMe₃)_4 and Zr(NMe₂)_4 were successful, as shown in Scheme 3.

Reaction of Zr(CH₂SiMe₃)₄ with 1 equiv of 13, 14, or 15 gave the corresponding alkyl complexes $Zr(N_3^{Ts}N)$ - (CH_2SiMe_3) (**30**), $Zr(N_3^{Ms}N)(CH_2SiMe_3)$ (**31**), and $Zr-(N_3^{ArF}N)(CH_2SiMe_3)$ (**32**), respectively, in 60–89% yield after recrystallization. When followed in C_6D_6 on the NMR tube scale, the yields were effectively quantitative and the expected SiMe₄ side product was observed. These alkyl compounds were readily handled using normal Schlenk line and drybox techniques. Reaction of Zr(NMe₂)₄ with 1 equiv of 13-15 in CD₂Cl₂ likewise showed quantitative conversions and the expected HNMe2 side product. However, scale up of these reactions met with considerable difficulties associated with simultaneous formation of hydrolysis products, apparently arising from adventitious water. Only in one instance, the reaction of Zr(NMe₂)₄ with the electrondeficient $H_3N_3^{ArF}N$ (15), could a pure product be obtained on scale up. $Zr(N_3^{ArF}N)(NMe_2)$ (33) was obtained in 82% yield after careful recrystallization from rigorously dried THF and crystallographically authenticated (vide infra). The hydrolysis product of 33 was identified as the μ -oxo dimer $\{Zr(N_3^{ArF}N)\}_2(\mu$ -O) (34). This could be prepared by repeated slurrying of pure 33 in "wet" Et₂O (eq 4). The solidstate structure of 34 has been determined and confirms that

shown in eq 4. Further details are given in the Supporting Information.



The solid-state structures of the alkyl complexes 30 and 32 as well as the amide complex 33 have been determined. The molecular structures of 30 and 33 are given in Figures 6 and 7, and selected distances and angles are given in Tables 4 and 5. The structure of 32 is analogous to that of 30. A displacement elipsoid and selected metric parameters are given in the Supporting Information.

Compound **30** (and its analogue **32**) exists as a centrosymmetric, eight-coordinate dimer in the solid state. In addition to the four Zr–N bonds, two –NSO₂Ts groups (N(2), N(3)) of the N₃^{Ts}N ligand also act as $\kappa^2(N,O)$ donors to one zirconium, and for one of these there is an additional bridging S=O···Zr interaction to the other metal center (O(2), O(2A)). The eighth coordination site is occupied by a terminal CH₂SiMe₃ ligand with Zr–CH₂ and Zr–CH₂– SiMe₃ parameters within the expected ranges.⁸⁶ The geometry around the zirconium centers (see Figure 6 (bottom)

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Figure 6. Displacement ellipsoid plots (25% probability) of $Zr(N_3^{Ts}N)(CH_2SiMe_3)$ (**30**). H atoms are omitted for clarity. Top: full structure. Bottom: details of the metal coordination environment.

for a clearer view) is intermediate between a distorted square antiprism (the two planes being $\{N(1)-N(3), O(3)\}$ and $\{C-N(3), O(3)\}$ (28), N(4), O(1), O(2A)}) and a distorted, face-capped pentagonal bipyramid. In this latter description, C(28) and N(2)occupy the axial sites, the equatorial donors are O(1)-O(3), N(3), and N(4), and the capping atom is the tertiary amine nitrogen N(1) with a relatively long $Zr(1) \cdots N(1)$ bond of 2.670(2) Å. As mentioned, $Zr(N_3^{AirF}N)(CH_2SiMe_3)$ (32) is also eight-coordinate and dimeric in the solid state (see the Supporting Information) with an analogous geometry to that of 30. The only structural difference is that while 30 features $\kappa^2(N,O)$ coordination of one terminal and one bridging $-NSO_2Ts$ group, in 32 $\kappa^2(N,O)$ coordination is found for the two nonbridging $-NSO_2Ar^F$ groups and not for the bridging one. The Zr-NSO₂Ts distances in 30 are marginally shorter (av 2.223 Å, range 2.201(2)–2.238(2) Å) than the $Zr-NSO_2Ar^F$ distances in **32** (av 2.245 Å, range 2.217(4)-2.272(4) Å).

In contrast, the dimethylamido complex **33** is monomeric in the solid state but still possesses an eight-coordinate zirconium atom. In addition to the NMe₂ group, the N₃^{ArF}N ligand occupies seven coordination sites, with each SO₂Ar^F donor being $\kappa^2(N,O)$ coordinated. The coordination geometry is best described as a distorted pentagonal bipyramid (cf. Figure 7, bottom), with N(5) and N(3) being in the axial sites and the capping interaction again being to the tertiary amine donor of N₃^{ArF}N ligand (Zr(1)···(N4) = 2.725(4) Å). The N atom of the NMe₂ ligand is sp² hybridized (sum of



Figure 7. Displacement ellipsoid plots (25% probability) of Zr- $(N_3^{ArF})(NMe_2)$ (**33**). H atoms omitted for clarity. Top: full structure. Bottom: details of the metal coordination environment.

Table 4. Selected Bond Distances (\AA) and Angles (deg) for $Zr(N_3^{Ts}N)(CH_2SiMe_3)$ (30)

		, . ,	
Zr(1)-C(28)	2.251(2)	Zr(1)-N(1)	2.670(2)
Zr(1) - N(2)	2.232(2)	Zr(1) - N(3)	2.201(2)
Zr(1) - N(4)	2.238(2)	Zr(1) - O(1)	2.672(2)
Zr(1) - O(3)	2.292(2)	Zr(1)-O(2A)	2.272(2)
S(1) - O(1)	1.452(2)	S(1) - O(2)	1.468(2)
S(2) - O(3)	1.486(2)	S(2) - O(4)	1.433(2)
S(3) - O(5)	1.440(2)	S(3)-O(6)	1.446(2)
Zr(1) - N(2) - S(1)	107.62(9)	Zr(1) - N(2) - C(2)	130.6(1)
S(1) - N(2) - C(2)	119.9(1)	Zr(1) - N(3) - S(2)	100.6(9)
Zr(1) - N(3) - C(11)	127.8(1)	S(2)-N(3)-C(11)	121.9(2)
Zr(1) - N(4) - S(3)	129.8(1)	Zr(1) - N(4) - C(20)	113.9(1)
S(3) - N(4) - C(20)	112.1(1)	Zr(1) - C(28) - Si(1)	134.4(1)

Table 5. Selected Bond Distances (Å) and Angles (deg) for $Zr(N_2^{ArF})(NMe_2)$ (33)

		(33)	
Zr(1) - N(1)	2.231(5)	Zr(1) - N(2)	2.280(5)
Zr(1) - N(3)	2.198(4)	Zr(1) - N(4)	2.725(4)
Zr(1) - N(5)	2.038(5)	Zr(1) - O(1)	2.471(4)
Zr(1) - O(3)	2.322(4)	Zr(1) - O(5)	2.365(4)
S(1) - O(1)	1.467(4)	S(1) - O(2)	1.441(4)
S(2) - O(3)	1.481(4)	S(2) - O(4)	1.437(4)
S(3)-O(5)	1.482(4)	S(3)-O(6)	1.430(4)
Zr(1) - N(1) - S(1)	101.9(2)	Zr(1) - N(1) - C(3)	127.3(4)
S(1)-N(1)-C(3)	119.3(4)	Zr(1) - N(2) - S(2)	96.3(2)
Zr(1) - N(2) - C(5)	124.6(4)	S(2) - N(2) - C(5)	117.8(4)
Zr(1) - N(3) - S(3)	102.4(2)	Zr(1) - N(3) - C(7)	132.7(4)
S(3) - N(3) - C(7)	124.8(4)	Zr(1) - N(5) - C(1)	131.3(4)
Zr(1) - N(5) - C(2)	119.2(4)	C(1) - N(5) - C(2)	109.5(5)

angles subtended at N(5) = $360(1)^{\circ}$) as expected due to $2p_{\pi}-4d_{\pi}$ bonding interactions,^{79–82} and the Zr–NMe₂ distance of

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2.038(5) Å is within the usual general ranges.⁸⁶ A more detailed comparison of 33 can be made with Scott's structurally authenticated tris(amido)amine complexes Zr{N(CH2- CH_2NR_3 (NMe₂) (R = SiMe₂^tBu or 2,4,6-C₆H₂Me₃), having more "innocent" (or conventional) N-substituents than the sulforyl groups in $N_3^{SO2R}N$.^{87,88} In these compounds the five-coordinate Zr atoms have trigonal-bipyramidal geometries with average Zr-NR distances to the tren amide donors of ca. 2.116 Å in each case. These are considerably shorter than in 33 (av $Zr-N_{ArF} = 2.236(3)$, range 2.198(4)-2.280(5) Å). This reflects both the electron-withdrawing nature of the sulfonyl groups (as noted elsewhere⁶⁸) and the higher coordination number in the case of 33. Despite this higher coordination number, the $Zr-NMe_2$ distance (2.038(5)) Å) is marginally shorter that in $Zr{N(CH_2CH_2NR)_3}(NMe_2)$ (2.063(2) and 2.044(3) Å).

The $\kappa^2(N,O)$ coordination of the sulfonamide groups in **30** and **32–34** is well precedented in the literature for transition and main group metals in general.^{74,76,89–91} With regard to zirconium, three related sulfonamide complexes have been structurally authenticated previously. These are $Zr(CyN_2^{Ts})$ -(NMe₂)₂(NHMe₂) (the analogue of **25** and **26** possessing two $\kappa^2(N,O)$ -bound –NTs donors and a trigonal-bipyramidal Zr),⁸⁹ Zr(O₂N^{Ts}N^{Dy})(NMe₂)₂ (one $\kappa^1(N,O)$ and one $\kappa^2(N,O)$ –NTs), and Zr(O₂N^{Ts}N^{OMe})(NMe₂)₂ (two $\kappa^1(N,O)$ –NTs)).⁶⁸ The Zr–NSO₂R distances in **30** and **32–34** are comparable to those in these previous examples. As noted previously, the S=O distances of the bridging sulfonyl oxygens in **30** and **32–34** are significantly longer than for the terminal ones.

As mentioned, the N atom of the NMe₂ ligand in **33** is trigonal planar (sum of the angles subtended at N(5) 360-(1)°), which is the usual case for early transition metal amide ligands.⁸⁰ In contrast, the angles subtended at the sulfonamide donor nitrogens in the four complexes **30** and **32–34** are much more varied, spanning the range 336(1)–360(1)°. Such behavior has been seen elsewhere in the literature (e.g., for Zr(CyN₂^{Ts})(NMe₂)₂(NHMe₂) the corresponding sums of angles are 340° and 357°) and may reflect the diminished $2p_{\pi}-4d_{\pi}$ bonding in sulfonamides compared to conventional amide ligands. In general, across the four structures, there is no overall correlation between Zr–NSO₂R distance and degree of pyramidalization of the respective nitrogen.

and degree of pyramidalization of the respective nitrogen. At first sight, it is not clear why $Zr(N_3^{ArF}N)(NMe_2)$ (33) is so moisture sensitive compared to the alkyls $Zr(N_3^{R}N)$ -(CH₂SiMe₃) (30–32), readily eliminating HNMe₂. For example, 33, 30, and 32 all contain coordinatively saturated, eight-coordinate metals centers and, as mentioned, the $Zr-NMe_2$ bond length in 33 is normal. One reason might be connected with the aforementioned distortions of the sulfonamide donor nitrogens from planarity. Although the average $Zr-NSO_2R$ distances in 30 and 32-34 are very similar (range of averages 2.224–2.241 Å) and comparable to those in 6 and 8 (av 2.238 Å), the sulfonamide nitrogens in 33 appear to be somewhat more distorted from planarity (av

sum of angles at $NSO_2R = 348^\circ$) than in the other compounds (range of averages $354-360^{\circ}$). In particular N(1) and N(2) (sum of angles $348(1)^{\circ}$ and $336(1)^{\circ}$), which lie in the pentagonal-bipyramid equatorial plane of 33, are particularly distorted. In the μ -oxo hydrolysis product, 34, the sums of the angles at NSO₂Ar^F (351(1)-360(1)°) again lie in the normal range. We propose that the relief of this distortion on going from 33 to 34 might provide a thermodynamic driving force for hydrolysis and that the distortion is partially driven by effective $2p_{\pi} \rightarrow 4d_{\pi} \pi$ -donation from the NMe₂ ligand into the remaining $4d_{\pi}$ acceptor orbital of the eight-coordinate metal center. The NSO₂Ar^F distortions from planarity would relieve unfavorable filled-orbital-filled-orbital interactions between the strongly π -donating NMe₂ lone pair and (more weakly) π -donating sulfonamide nitrogens. Such π donating ligand conflicts are well recognized in early metal chemistry.^{80,81}

Although the alkyls $Zr(N_3^RN)(CH_2SiMe_3)$ (30–32) have complex structures in the solid state, the solution NMR spectra in the range 20–40 °C are relatively simple, indicative of monomeric, C_3 -symmetric species in solution (or dimeric structures in the fast exchange regime). Cooling these solutions leads to more complex spectra. The NMR spectra of 33 and 34 are consistent with the solid-state structures, indicating C_3 and C_1 molecular symmetry, respectively.



As mentioned, metal-alkoxide compounds are superior initiators compared to their amide and alkyl counterparts due to more favorably balanced rates of initiation and propagation for the former. Since zirconium alkoxides of the type $Zr(N_3^R N)(O^i Pr)$ were not accessible from the protioligands H₃N₃^RN and Zr(OⁱPr)₄·ⁱPrOH (vide supra), we attempted to prepare them by protonolysis starting from the alkyl or amide compounds 30-33. As shown in eq 5 for $Zr(N_3^{Ts}N)(CH_2SiMe_3)$ (30), reaction with ⁱPrOH on the NMR scale in C_6D_6 quantitatively yielded the corresponding alkoxide species $Zr(N_3^{Ts}N)(O^{1}Pr)$ (35). Likewise, reaction of one equivalent of ArOH with $Zr(N_3^{ArF}N)(NMe_2)$ (33) on the NMR scale in C_6D_6 gave the aryloxide species $Zr(N_3^{ArF}N)$ -(OAr) (Ar = 2,6-C₆H₃Me₂) (**36**). However, once again with these π -donor alkoxide/aryloxide ligands the compounds were difficult to obtain pure on the preparative scale. For the purposes of the ROP studies discussed below we therefore generated the isoproposides $Zr(N_3^RN)(O^iPr)$ in situ from the well-defined alkyl compounds. In situ generation of alkoxide initiators from stable alkyl or related intermediates has been widely employed in the literature.^{17,22,92-98}

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Table 6. Solution Polymerization of ε -CL by Ti(N ₂ ^{Ms} N ^{OMe})(NMe ₂) ₂ (18), Ti(N ₂ ^{Ts} N ^{Ph})(NMe ₂) ₂ (19), Ti(N ₂ ^{Ms} N ^{Ph})(NMe ₂) ₂ (20),
$Ti(N_{2}^{Ts}N^{Ph})(O^{i}Pr)(NMe_{2}) (24), Ti(N_{2}^{Ms}N^{OMe})(O^{i}Pr)_{2} (21), Ti(N_{2}^{Ts}N^{Ph})(O^{i}Pr)_{2} (22), Ti(N_{2}^{Ms}N^{Ph})(O^{i}Pr)_{2} (23), Ti(CyN_{2}^{Ts})(O^{i}Pr)_{2} (23), Ti(N_{2}^{Ms}N^{OMe})(O^{i}Pr)_{2} (23$
(25), and Ti(CvN ₂ ^{SO₂Mes)} ($O^{i}Pr$) ₂ (26) ^{<i>a</i>}

entry	initiator	yield $(\%)^b$	time (h)	$k_{\rm app} ({\rm min}^{-1})$	$M_{\rm n}({ m GPC})^c$	$M_{\rm n}({\rm calcd})^d$	$M_{\rm w}/M_{\rm n}$	ref
1	$Ti(N_2^{Ts}N^{OMe})(NMe_2)_2$ (29)	95	22	е	14 260	5750	1.60	68
2	$Ti(N_2^{Ms}N^{OMe})(NMe_2)_2$ (18)	83	8	е	12650	5750	1.46	f
3	$Ti(N_2^{Ts}N^{Ph})(NMe_2)_2(19)$	90	6	е	12010	5750	1.35	f
4	$Ti(N_2^{Ms}N^{Ph})(NMe_2)_2$ (20)	94	4	0.005(3)	11050	5750	1.39	f
5	$Ti(N_2^{Ts}N^{Ph})(O^iPr)(NMe_2)$ (24)	90	4	0.0130(4)	12370	5770	2.08	f
6	$Ti(N_2^{Ts}N^{py})(O^iPr)_2$ (7)	97	9	0.007(1)	5720	5770	1.80	68
7	$Ti(N_2^{Ts}N^{OMe})(O^iPr)_2$ (5)	87	1	0.065(3)	6390	5770	1.39	68
8	$Ti(N_2^{Ms}N^{OMe})(O^iPr)_2$ (21)	89	3	0.023(1)	7390	5770	1.57	f
9	$Ti(N_2^{Ts}N^{Ph})(O^{Pr})_2(\tilde{22})$	96	1.5	0.042(2)	6370	5770	1.73	f
10	$Ti(N_2^{Ms}N^{Ph})(O^iPr)_2$ (23)	94	0.5	0.105(8)	6500	5770	1.41	f
11	$Ti(CvN_2^{Ts})(O^iPr)_2$ (25)	96	0.2	0.510(30)	5080	5770	1.28	f
12	$Ti(CvN_2^{SO_2Mes})(O^iPr)_2$ (26)	91	1	0.039(2)	12640	5770	1.87	f

^{*a*} Data for the previously studied compounds are given for comparison.⁶⁸ Conditions: [ϵ -CL]:[initiator] = 100:1, 6.8 mL of toluene at 100 °C. See Experimental Section for other details. ^{*b*} Isolated yield at 100% NMR conversion. ^{*c*} Molecular weights (g mol⁻¹) determined from GPC using the appropriate Mark–Houwink corrections. ^{*d*} Expected M_n (g mol⁻¹) for two chains growing per initiator at 100% conversion. ^{*e*} Not determined. ^{*f*} This work.

 $\begin{array}{l} \text{Table 7. Solution Polymerization of } \varepsilon\text{-CL by } Zr(N_3^{\ Ts}N)(CH_2SiMe_3)\ (30), \\ Zr(N_3^{\ Ms}N)(CH_2SiMe_3)\ (31), \\ Zr(N_3^{\ ArF}N)(CH_2SiMe_3)\ (32), \\ \text{and } Zr(N_3^{\ ArF}N)(NMe_2)\ (33)^a \end{array}$

entry	initiator	co-initiator	yield $(\%)^b$	time (h)	$k_{\text{app.}} (\min^{-1})$	$M_{\rm n}({ m GPC})^c$	$M_{\rm n}({\rm calcd})^d$	$M_{ m w}/M_{ m n}$	ref
1	$Zr(N_3^{Ts}N)(CH_2SiMe_3)$ (30)		91	1	0.11(1)	22 270	11 500	1.39	е
2	$Zr(N_3^{Ms}N)(CH_2SiMe_3)$ (31)		96	1	0.057(1)	15090	11 500	1.33	е
3	$Zr(N_3^{ArF}N)(CH_2SiMe_3)$ (32)		93	1.5	f $($	17600	11 500	1.19	е
4	$Zr(N_3^{ArF}N)(NMe_2)$ (33)		92	1.4	0.069(1)	13720	11450	1.45	е
5	$Zr(N_2^{Ts}N^{OMe})(O^iPr)_2$ (6)		93	1	0.121(4)	7770	11470	1.18	68
6	$Zr(N_2^{Ts}N^{py})(O^{i}Pr)_2(8)$		91	1	0.108(5)	5180	11470	1.19	68
7	$Zr(N_3^{Ts}N)(CH_2SiMe_3)$ (30)	ⁱ PrOH	96	0.9	0.071(1)	11630	11470	1.17	е
8	$Zr(N_3^{Ms}N)(CH_2SiMe_3)$ (31)	ⁱ PrOH	96	0.7	0.093(2)	10850	11,470	1.16	е
9	$Zr(N_3^{ArF}N)(CH_2SiMe_3)$ (32)	ⁱ PrOH	89	0.6	f ()	11 280	11,470	1.18	е

^{*a*} Data for the previously studied compounds are given for comparison.⁶⁸ Conditions: [ϵ -CL]:[initiator] = 100:1, 6.8 mL of toluene at 100 °C. See Experimental Section for other details. ^{*b*} Isolated yield at 100% NMR conversion. ^{*c*} Molecular weights (g mol⁻¹) determined from GPC using the appropriate Mark–Houwink corrections. ^{*d*} Expected M_n (g mol⁻¹) for one chain growing per initiator at 100% conversion. ^{*e*} This work. ^{*f*} Neither first nor second order in ϵ -CL.

Ring-Opening Polymerization of *e*-Caprolactone. A principal aim of this work was to determine the effect of structural variations of poly(sulfonamide)amine-supported group 4 complexes on the ROP of *ɛ*-CL and *rac*-LA. The titanium amide and alkoxide complexes 18-26, the zirconium alkyl and amide complexes 30-33, and the corresponding *in situ* generated zirconium isopropoxide complexes were evaluated. Polymerizations were performed in toluene at 100 °C so as to allow direct comparison with the bis(sulfonamide)amine initiators 5-8 and 29 previously investigated.^{68,69} The progress of each reaction was monitored by regular sampling, and the results summarized in Tables 6 and 7 correspond to the point at which the polymerizations eventually reached 100% conversion. The molecular weights and PDIs were determined by GPC using the appropriate Mark-Houwink corrections,⁹⁹⁻¹⁰¹ and the stated yields refer to the amount of poly(ε -CL) isolated. The M_n (calcd) values are those expected for either one or two polymer chains growing per initiator at 100% conversion of monomer. The results for titanium and zirconium are discussed in turn.

Titanium Initiators. Table 6 lists the results for the ROP of ε -CL using the new titanium initiators. The results pre-viously obtained with Ti(N₂^{Ts}N^{OMe})(NMe₂)₂ (**29**), Ti(N₂^{Ts}-N^{OMe})(OⁱPr)₂ (**5**), and Ti(N₂^{Ts}N^{py})(OⁱPr)₂ (**7**) are given for comparison. Of the nine new titanium initiators studied, the bis(dimethylamide) systems 18-20 were the slowest (entries 2–4). The GPC data are indicative of only one $poly(\varepsilon-CL)$ chain forming per metal on average $(M_n(\text{GPC}) = 11050 - 12650 \text{ g mol}^{-1} \text{ vs } M_n(\text{calcd}) = 11450 \text{ g mol}^{-1})$, consistent with the six-coordinate bis(dimethylamide) complexes studied previously (cf. entry 1 (**29**)).⁶⁸ The polymerization is relatively well controlled, as indicated by PDIs in the range 1.35-1.46 and good agreement between found and calculated $M_{\rm n}$ (assuming one chain per metal). In order to evaluate these bis(dimethyl)amide initiators further, the most efficient one (20, entry 4) was monitored throughout the course of polymerization. The consumption of monomer followed first-order kinetics, and a reasonably linear plot of $M_{\rm p}({\rm GPC})$ vs percent conversion was obtained (see the Supporting Information). There was also an induction period of around 60 min, as expected, 22,53,102 owing to the slow first ε -CL insertion into the Ti-NMe₂ bond.

The apparent first-order rate constant (k_{app}) of 0.005(3) s⁻¹ for the ROP using **20** is 200 times less than that for the

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Figure 8. First-order plot for ε -CL consumption using Ti- $(N_2^{Ts}N^{Ph})(O^{i}Pr)_2$ (22). Conditions: $[\varepsilon$ -CL₀]:[22] = 100:1, 6.8 mL of toluene, 100 °C, 0.1 mL aliquots taken at the given intervals. See Experimental Section for other details. Linear fit (r^2 = 0.995) shown is for the first-order region after the induction period.



Figure 9. Plots of M_n and PDI (determined by GPC) vs conversion for the ROP of ε -CL using Ti(N₂^{Ts}N^{Ph})(OⁱPr)₂ (22). Conditions: [ε -CL₀]:[22] = 100:1, 6.8 mL of toluene, 100 °C, 0.1 mL aliquots taken at the given intervals. Hollow diamonds correspond to M_n and hollow circles to PDI.

corresponding bis(isopropoxide) initiator (**23**, entry 10) with the same supporting ligand. This would suggest that the spectator NMe₂ in the propagating species Ti(N₂^RN^X)-(NMe₂){poly(ϵ -CL)} has a detrimental effect on the rate on ϵ -CL insertion into the Ti–OCH₂ bond of the growing polymeryl chain. This is attributed to a combination of steric and strong π -donation effects of NMe₂ (inhibiting monomer coordination) in comparison with those from a second growing polymeryl chain (i.e., the situation found starting from the bis(isopropoxide) initiators). The slower rates of propagation for the bis(dimethylamide) systems **18–20** compared to their bis(isopropoxide) analogues (**21–23**, entries 8–10) parallels the behavior of the six-coordinate initiators **29** and **5** (entries 1 and 7) reported previously.⁶⁸

To test this interpretation further, the mixed isopropoxide bis(dimethylamide) complex Ti(N₂^{Ts}N^{Ph})(OⁱPr)(NMe₂) (**24**, entry 5) was also evaluated. The measured M_n was in close agreement with one polymeryl chain growing per metal center. The ¹H NMR spectrum of the poly(ε -CL) was dominated by $-O^{i}$ Pr end groups, consistent with preferred initial insertion into the Ti $-O^{i}$ Pr bond of **24**. The MALDI-ToF-MS spectra were also consistent with this, but also showed a minor distribution indicative of amide initiation (see the Supporting Information). When the polymerization process was followed by regular sampling, it was found that ROP using **24** had an induction period of ca. 30 min (see the Supporting Information), which is significantly shorter than that for the related bis(amide) **20**. However the bis(alkoxide) analogue **22** showed a negligible induction period of ca. 10 min (Figure 8). Consistent with the apparent detrimental effect of a spectator NMe₂ group, the propagation rate constant for **24** of 0.0130(4) s⁻¹ was significantly slower than for the otherwise identical **22** ($k_{app} = 0.042 \text{ s}^{-1}$, entry 9). As had been observed previously for **5** and **7** (entries 7 and

6),⁶⁸ changing from the bis(amide) initiators to the corresponding bis(alkoxides) (entries 8-12) gives a clear switch from ca. one to ca. two $poly(\varepsilon-CL)$ chains per metal center and also a significant increase in activity. The behavior of all these bis(alkoxides) was investigated in detail (see Figures 8 and 9 for representative plots and the Supporting Information for remaining plots; k_{app} values are given in Table 6). All the initiators showed a fairly short induction period followed by a polymerization process that was first order with respect to ε -CL concentration (Figure 8). Similar induction periods have been observed for main group and transition metal isopropoxide initiators.^{22,53,102} Linear relationships between $M_{\rm n}$ and percent conversion were found, and in the case of $Ti(CyN_2^{Ts})(O^iPr)_2$ (25, entry 11) there was excellent agreement between the measured and predicted $M_{\rm n}$ (5080 vs 5720 g mol⁻¹) and the PDI was only 1.28. Compound **25** was also the fastest initiator, with an induction period of just 2 min, and polymerized 100 equiv of ε -CL to completion within 10 min after the induction period.

There are some fairly well-defined relationships between bis(sulfonamide) supporting ligand type and the rates of polymerization. For a given sulfonyl substituent $-SO_2R$, moving from a tetradentate ligand ($N_2^R N^{OMe}$ or $N_2^R N^{py}$) to a tridentate one generally gave a noticeable increase in activity (cf. **29** vs **19**; **18** vs **20**; **21** vs **23**) and also a narrower PDI and better agreement between measured and predicted M_n . An apparent exception is **5** vs **22** ($N_2^{Ts}N^{OMe}$ vs N_2^{Ts} - N^{Ph}), where the latter was slightly slower and had a poorer PDI. On the other hand, **22** is certainly much faster than the previously reported **7** ($N_2^{Ts}N^{Ph}$ vs $N_2^{Ts}N^{py}$), the latter having the better (pyridyl) donor. Compound **25** was the fastest of all the *N*-tosyl sulfonamide initiators (**7**, **5**, **22**, **25**). Although **25** is not formally four-coordinate, since both $-NSO_2Ts$ donors have $\kappa(N,O)$ bidentate coordination, ⁷⁶ the change from the bis(sulfonamide)amine ligands $N_2^{Ts}N^R$ to CyN_2^{Ts}

For a given ligand type $(N_2^R N^{OMe}, N_2^R N^{Ph}, CyN_2^R)$ there are also some reasonably consistent relationships between activity and sulfonyl substituent $-SO_2R$ (R = Tol, Me, or Mes). The most noticeable differences are between **25** and **26** $(CyN_2^{Ts} vs CyN_2^{SO_2Mes})$ in terms of improved activity (k_{app} of 0.510(3) and 0.039(2) s⁻¹) and a narrower PDI in the case of **25**. Furthermore, the measured M_n values of 5080 and 12 640 g mol⁻¹ show that the greater steric constraints associated with $CyN_2^{SO_2Mes}$ prevent the formation of two polymer chains per metal center. Comparison of **19** and **20**, and **22** and **23** $(N_2^{Ts}N^{Ph} vs N_2^{Ms}N^{Ph})$ shows a smaller increase in activity on changing from $-SO_2$ Tol to $-SO_2Me$, which may also be due to steric factors. Comparison of **29** and **18** $(N_2^{Ts}N^{OMe} vs N_2^{Ms}N^{OMe})$ also reveals an increase in activity on changing from $-SO_2$ Tol to $-SO_2Me$. In contrast, comparing **5** and **21** with the same $N_2^{Ts}N^{OMe}$ and $N_2^{Ms}N^{OMe}$ ligands revealed that **21** was the slowest with somewhat poorer control.

Zirconium Initiators. The zirconium complexes Zr- $(N_3^{Ts}N)(CH_2SiMe_3)$ (**30**), Zr $(N_3^{Ms}N)(CH_2SiMe_3)$ (**31**), Zr- $(N_3^{ArF}N)(CH_2SiMe_3)$ (**32**), and Zr $(N_3^{ArF}N)(NMe_2)$ (**33**)

 $\begin{array}{l} \text{Table 8. Solution Polymerization of } rac\text{-Lactide by } \text{Ti}(N_2^{\ Ts}N^{OMe})(O^iPr)_2 \ (5), \ \text{Ti}(N_2^{\ Ts}N^{py})(O^iPr)_2 \ (7), \ \text{Ti}(N_2^{\ Ts}N^{Ph})(O^iPr)_2 \ (22), \ \text{Ti}(N_2^{\ Ms}N^{Ph})(O^iPr)_2 \ (23), \ \text{Ti}(CyN_2^{\ Ts})(O^iPr)_2 \ (25), \ \text{and} \ \text{Ti}(CyN_2^{\ SO_2Mes})(O^iPr)_2 \ (26)^a \end{array}$

entry	initiator	co-initiator	conversion $(\%)^b$	time (h)	$k_{\rm app} ({\rm h}^{-1})$	$M_{\rm n}({ m GPC})^c$	$M_{\rm n}({\rm calcd})^d$	$M_{ m w}/M_{ m n}$	ref
1	$Ti(N_2^{Ts}N^{OMe})(O^iPr)_2$ (5)		90	24	е	8990	6540	1.21	f
2	$Ti(N_2^{Ts}N^{py})(O^iPr)_2(7)$		73	24	е	7230	5320	1.16	f
3	$Ti(N_2^{Ts}N^{Ph})(O^iPr)_2$ (22)		71	11	0.119(4)	7900	5160	1.13	f
4	$Ti(N_2^{Ms}N^{Ph})(O^iPr)_2$ (23)		44	2	0.29(2)	3980	3230	1.09	f
5	$Ti(CvN_2^{Ts})(O^iPr)_2$ (25)		32	4	0.11(1)	3620	2370	1.16	f
6	$Ti(CyN_2^{SO_2Mes})(O^iPr)_2 (26)$		46	4	0.15(1)	4880	3370	1.22	f

^{*a*} Conditions: [*rac*-LA]:[initiator] = 100:1, 6.8 mL of toluene at 70 °C. See Experimental Section for other details. ^{*b*} NMR conversion. ^{*c*} Molecular weights (g mol⁻¹) determined from GPC using the appropriate Mark–Houwink corrections. ^{*d*} Expected M_n (g mol⁻¹) for two chains growing per initiator at the given conversion. ^{*e*} Not determined. ^{*f*} This work.

Table 9. Solution Polymerization of *rac*-Lactide by $Zr(N_3^{Ts}N)(CH_2SiMe_3)$ (30), $Zr(N_3^{Ms}N)(CH_2SiMe_3)$ (31), $Zr(N_3^{ArF}N)(CH_2SiMe_3)$ (32), and $Zr(N_3^{ArF}N)(NMe_2)$ (33)^{*a*}

entry	initiator	co-initiator	conversion $(\%)^b$	time (h)	$k_{\rm app} ({\rm h}^{-1})$	$M_{\rm n}({ m GPC})^c$	M_n (calcd) ^d	$M_{\rm w}/M_{\rm n}$	ref.
1	$Zr(N_2^{Ts}N^{OMe})(O^iPr)_2$ (6)		94	6	0.468(2)	8290	13610	1.15	68
2	$Zr(N_3^{Ts}N)(CH_2SiMe_3)$ (30)		84	61	0.033(2)	23 690	12190	1.19	е
3	$Zr(N_3^{Ms}N)(CH_2SiMe_3)$ (31)		83	65	0.021(1)	18920	12050	1.38	е
4	$Zr(N_3^{ArF}N)(NMe_2)$ (33)		66	66	0.018(1)	29 260	9550	1.19	е
5	$Zr(N_3^{Ts}N)(CH_2SiMe_3)$ (30)	ⁱ PrOH	96	20	0.154(2)	14 340	13890	1.08	е
6	$Zr(N_3^{Ms}N)(CH_2SiMe_3)$ (31	ⁱ PrOH	95	24	0.170(3)	15600	13750	1.11	е
7	$Zr(N_3^{ArF}N)(CH_2SiMe_3)$ (32)	ⁱ PrOH	89	24	0.134(4)	13 005	12880	1.08	е

^{*a*} Data for the previously studied compound **6** are given for comparison.⁶⁸ Conditions: [*rac*-LA]:[initiator]:[co-initiator] = 100:1:1, 6.8 mL of toluene at 70 °C. See Experimental Section for other details. ^{*b*} NMR conversion. ^{*c*} Molecular weights (g mol⁻¹) determined from GPC using the appropriate Mark–Houwink corrections. ^{*d*} Expected M_n (g mol⁻¹) for one chain growing per initiator at the given conversion. ^{*e*} This work.

were also all evaluated for the ROP of ε -CL. *In situ* generation of zirconium alkoxides was performed by reaction of Zr(N₃^RN)(CH₂SiMe₃) with ⁱPrOH immediately prior to monomer addition. The results are summarized in Table 7, along with the corresponding data for the previously reported bis(sulfonamide)amine-supported initiators Zr(N₂^{Ts}N^{OMe})-(OⁱPr)₂ (6) and Zr(N₂^{Ts}N^{Py})(OⁱPr)₂ (8). Plots of monomer conversion vs time and the corresponding first-order kinetic plots, and plots of M_n and PDI vs conversion, are given in the Supporting Information for all four initiators.

Entries 1-4 of Table 7 show the ROP results for 30-33 in the absence of ⁱPrOH co-initiator. As expected for metalalkyl and -amide initiating groups, the experimental $M_{\rm p}$ values $(13720-22270 \text{ g mol}^{-1})$ are all somewhat higher than expected at 100% conversion of monomer (11 410 g mol⁻¹) and one chain growing per inititing group, and the PDIs are moderately broad. Despite the higher than expected $M_{\rm n}$ values, the $M_{\rm n}$ (GPC) vs conversion plots show good linearity. This may indicate that there is some instability of the preinitiators (or some other reason for not all the complexes initiating ROP), but once they enter the catalytic cycle, the polymerization proceeds in a living fashion. The MAL-DI-ToF mass spectra of the poly(ε -CL)s showed the presence of the expected CH₂SiMe₃ or NMe₂ end-groups. For 32 the consumption of ε -CL was neither first nor second order, whereas that for the amide homologue 33 did follow firstorder kinetics (see the Supporting Information). Compound 30 showed an induction period of ca. 20-30 min, whereas 31 and 32 had shorter ones. The induction period for 33 of ca. 20-30 min is consistent with Zr-NMe₂ being a less efficient initating group than Zr-CH₂SiMe₃, and the broader PDI for the poly(ε -CL) formed with 33 (1.45 vs 1.19 with 32) also supports this assertion.

Entries 7–9 of Table 7 show the effects of adding 1 equiv of ⁱPrOH co-initiator to **30–32** prior to introducing the ε -CL. As expected, this had a beneficial effect on several aspects of the ROP. The induction periods were all reduced (Zr-O'Pr being a more efficient initiating group than CH₂SiMe₃ or NMe₂), and consequently, the PDIs of the polymers were also narrower (range 1.16-1.18). The experimental M_n values (10850-11630 g mol⁻¹) were also in much better agreement with the calculated ones $(11470 \text{ g mol}^{-1})$. The ¹H NMR and MALDI-ToF mass spectra of the polymers showed the expected $-O^{i}Pr$ chain ends. There was no specific effect on the apparent propagation rate constant compared to the ⁱPrOH-free systems. This is as expected since the propagating species $Zr(N_3^R N) \{ poly(\varepsilon - CL) \}$ are indentical for each N₃^RN ligand (except for the polymeryl chain end). For $32 + {}^{i}$ PrOH the consumption of ε -CL was once again neither first nor second order. Whereas Zr- $(N_3^{ArF}N)(CH_2SiMe_3)$ (32) + ⁱPrOH gave poly(ϵ -CL) with exclusively -OⁱPr chain ends, initial results showed that use of $Zr(N_3^{\text{ÅrF}}N)(NMe_2)$ (33) + ⁱPrOH gave polymers with both -NMe₂ and -OⁱPr end-groups. Since NMR tube studies showed that 33 was immediately and quantitatively convered to the corresponding isopropoxide complex, the -NMe₂-terminated polymer may arise through an activated monomer mechanism (initiated by HNMe₂), as we have discussed recently.103

Although the ROP activity using 30-32 (with or without co-initiator) was fairly efficient for a group 4 system in general,¹¹ there was no improvement on the previous systems 6 and 8 (entries 5 and 6) as judged by the propagation rate constants. Furthermore, the activities of 30-32 are not significantly better on average than the five-coordinate titanium initiators 22 and 23. At first sight this seems surprising, given the results of Kol and Davidson with the tris(phenolate)amine systems 4 (Figure 1, *vide supra*).^{57,59} However, the solid-state structures of 30, 32, and 33 show that the systems $Zr(N_3^RN)X$ (X = alkyl, amide, alkoxide) are not five-coordinate analogues of 4, and in fact all possess eight-coordinate metal centers (and

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Figure 10. First-order plot for *rac*-LA consumption using Zr- $(N_3^{Ms}N)(CH_2SiMe_3)$ (**31**) with ⁱPrOH co-initiator. Conditions [*rac*-LA₀]:[**31**]:ⁱPrOH = 100:1:1, 6 mL of toluene, 70 °C, 0.1 mL aliquots taken at the given intervals. See Experimental Section for other details. Linear fit ($r^2 = 0.998$).



Figure 11. Plots of M_n and PDI (determined by GPC) vs conversion for the ROP of *rac*-LA using $Zr(N_3^{Ms}N)(CH_2SiMe_3)$ (**31**) with ⁱPrOH co-initiator. Conditions: [rac-LA₀]:[**31**]:ⁱPrOH = 100:1:1, 6.0 mL of toluene, 70 °C, 0.1 mL aliquots taken at the given intervals. Hollow diamonds correspond to M_n and hollow circles to PDI.

indeed might be dimeric under polymerization conditions, although this seems less likely). The ability of the $-NSO_2R$ donors to act as bidentate $\kappa(N,O)$ donors saturates the zirconium coordination spheres, and presumably one or more sulfonamide groups need to change to a monodentate coordination mode to accept the incoming ε -CL prior to insertion into the growing Zr-polymeryl chain.

Ring-Opening Polymerization of *rac*-Lactide. Polymerization studies with *rac*-LA were carried out in toluene at 70 °C as for the previously studied complex $Zr(N_2^{Ts}N^{OMe})(O^{i}Pr)_2$ (6).⁶⁸ Reactions were monitored by regular sampling for the determination of *rac*-LA conversion and experimental M_n values. The data are summarized in Tables 8 and 9 for a number of titanium and zirconium initiators, respectively. Some representative plots using $Zr(N_3^{Ms}N)(CH_2SiMe_3)$ (31) with ⁱPrOH co-initiator are given in Figures 10 and 11 and will be discussed below. Further details are given in the Supporting Information (conversion vs time, M_n and PDI vs conversion, and first-order log plots).

Titanium Initiators. Table 8 summarizes the ROP performance of a number of titanium bis(isopropoxide) complexes.

Of the new titanium compounds reported herein, the fiveand four-coordinate initiators 22, 23, 25, and 26 were chosen for rac-LA since these had demonstrated the best behavior for the ROP of ε -CL. Table 8 also gives ROP data for the pre-viously reported Ti(N₂^{Ts}N^{OMe})(OⁱPr)₂ (5) and Ti(N₂^{Ts}N^{py})- $(O^{i}Pr)_{2}$ (7) for comparison (entries 1 and 2) since these had not been included in our earlier studies. These two sixcoordinate compounds gave 90% and 73% conversion of 100 equiv of LA to poly(rac-LA) after 24 h. The polymers formed had reasonably narrow PDIs, although the experimental $M_{\rm n}$ values were somewhat higher than expected for two chains per initiator (i.e., one chain per Ti-OⁱPr bond). Analogous behavior was found previously for Zr(N2^{Ts}N^{OMe})- $(O^{i}Pr)_{2}(6)^{68}$ (Table 9, entry 1), with 7 achieving 94% conversion after 6 h (cf. 90% after 24 h for the titanium congener 5). The higher conversions achieved with 6 are consistent with literature trends and more facile access to the metal center for the larger metal. The lower conversion with 7 compared to 5 is in line with the ε -CL ROP results (Table 6, entries 6 and 7) and may reflect the stronger binding of the pyridyl pendant donor in 7. In all cases, the ¹H NMR and MALDI-ToF mass spectra showed the presence of -O'Pr chain ends. The MALDI-ToF spectra showed peak envelopes separated by m/z values of 72 (i.e., one-half of a LA unit), consistent with extensive transesterification, as was found with 6 previously. Disappointingly (as was also found for 6), all of the polymers produced were atactic $(P_{\rm r} \approx 0.50)$, as judged by the selectively homonuclear decoupled ¹H NMR spectra.¹⁰⁴

The five- and four-coordinate initiators 22, 23, 25, and 26 were apparently unstable for extended polymerization times (see the Supporting Information for detailed conversion vs time plots). Each compound initially catalyzed the well-controlled ROP of rac-LA, as judged by wellbehaved first-order kinetics, linear M_n vs time plots, and relatively narrow PDIs in the range ca. 1.1-1.2 (entries 3-6). All four gave polymers with M_n values slightly higher than expected for two chains growing per metal center (cf. compounds 5-7). However, after the times listed in Table 8 polymerization activity halted. Nonetheless, some structure--activity trends can be inferred from the data and the apparent propagation rate constants (k_{app}) listed in Table 8, which correspond to the kinetically well-behaved parts of the ROP process. As found for the ε -CL studies, changing from six-coordinate 5 and 7 to five-coordinate 22 and 23 $(N_2^R N^X)$ vs $N_2^{Ts}N^{Ph}$) gave an increase in activity (e.g., 73% and 71%) conversion after 24 and 11 h for 5 and 22, respectively) and reduction in PDI. Changing from 22 to 23 (-NSO₂Tol vs $-NSO_2Me$) also gave an increase in activity, as judged by $k_{\rm app}$, and again a decrease in PDI. However, there was surprisingly little difference between 25 and 26 (-NSO₂Tol vs $-NSO_2Mes$) in terms of chains per metal and rate, despite the different steric demands of the two CyN2^R ligands. Overall, in terms of rate, PDI, and agreement between found and predicted M_n the five-coordinate Ti(N₂^{Ms}N^{Ph})(OⁱPr)₂ (23) gave the best ROP performance, although the longerterm stability was poor (44% conversion when the ROP ceased after 2 h).

Zirconium Initiators. Table 9 summarizes the ROP results for **30**, **31**, and **33** (entries 2–4) and also the previously studied $Zr(N_2^{Ts}N^{OMe})(O^iPr)_2$ (6, entry 1), which, as mentioned,

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forms between one and two poly(*rac*-LA) chains per metal center with 94% conversion of 100 equiv of *rac*-LA after 6 h. As with the ε -CL study, the alkyl and amide complexes were active for ROP of *rac*-LA. Although the polymerization proceeded very slowly (66–84% conversion after 61–66 h) and formed poly(*rac*-LA) with much higher than expected M_n values, the M_n (GPC) vs percent conversion plots were fairly linear. This may indicate that there is some instability or side reactions of the complexes prior to initiation, but that once they have entered the catalytic cycle the polymerization proceeds in a living fashion, as had been observed for ε -CL. The MALDI-ToF mass spectra of low molecular weight polymer samples showed the expected –CH₂SiMe₃ or –NMe₂ end groups, as well as evidence of extensive transesterification, with peak envelopes of m/z = 72 apart.

As for the ε -CL studies, in situ generation of alkoxide initiators from 31-32 (entries 5-7) gave a much more efficient and better controlled polymerization process. Linear relationships between M_n and conversion were obtained that remained effectively constant throughout the reaction. (Figures 10 and 11 and the Supporting Information). The resulting polymers had extremely narrow PDIs (1.08-1.11), and there was very good agreement between experimental and predicted molecular weights. Consistent with this, the gradients of the M_n vs percent conversion plots were in the range $144(2)-159(4) \text{ g mol}^{-1}$ (% conversion)⁻¹, in agreement with that expected (144.1 g mol⁻¹ (% conversion)⁻¹) for one poly(*rac*-LA) chain growing per metal center. The MALDI-ToF mass spectra showed exclusively isopropoxide-terminated poly(rac-LA) chains with peak envelope separations of m/z = 72. Regrettably, all of the poly-(rac-LA)s produced with these initiators were atactic ($P_r \approx$ 0.5), as has been observed for all other poly(sulfonamide)supported group 4 and aluminum ROP initiators. All of these data are consistent with these species acting as initiators for the living ROP of *rac*-lactide. The k_{app} values show a dependence on the sulfonamide group with the general order of Ms $(31) > Ts (30) > Ar^{F}(32)$. This may indicate easier access of the monomer to metal center as steric demands of the sulfonyl S-substituent diminish. However, in comparison to six-coordinate 6, the alkoxide initiators derived from 30-32 were 3 to 4 times slower. This is consistent with the slightly slower rates found for 30-32 for ε -CL ROP (vide supra). Again, the bidentate $\kappa(N,O)$ coordination of the -NSO₂R donors presumably inhibits monomer coordination to the metal center.

Conclusion

In this contribution we have carried out systematic bis-(sulfonamide) ligand variations leading to improved ROP activity and control for the thermally robust group 4 complexes of these ligands. The new bis(dimethylamide) complexes $Ti(N_2^{Ms}N^{OMe})(NMe_2)_2$ (18), $Ti(N_2^{Ts}N^{Ph})(NMe_2)_2$ (19), and $Ti(N_2^{Ms}N^{Ph})(NMe_2)_2$ (20) were easily prepared under mild conditions from $Ti(NMe_2)_4$. Similarly, the bis-(isopropoxide) complexes $Ti(N_2^{Ms}N^{OMe})(O^iPr)_2$ (21), $Ti-(N_2^{Ts}N^{Ph})(O^iPr)_2$ (22), and $Ti(N_2^{Ms}N^{Ph})(O^iPr)_2$ (23) could be synthesized from $Ti(O^iPr)_2(NMe_2)_2$ and the appropriate protio-ligand. Reaction between an excess of $H_2N_2^{Ts}N^{Ph}$ and $Ti(O^iPr)_2(NMe_2)_2$ gave $Ti(N_2^{Ts}N^{Ph})(O^iPr)(NMe_2)$ (24). In accordance with our previous study, the amides were poorer initiators than the alkoxides toward the ROP of ε -CL. Certain structure–activity relationships were observed with titanium, with lower coordination number and less sterically encumbered ligands giving the most active and best controlled initiators. The previously reported $\text{Ti}(\text{CyN}_2^{\text{Ts}})$ - $(\text{O}^{\text{i}}\text{Pr})_2$ (25) was the most active initiator of those surveyed for the ROP of ε -CL. All of the titanium complexes were poor initiators for the ROP of *rac*-lactide, giving poor conversions (30–70%), although bulkier groups on a given ligand backbone generally gave higher conversions.

 C_3 -Symmetric zirconium initiators were also investigated. The protio-ligands $H_3N_3^RN$ reacted readily with Zr(CH₂-SiMe₃)₄ to form Zr(N₃^RN)(CH₂SiMe₃) (R = Ts (**30**), Ms (**31**), or Ar^{F} (**32**)). Reaction of $Zr(NMe_{2})_{4}$ with $H_{3}N_{3}^{ArF}N$ gave the corresponding amide complex $Zr(N_{3}^{ArF}N)(NMe_{2})$ (**33**), which was found to be highly moisture sensitive, giving ${Zr(N_3^{ArF}N)}_2(\mu$ -O) (34) in the presence of trace amounts of water. In situ protonolysis reactions with Zr(N3^{Ts}N)(CH2-SiMe₃) (30) or 33 yielded the corresponding alkoxide or aryloxide complexes. As has been observed elsewhere, the zirconium complexes generally provided more active ROP initiators than the titanium analogues, although $Ti(CyN_2^{Ts})$ - $(O^{i}Pr)_{2}$ was the most active of all those surveyed for ε -CL. In situ generation of alkoxide initiators from the zirconium alkyl complexes gave well-controlled rac-LA initiators with narrow polymer PDIs and good agreement between experimental and predicted M_n values. Of these compounds, the least bulky sulfonyl substituents yielded the most active initiator for rac-lactide. However, these initiators were generally found to be less active than the six-coordinate zirconium complexes investigated previously,⁶⁸ which is attributed to the saturating effects of the $\kappa^2(N,O)$ coordination.

Experimental Section

General Methods and Instrumentation. All manipulations were carried out using standard Schlenk line or drybox techniques under an atmosphere of argon or dinitrogen. Solvents were degassed by sparging with dinitrogen and dried by passing through a column of the appropriate drying agent. Toluene was refluxed over sodium and distilled. Deuterated solvents were dried over sodium (C6H6) or P2O5 (CDCl3 and CD2Cl2), distilled under reduced pressure, and stored under dinitrogen in Teflon valve ampules. NMR samples were prepared under dinitrogen in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. ¹H and ¹³C{¹H} NMR spectra were recorded on Varian Mercury-VX 300 and Varian Unity Plus 500 spectrometers at ambient temperature unless stated otherwise and referenced internally to residual protio-solvent (¹H) or solvent (¹³C) resonances and are reported relative to tetramethylsilane ($\delta = 0$ ppm). Assignments were confirmed using two-dimensional ¹H⁻¹H and ¹³C⁻¹H NMR correlation experiments. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. IR spectra were recorded on a Nicolet Magna 560 ESP FTIR spectrometer. Samples were prepared in a drybox as Nujol mulls between NaCl plates, and the data are quoted in wavenumbers (cm^{-1}) . Elemental analyses were carried out by the Elemental Analysis Service at the London Metropolitan University.

MALDI-ToF-MS analysis was performed on a Waters MALDI micro equipped with a 337 nm nitrogen laser. An accelerating voltage of 25 kV was applied. The polymer samples were dissolved in THF at a concentration of 1 mg mL⁻¹. The cationization agent used was potassium trifluoroacetate (Fluka, >99%) dissolved in THF at a concentration of 5 mg mL⁻¹. The matrix used was *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) (Fluka) and was dissolved in THF at a concentration of 40 mg mL⁻¹. Solutions of matrix, salt, and polymer were mixed in a volume ratio of 4:1:4, respectively. The mixed solution was hand-spotted on a stainless steel MALDI target and left to dry. The spectra were recorded in the refectron mode.

Polymer molecular weights (M_n, M_w) were determined by GPC using a Polymer Laboratories Plgel Mixed-D column (300 mm length, 7.5 mm diameter) and a Polymer Laboratories PL-GPC50 Plus instrument equipped with a refractive index detector. THF (HPLC grade) was used as an eluent at 30 °C with a rate of 1 mL min⁻¹. Linear polystyrenes were used as primary calibration standards, and Mark–Houwink corrections for poly(ε -CL) or poly(*rac*-LA) in THF were applied for the experimental samples.^{99–101}

Starting Materials. Ti(NMe₂)₄,^{105,106} Ti(NMe₂)₂(OⁱPr)₂,^{107,108} Zr(CH₂SiMe₃)₄,¹⁰⁹ Zr(NMe₂)₄,¹¹⁰ H₂CyN₂^{Ts},⁷¹ H₂CyN₂^{SO₂Mes,⁷²} H₃N₃^{Ts}N,⁷⁰ *N*-mesylaziridine,¹¹¹ H₂N₂^{Ts}N^{Ph},⁶⁹ H₂N₂^{Ms}N^{Ph,69} and *N*-tosylaziridine⁷⁵ were synthesized according to published procedures. ε -CL was dried over freshly ground CaH₂ and distilled before use. *rac*-LA was recrystallized twice from toluene and then sublimed twice prior to use. Other reagents were purchased from Sigma-Aldrich and used without further purification.

 $H_2N_2^{Ms}N^{OMe}$ (12). To a solution 1-(methylsulfonyl)aziridine (4.42 g, 0.036 mol) in EtOH (200 mL) at room temperature was added 2-methoxyethylamine (1.44 g, 0.017 mol) dropwise. The resulting orange solution was stirred at 40 °C for 16 h, filtered, and concentrated under reduced pressure. An analytically pure sample was obtained by column chromatography (SiO₂, eluent system ethyl acetate-pentane-NH₄OH(aq), 50:10:1) to give a light orange oil. Yield: 5.64 g (50%). ¹H NMR (CDCl₃, 293 K, 300.7 MHz): δ 3.40 (2H, t, ${}^{3}J = 4.9$ Hz, CH₂OMe), 3.10 (4H, t, ${}^{3}J = 5.4$ Hz, CH₂NHS), $3.36 (3H, s, OMe), \overline{2.90} (6H, s, SO_{2}Me),$ 2.68 (4H, t, ${}^{3}J = 5.4$ Hz, CH₂CH₂NHS), 2.60 (2H, t, ${}^{3}J = 4.9$ Hz, CH₂CH₂OMe). ¹³C{¹H} NMR (CDCl₃, 293 K, 75.4 MHz): δ 70.8 (CH₂CH₂OMe), 59.0 (OMe), 54.0 (CH₂CH₂NS), 52.8 (SO_2Me) , 42.0 (CH₂NHS), 40.0 (CH₂OMe). IR (KBr plates, Nujol mull cm⁻¹): 3285 (m), 3015 (w), 2847 (s), 2361 (w), 2340 (w), 1736 (w), 1718 (w), 1700 (w), 1684 (w), 1653 (m), 1645 (m), 1636 (m), 1559 (w), 1378 (s), 1199 (w), 1057 (m), 1012 (w), 973 (m), 769 (m), 668 (w), 523 (w). ES-HRMS: m/z = 318.1142

 $([M + 1]^+; \text{ calcd for } C_9H_{23}N_3O_5S_2 318.1157).$ H₃N₃^{Ms}N (14). To a solution of tris(2-aminoethyl)amine (25.2 g, 26.0 mL, 0.170 mol) and NaOH (22.0 g, 0.550 mol) in H₂O (100 mL) was added dropwise a solution of methanesulfonyl chloride (59.2 g, 40.0 mL, 0.520 mol) in diethyl ether (300 mL), and the mixture was stirred at RT for 2 h. The resulting solution was evaporated under reduced pressure, and the resulting white solid recrystallized from H₂O (30 mL) at 100 °C. The resulting white crystalline solid was filtered and dried in vacuo. Yield: 12.0 g (18%). ¹H NMR ((CD₃)₂SO, 299.8 MHz, 298 K): δ 7.00 (3H, br s, NH), 3.15 (6H, br s, $SNCH_2CH_2N$), 3.07 (9H, s, SO_2Me), 2.65 (6H, br s, $SNCH_2CH_2N$) ppm. ¹³C{¹H} NMR ((CD₃)₂SO, 75.4 MHz, 298 K): δ 67.8 (SNCH₂CH₂N), 65.5 (SNCH₂CH₂N), 54.7 (SO₂Me) ppm. IR (KBr plates, Nujol mull cm^{-T}): 3301 (m), 3242 (s), 3224 (s), 2725 (w), 1419 (w), 1348 (w), 1305 (s), 1261 (m), 1234 (w), 1224 (m), 1162 (s), 1137 (s), 1091 (m), 1068 (w), 1046 (w), 1026 (w), 1000 (w), 986 (m), 962 (s), 926 (m), 909 (w), 807 (m), 772 (s), 721 (w), 668 (w). ES-HRMS: m/z = 381.0926 $([M + H]^+; calcd for C_9H_{25}N_4O_6S_3 381.0936)$. Anal. Found (calcd for C₉H₂₄N₄O₆S₃): C, 28.41 (28.41); H, 6.43 (6.36); N, 14.65 (14.72).

 $H_3N_3^{ArFN}$ (15). To a solution of tris(2-aminoethyl)amine (2.34 g, 2.40 mL, 16.0 mmol) and NaOH (2.00 g, 34.2 mmol) in H₂O (105 mL) was added dropwise a solution of 3,5-bis-

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(trifluoromethyl)benzene sulfonyl chloride (15.00 g, 48.1 mmol) in diethyl ether (210 mL), and the mixture was stirred at RT for 2 h. The white solid that formed was filtered and washed with $H_2O(3 \times 15 \text{ mL})$ and diethyl ether $(3 \times 20 \text{ mL})$. The product was recrystallized from acetonitrile (40 mL) and methanol (50 mL). Yield: 12.37 g (79%). ¹H NMR ((CD₃)₂SO, 299.8 MHz, 298 K): δ 8.43 (3H, s, 4-C₆H₃(CF₃)₂), 8.31 (6H, s, 2-C₆H₃(CF₃)₂), 7.90 (3H, br s, NH), 2.76 (6H, t, ³J = 6.1 Hz, SNCH₂CH₂N), 2.29 (6H, t, ³J = 6.1 Hz, SNCH₂CH₂N) ppm. ¹³C{¹H} NMR ((CD₃)₂SO, 75.4 MHz, 298 K): δ 143.5 (1-C₆H₃(CF₃)₂), 131.4 $(CF_3, {}^{I}J = 33.2 \text{ Hz}), 127.0 (2-C_6H_3(CF_3)_2), 124.4 (3-C_6H_3-C_6H_3))$ $(CF_3)_2$), 120.8 (4-C₆H₃(CF₃)₂), 53.2 (SNCH₂CH₂N), 40.4 (SNCH₂CH₂N) ppm. ¹⁹F NMR ((CD₃)₂SO, 282.1 MHz, 298 K): -61.7 (18F, s, CF₃) ppm. IR (KBr plates, Nujol mull cm⁻¹): 3292 (s), 3227 (m), 3091 (w), 1627 (w), 1408 (w), 1336 (m), 1298 (s), 1282 (s), 1268 (w), 1195 (m), 1139 (s), 1111 (m), 1089 (w), 1046 (w), 1018 (w), 959 (w), 950 (w), 906 (s), 947 (m), 838 (w), 794 (w), 726 (w), 697 (m), 682 (m), 629 (w). Anal. Found (calcd for C₃₀H₂₄F₁₈N₄O₆S₃): C, 37.03 (36.97); H, 2.48 (2.50); N, 5.84 (5.75).

 $Ti(N_2^{Ms}N^{OMe})(NMe_2)_2$ (18). A solution of $H_2N_2^{Ms}N^{OMe}$ (0.50 g, 0.002 mol) in benzene (20 mL) was added dropwise to Ti(NMe₂)₄ (1.06 g, 0.005 mol) in benzene (20 mL) and stirred for 4 h. The resulting red solution was filtered and volatiles were removed under reduced pressure to give 18 as a red solid. Further solid was obtained by recrystallization from toluene (50 mL) at -80 °C, combined, and dried in vacuo. Yield: 0.11 g (40%). ¹H NMR (C₆D₆, 298 K, 300.7 MHz): δ 3.40 (12H, s, NMe_2 , 3.40 (2H, m, CH₂NS), 2.90 (3H, s, OMe), 2.80 (2H, t, ${}^{3}J =$ $4.\overline{3}$ Hz, CH₂OMe), $2.5\overline{0}$ (6H, s, SO₂Me), 2.40 (2H, t, ${}^{3}J$ = 7.2 Hz, NCH₂CH₂OMe), 2.20 (4H, t, ${}^{3}J = 6.4$ Hz, NCH₂CH₂NS). $^{13}C{^{T}H} (C_6D_6, 298 \text{ K}, 75.4 \text{ MHz}): \delta 68.0 (\text{NMe}_2), 60.0 (\text{CH}_2\text{OMe}),$ 53.0 (CH₂CH₂NS), 52.0 (CH₂CH₂O),49.0 (CH₂CH₂NS). IR data (KBr plates, Nujol mull, cm⁻¹): 1734 (w), 1717 (w), 1700 (w), 1684 (w), 1653 (w), 1646 (w), 1636 (w), 1616 (w), 1576 (w), 1559 (w), 1540 (w), 1521 (w), 1507 (w), 1418 (m), 1376 (m), 1259 (s), 1181 (w), 1154 (s), 1118 (m), 1020 (m), 949 (s), 788 (s), 667 (w), 593 (m), 502 (s). EI-HRMS: m/z = 407.0904 ([M - NMe₂]⁺; calcd for $C_{13}H_{33}N_5O_5S_2Ti$ 407.0902). Anal. Found (calcd for C₁₃H₃₃N₅O₅S₂Ti): C, 34.47 (34.59); H, 7.19 (7.37); N, 15.64 (15.51).

 $Ti(N_2^{Ts}N^{Ph})(NMe_2)_2$ (19). To a solution of $H_2N_2^{Ts}N^{Ph}$ (2.00) g, 4.0 mmol) in benzene (50 mL) was added a solution of Ti(NMe₂)₄ (0.94 mL, 12.0 mmol) in benzene (30 mL). The mixture was stirred for 2 h, resulting in a red solution. The solution was concentrated under reduced pressure to yield a yellow solid, which was recrystallized from a concentrated benzene solution (20 mL) layered with pentane (30 mL) to yield 19 as red diffraction-quality crystals, which were washed with pentane $(3 \times 20 \text{ mL})$ and dried *in vacuo*. Yield: 2.18 g (86%). ¹H NMR (CD₂Cl₂, 499.9 MHz, 248 K): δ 7.73 (4H, d, ³J = 10.0 Hz, 2-C₆H₄Me), 7.36–7.32 (3H, m, overlapping 3-C₆H₅ and 4-C₆H₅), 7.29 (4H, d, ${}^{3}J = 10.0$ Hz, 3-C₆H₄Me), 7.06 (2H, d, ${}^{3}J = 9.5$ Hz, 2-C₆H₅), 3.72 (2H, s, C<u>H</u>₂C₆H₅), 3.57 (8H, s, overlapping NMe2 and TsNCH2CH2N), 3.31 (8H, s, overlapping NMe₂ and TsNCH₂CH₂N), 2.68 (2H, m, TsNCH₂CH₂N), 2.57 (2H, m, TsNCH₂CH₂N), 2.37 (6H, s, C₆H₄Me) ppm. $^{13}C{^{1}H}$ NMR (CD₂Cl₂, 248 K, 75.4 MHz): δ 142.0 (1- C_6H_4Me), 139.0 (4- C_6H_4Me), 131.3 (4- C_6H_5), 130.0 (1- C_6H_5), 129.3 $(3-C_6H_4Me)$, 128.7 $(4-C_6H_5)$, 128.5 $(3-C_6H_5)$, 127.1 (2-C₆H₄Me), 54.6 (CH₂C₆H₅), 50.9 (NMe₂), 47.8 (TsNCH₂-<u>CH</u>₂N), 47.7 (NMe₂), 45.6 (TsN<u>CH</u>₂CH₂N), 21.3 (C₆H₄Me) \overline{ppm} . IR (KBr plates, Nujol mull cm^{-1}): 2774 (w), 1342 (w), 1294 (m), 1280 (s), 1268 (m), 1249 (m), 1205 (w), 1144 (s), 1082 (s), 909 (m), 868 (w), 813 (m), 797 (w), 773 (w), 730 (w), 712 (w), 703 (w), 676 (m), 663 (m), 650 (w). Anal. Found (calcd for C₂₉H₄₁N₅O₄S₂Ti): C, 55.18 (54.79); H, 6.56 (6.50); N, 11.02 (10.70).

 $Ti(N_2^{Ms}N^{Ph})(NMe_2)_2$ (20). A solution of $H_2N_2^{Ms}N^{Ph}$ (0.500 g, 1.43 mmol) in benzene (50 mL) was added dropwise to a solution

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of Ti(NMe₂)₄ (0.231 g, 1.43 mmol) in benzene (30 mL), and the mixture was stirred for 2.5 h. The volatiles were removed under reduced pressure, and the residue was dissolved in toluene and cooled to -80 °C to yield a red crystalline product, which was filtered and dried in vacuo. Yield: 0.30 g, (45%). ¹H NMR (CD₂Cl₂, 213 K, 499.9 MHz): δ 7.16 (2H, s, 3-C₆H₅), 7.08 (1H, s, 4-C₆H₅), 6.58 (2H, d, ${}^{3}J = 8.3$ Hz, 2-C₆H₅), 3.79 (2H, s, C<u>H</u>₂C₆H₅), 3.73 $(2H, t, {}^{3}J = 6.1 \text{ Hz}, \text{CH}_2\text{NS}), 3.36 (6H, s, \text{NMe}_2), 3.32 (6H, s, s)$ NMe₂), 2.63 (2H, t, ${}^{3}J = 6.1$ Hz, CH₂NS), 2.47 (6H, s, SO₂Me), $1.\overline{95}(2H, t, {}^{3}J = 6.0 \text{ Hz}, \text{NCH}_{2}\text{CH}_{2}\overline{\text{NS}}), 1.68(2H, t, {}^{3}J = 6.0 \text{ Hz},$ NCH₂CH₂NS) ppm. ${}^{13}C{}^{1}H{}^{\overline{}}(CD_2Cl_2, 213 \text{ K}, 75.5 \text{ MHz}): \delta 131.9$ $(2-C_6H_5)$, 131.4 $(1-C_6H_5)$, 130.0 $(4-C_6H_5)$, 129.0 $(3-C_6H_5)$, 57.3 (CH₂C₆H₅), 51.4 (NMe₂), 48.9 (NCH₂CH₂NS), 44.1 (SO₂Me), 40.5 (CH₂NS). IR (KBr plates, Nujol mull cm⁻¹): 2924 (s), 2361 (m), 2338 (w), 1734 (w), 1684 (w), 1636 (m), 1559 (w), 1540 (w), 1521 (w), 1507 (m), 1377(m), 1260 (m), 805 (w), 666 (w), 477 (s). Anal. Found (calcd for C₁₇H₃₃N₅O₄S₂Ti): C, 42.18 (42.23); H, 6.91

(6.88); N, 14.39 (14.49). $Ti(N_2^{Ms}N^{OMe})(O^{i}Pr)_2$ (21). A solution of $H_2N_2^{Ms}N^{OMe}$ (0.340 g, 0.0011 mol) in benzene (20 mL) was added dropwise to a solution of Ti(NMe₂)₂(OⁱPr)₂ (0.550 g, 0.0022 mol) in benzene (20 mL). The resulting bright orange solution was stirred for 2 h at room temperature, and volatiles were removed under reduced pressure. The residue was extracted into toluene (50 mL) and cooled to -80 °C for 16 h. The resulting orange solution was filtered and dried in vacuo to yield 21 as an orange powder. Yield: 0.23 g (44%). Red single crystals suitable for an X-ray diffraction study were obtained by recrystallization from a concentrated toluene-hexane solution (1:3) at -80 °C. ¹H NMR (C₆D₆, 353 K, 499.2 MHz): δ 5.01 (2H, sep, ³J = 6.1 Hz, OCHMe₂), 3.19 (3H, s, OMe), 3.05 (2H, t, ³J = 5.1 Hz, CH₂NS), 2.77 (4H, app. q, ${}^{3}J = 5.7$ Hz, overlapping NCH₂CH₂NS and CH₂CH₂OMe), 2.54 (6H, s, SO₂Me), 2.18 (2H, $\overline{t_1}^3 J = 5.5$ Hz, CH_2CH_2OMe), 1.27 (12H, d, ${}^{\overline{3}}\overline{J}$ = 6.1 Hz, OCHMe₂) ppm. $^{13}\overline{C}{^{1}H}$ (C₆D₅CD₃, 353 K, 75.5 MHz): δ 70.5 (OCHMe₂), 63.0 (OMe), 59.0 (CH₂CH₂NS), 58.0 (CH₂CH₂OMe), 54 (CH₂OMe), 49.5 (SO₂Me), 39.5 (CH₂NS), 26.0 (OCHMe₂) ppm. IR (KBr plates, Nujol mull, cm⁻¹): 1653 (w), 1559 (w), 1321 (s), 1363 (m), 1261 (w), 1162 (s), 1007 (m), 851 (w), 805 (w), 666 (w), 617 (w), 488 (m). EI-HRMS: m/z = 422.0889 ([M - OiPr]⁺; calcd for C₂₁H₂₉-N₃O₇S₂Ti 422.0899). Anal. Found (calcd for C₂₁H₂₉N₃O₇S₂Ti): C, 37.51 (37.42); H, 7.27 (7.25); N, 8.69 (8.73).

 $Ti(N_2^{Ts}N^{Ph})(O^iPr)_2$ (22). To a solution of $H_2N_2^{Ts}N^{Ph}$ (0.500 g, 1.00 mmol) in chlorobenzene (30 mL) was added Ti(NMe₂)₂-(OⁱPr)₂ (0.254 g, 1.00 mmol) in chlorobenzene (30 mL). The resulting light yellow solution mixture was stirred for 2 h and concentrated under reduced pressure to yield a yellow solid, which was recrystallized from a concentrated dichloromethane (10 mL) solution layered with pentane (30 mL) to yield 22 as a light yellow solid, which was washed with pentane $(3 \times 20 \text{ mL})$ and dried *in vacuo*. Yield: 0.31 g (47%). ¹H NMR (CD₂Cl₂, 299.9 MHz, 246 K): δ 8.16 (4H, d, ³J = 9.2 Hz, 2-C₆H₄Me), 6.98 (4H, m, overlapping 3-C₆H₅ and 4-C₆H₅), 6.95 (4H, d, ${}^{3}J = 9.2$ Hz, $3-C_6H_4Me$), 6.70 (2H, d, ${}^{3}J = 8.5$ Hz, $2-C_6H_5$), 5.51 (1H, sept., ${}^{3}J = 6.2$ Hz, OCHMe₂), 5.31 (1H, sept., ${}^{3}J = 5.9$ Hz, OCHMe₂), 4.15 (2H, s, CH₂C₆H₅), 3.34 (4H, app. t, ${}^{3}J = 6.3$ Hz, $T_{sNCH_{2}CH_{2}N}$, 2.22 (4H, app. t, ³J = 6.3 Hz, $T_{sNCH_{2}CH_{2}N}$), 1.98 ($\overline{6H}$, s, C₆H₄Me), 1.61 (12H, 2 × overlapping d, ${}^{3}J = \overline{6.2}$ and 5.9 Hz, OCHMe₂) ppm. ${}^{13}C{}^{1}H{}$ NMR (CD₂Cl₂, 246 K, 75.4 MHz): $\delta 142.5 (1-C_6H_4Me)$, 139.0 (4-C₆H₄Me), 131.5 (4-C₆H₅), 131.0 (1-C₆H₅), 129.5 (3-C₆H₄Me), 129.0 (4-C₆H₅), 128.8 (3-C₆H₅), 127.4 (2-C₆H₄Me), 84.4 (OCHMe₂), 83.4 (OCHMe₂), 57.1 (CH₂C₆H₅), 50.8 (TsNCH₂CH₂N), 47.7 (TsNCH₂CH₂N), 25.4 (OCHMe₂), 24.9 (OCHMe₂), 21.3 (C₆H₄Me) ppm. IR (KBr plates, Nujol mull cm⁻¹): 2723 (w), 1298 (m), 1152 (s), 1109 (m), 1086 (m), 1028 (w), 997 (w), 946 (m), 906 (w), 814 (m), 772 (w), 732 (m), 667 (m). Anal. Found (calcd for C31H43N3O6S2Ti): C, 55.63 (55.29); H, 6.39 (6.34); N, 6.19 (6.45).

 $Ti(N_2^{Ms}N^{Ph})(O^iPr)_2$ (23). A soultion of $H_2N_2^{Ms}N^{Ph}$ (0.370 g, 1.073 mmol) in benzene (50 mL) was added dropwise to a

solution of Ti(NMe₂)₂(OⁱPr)₂ (0.300 g, 1.18 mmol) in benzene (20 mL). The resulting solution was stirred for 2 h, and volatiles were removed under reduced pressure. The residue was extracted into benzene, and volatiles were removed under reduced pressure. The resulting red solid was washed with hexane (3 \times 15 mL) and dried *in vacuo*, yielding 23 as a red powder. Yield: 0.30 g, (56%). ¹H NMR (CD₂Cl₂, 223 K, 449.9 MHz): δ 7.16 $(2H, m, 3-C_6H_5), 7.10(1H, s, 4-C_6H_5), 6.77(2H, d, {}^{3}J = 7.0 Hz,$ $2-C_6H_5$, 5.23 (1H, q, ${}^{3}J = 5.4$ Hz, OCHMe₂), 5.14 (1H, q, {}^{3}J = 5.4 Hz, OCHMe₂), 5.14 (1H, q, {} 6.3 Hz, OC<u>H</u>Me₂), 4.11 (2H, s, C<u>H</u>₂C₆H₅), 3.72 (2H, q, ${}^{3}J = 5.6$ Hz, CH₂NS), 2.93 (2H, t, ${}^{3}J = 6.9$ Hz, NCH₂CH₂NS), 2.64 (6H, s, SO₂Me), 2.21 (2H, t, ${}^{3}J = 5.4$ Hz, CH₂NS), 1.93 (2H, t, ${}^{3}J =$ 6.2 Hz, NCH₂CH₂NS), 1.47 (6H, d, ${}^{3}J = 6.3$ Hz, OCHMe₂), 1.16 (6H, d, ${}^{3}J = 5.4$ Hz, OCHMe₂) ppm. ${}^{13}C{}^{1}H{}$ (CD₂Cl₂, 293 K, 75.5 MHz): δ 132.4 (1- $\overline{C_6H_5}$). 132.0 (2- C_6H_5), 129.0 (4-C₆H₅), 128.9, (3-C₆H₅), 83.5 (OCHMe₂), 58.6 (CH₂C₆H₅), 51.5 (NCH_2CH_2NS) , 48.7 (SO_2Me) , $\overline{39}$.4 (CH_2NS) , $\overline{26.1}$ $(OCHMe_2)$. IR (KBr plates, Nujol mull, cm⁻¹): 3853 (m), 3838 (w), 3821 (s), 3801 (w), 3751 (m), 3745 (w), 3735 (m), 3676 (w), 3649 (m), 3629 (m), 3583 (w), 2361 (s), 2341 (m), 2275 (s), 2120 (m), 2050 (m), 1772 (w), 1740 (w), 1717 (w), 1700 (w), 1684 (w), 1670 (w), 1653 (w), 1636 (w), 1617 (w), 1570 (m), 1559 (w), 1541 (w), 1521 (s), 1507 (m), 1377 (s), 1260 (s), 1019 (s), 802 (m), 721 (w), 666 (s), 542 (s), 446 (s). EI-HRMS: m/z = 453.0570, ([M - O¹Pr]⁺; calcd for $C_{19}H_{35}N_3O_6S_2Ti$: 453.0570), m/z = 348.0798 ([L]⁺, calcd for $C_{19}H_{35}N_3O_6S_2Ti$ 348.1130). Anal. Found (calcd for C₁₉H₃₅N₃O₆S₂Ti): C, 44.35 (44.44); H, 6.91 (6.87); N, 8.14 (8.18)

 $Ti(N_2^{Ts}N^{Ph})(O^iPr)(NMe_2)$ (24). To a solution of $Ti(NMe_2)_2$ -(OⁱPr)₂ (0.840 g, 3.30 mmol) in dichloromethane (30 mL) was added a solution of H₂N₂^{Ts}N^{Ph} (0.500 g, 1.00 mmol) in dichloromethane (30 mL). The mixture was stirred for 16 h, resulting in an orange solution. The solution was concentrated to ca. 15 mL, and hexane (40 mL) was added to precipitate the product, which was filtered. The orange solid was recrystallized from a concentrated dichloromethane solution layered with pentane to yield 24 as an orange solid, which was washed with pentane $(3 \times 20 \text{ mL})$ and dried in vacuo. The recrystallized product yielded crystals suitable for an X-ray diffraction study. Yield: 0.48 g (74%). ¹H NMR (CD₂Cl₂, 299.9 MHz, 248 K): δ 7.73 (4H, d, ³J = 9.0 Hz, 2-C₆H₄Me), 7.38 (2H, m, 2-C₆H₅), 7.29 (4H, d, ${}^{3}J = 9.0$ Hz, $3-C_6H_4Me$), 7.00 (3H, m, overlapping $3-C_6H_5$ and $4-C_6H_5$), 5.16 (1H, sept., ${}^{3}J = 6.1$ Hz, OC<u>H</u>Me₂), 3.73 (2H, s, CH₂C₆H₅), 3.43 (10H, s, overlapping NMe2 and TsNCH2CH2N), 2.74 (4H, m, TsNCH₂CH₂N), 2.37 (6H, s, C₆H₄Me), 1.61 (6H, d, ${}^{3}J = 6.1$ Hz, OCHMe₂) ppm. ${}^{13}C{}^{1}H$ NMR (CD₂Cl₂, 248 K, 75.4 MHz): δ 141.9 (1-C₆H₄Me), 139.6 (4-C₆H₄Me), 131.4 (4-C₆H₅), 129.8 (1-C₆H₅), 129.2 (3-C₆H₄Me), 128.9 (4-C₆H₅), 128.5 $(3-C_6H_5)$, 126.9 $(2-C_6H_4Me)$, 83.1 (OCHMe₂), 54.7 (CH₂C₆H₅), 52.7 (NMe₂), 47.6 (TsNCH₂CH₂N), 47.5 (TsNCH₂CH₂N), 25.8 $(OCHMe_2)$, 21.3 (C_6H_4Me) ppm. IR (KBr plates, Nujol mull cm⁻¹): 1623 (w), 1297 (s), 1168 (w), 1143 (m), 1085 (m), 1022 (m), 952 (s), 903 (w), 820 (w), 771 (w), 723 (m), 668 (m). Anal. Found (calcd for C₃₀H₄₂N₄O₅S₂Ti): C, 55.68 (55.92); H, 6.51 (6.58); N, 8.61 (8.44).

Alternative NMR Tube Scale Synthesis of $Ti(N_2^{Ts}N^{Ph})(O^iPr)$ -(NMe₂) (24). To a solution of $Ti(N_2^{Ts}N^{Ph})(NMe_2)_2$ (10 mg, 15.7 μ mol) in C₆D₆ (0.2 mL) was added a solution of $Ti(N_2^{Ts}N^{Ph})$ -(O^iPr)₂ (10.5 mg, 15.7 μ mol) in C₆D₆ (0.2 mL). Initial ¹H NMR indicated that no reaction had taken place. The reaction mixture was then heated at 80 °C for 4 days. A color change of the initially dark orange to light orange was observed. Analysis by ¹H NMR indicated that **14** had been formed quantitatively.

 $Zr(N_3^{Ts}N)(CH_2SiMe_3)$ (30). To a solution of $Zr(CH_2SiMe_3)_4$ (0.520 g, 1.20 mmol) in THF (15 mL) was added a solution of $H_3N_3^{Ts}N$ (0.710 g, 1.20 mmol) in THF (15 mL). The reaction was stirred at RT for 16 h, after which time the resulting light yellow solution was concentrated to ca. half the original volume and cooled to -78 °C. The resulting white crystalline solid was filtered, washed with pentane (3 × 15 mL), and dried *in vacuo*.

Yield: 0.63 g (67%). Crystals suitable for X-ray diffraction studies were obtained from slow evaporation of a THF solution at RT. ¹H NMR (CD₂Cl₂, 299.9 MHz, 298 K): δ 7.90 (6H, d, ³*J* = 6.4 Hz, 2-C₆H₄Me), 7.31 (6H, d, ³*J* = 6.4 Hz, 3-C₆H₄Me), 3.53 (6H, m, TsNCH₂CH₂N), 2.82 (6H, m, TsNCH₂CH₂N), 2.41 (9H, s, C₆H₄Me), 0.26 (2H, br s, CH₂Si), -0.30 (9H, s, SiMe₃) ppm. ¹³C{¹H} NMR (CD₂Cl₂, 75.4 MHz, 298 K): δ 141.9 (1-C₆H₄Me), 139.1 (4-C₆H₄Me), 129.8 (3-C₆H₄Me), 127.5 (2-C₆H₄Me), 60.8 (TsNCH₂CH₂N), 47.6 (TsNCH₂CH₂N), 21.5 (C₆H₄Me), 3.8 (CH₂Si), 2.4 (SiMe₃) ppm. IR (KBr plates, Nujol mull cm⁻¹): 1262 (s), 1161 (m), 1110 (m), 1019 (w), 968 (w), 814 (s), 668 (m), 635 (w). Anal. Found (calcd for C₂₉H₄₁N₅O₄S₂Ti): C, 47.42 (47.48); H, 5.76 (5.66); N, 7.09 (7.14).

 $Zr(N_3^{Ms}N)(CH_2SiMe_3)$ (31). To a solution of $Zr(CH_2SiMe_3)_4$ (0.500 g, 0.100 mmol) in toluene (10 mL) was added a slurry of $H_3N_3^{Ms}N$ (0.440 g, 0.100 mmol) in toluene (15 mL), and the mixture was heated to 100 °C for 3 h, after which time the solution was cooled to RT and filtered. The resulting light yellow solution was concentrated to ca. 5 mL, giving a white crystalline solid, which was filtered and washed with pentane $(3 \times 15 \text{ mL})$ and dried in vacuo. Yield: 0.35 g (60%). ¹H NMR (CD₂Cl₂, 299.9 MHz, 298 K): δ 3.47 (6H, t, ${}^{3}J = 6.0$ Hz, SNCH₂CH₂N), 3.08 (9H, s, SO₂Me), 2.74 (6H, t, ${}^{3}J = 6.0$ Hz, SNCH₂CH₂N), 0.29 (2H, br s, CH₂Si), -0.30 (9H, s, SiMe₃) ppm. $^{13}\overline{C}{}^{1}_{1}H$ NMR (CD₂Cl₂, 75.4 MHz, 298 K): 60.8 (SNCH₂CH₂N), 46.8 (SO₂Me), 40.7 (SNCH₂CH₂N), 3.1 (CH₂SiMe₃), 2.8 (SiMe₃) ppm. IR (KBr plates, Nujol mull cm⁻¹): 1324 (w), 1249 (s), 1150 (w), 1075 (m), 982 (s), 863 (m), 936 (m), 761 (w), 722 (w), 697 (w), 668 (w). Anal. Found (calcd for C13H32N4O6S3SiZr): C, 27.96 (28.09); H, 5.82 (5.80); N, 9.99 (10.08).

Zr(N3^{ArF}N)(CH2SiMe3) (32). To a solution of Zr(CH2SiMe3)4 (0.190 g, 0.200 mmol) in toluene (5 mL) was added a slurry of $H_3N_3^{ArF}N$ (0.400 g, 0.200 mmol) in toluene (15 mL), and the mixture was heated to 100 °C for 2 h, after which time the light yellow solution was cooled to 0 °C. A white crystalline product was isolated by filtration and dried in vacuo. Yield: 0.21 g (89%). Crystals suitable for X-ray diffraction studies were obtained from a concentrated benzene solution. ¹H NMR (CD₂Cl₂, 299.9 MHz, 313 K): δ 8.52 (6H, s, 2-C₆H₃(CF₃)₂), 8.14 (3H, s, 4-C₆H₃(CF₃)₂), 3.69 (6H, br s, SNCH₂CH₂N), 2.98 (6H, br s, SNCH₂CH₂N), 0.34 (2H, br s, CH₂Si), 0.36 (9H, s, SiMe₃) ppm. ¹³C{¹H} NMR (CD₂Cl₂, 75.4 $\overline{\text{MHz}}$, 313 K): 145.8 (1- $\overline{\text{C}_6}\text{H}_3(\text{CF}_3)_2$), 133.5 (CF₃, 1J = 34.3 Hz), 61.0 (SNCH₂CH₂N), 58.0 (SNCH₂CH₂N), 1.8 (SiMe₃) ppm. NMR (CD₂Cl₂, 282.1 MHz, 313 K): -61.5 (18F, s, CF₃) ppm. IR (KBr plates, Nujol mull cm⁻¹): 3102 (w), 2726 (w), 1624 (w), 1365 (s), 1282 (s), 1193 (s), 1141 (s), 1084 (m), 1044 (w), 1007 (w), 994 (w), 970 (m), 937 (m), 908 (s), 845 (s), 823 (m), 808 (m), 747 (w), 720 (w), 698 (m), 682 (s), 651 (w), 644 (m). Anal. Found (calcd for $\begin{array}{l} C_{34}H_{32}F_{18}N_4O_6S_3Zr); C, 35.47\,(35.51); H, 2.79\,(2.80); N, 4.78\,(4.87), \\ Zr(N_3^{ArF}N)(NMe_2)\,(33). \mbox{ To a solution of } Zr(NMe_2)_4\,(0.110\,g, \end{array}$

0.400 mmol) in THF (15 mL) was added a solution of $H_3N_3^{ArF}N_3$ (0.400 g, 0.410 mmol) in THF (15 mL), and the mixture was stirred at RT for 16 h, after which time the light yellow solution was concentrated to ca. half its original volume and cooled to -78 °C. The white crystalline product was isolated by filtration and dried in vacuo. Yield: 0.37 g (82%). Crystals suitable for X-ray diffraction studies were obtained from a concentrated THF solution. ¹H NMR (C₆D₆, 499.9 MHz, 298 K): δ 8.50 (6H, s, 2-C₆H₃-(CF₃)₂), 7.63 (3H, s, 4-C₆H₃(CF₃)₂), 2.99 (6H, br s, SNCH₂CH₂N), 2.86 (6H, s, NMe₂), 2.22 (6H, br s, SNCH₂CH₂N) ppm. ¹³C{¹H} NMR (CD₂Cl₂, 75.4 MHz, 298 K): 145.35 (1-C₆H₃(CF₃)₂), 133.1 $(CF_3, {}^{1}J = 33.9 \text{ Hz}), 126.2 (3-C_6H_3(CF_3)_2), 125.2 (2-C_6H_3(CF_3)_2),$ 121.6 $(4-C_6H_3(CF_3)_2)$, 60.45 $(SNCH_2CH_2N)$, 46.2 $(SNCH_2CH_2N)$, 44.1 (NMe_2) ppm. ¹⁹F NMR $(CD_2Cl_2, 282.1 \text{ MHz}, 298 \text{ K})$: -62.7 (18F, s, CF₃) ppm. IR (KBr plates, Nujol mull cm⁻¹): 1365 (m), 1280 (s), 1191 (m), 1125 (s), 1053 (w), 1016 (w), 956 (w), 937 (m), 924 (m), 901 (m), 780 (s), 738 (w), 720 (w), 698 (m), 682 (m), 644 (w). Anal. Found (calcd for C₃₂H₂₇F₁₈N₅O₆S₃Zr): C, 34.66 (34.72); H, 2.42 (2.46); N, 6.38 (6.33).

 $\{Zr(N_3^{ArF}N)\}_2(\mu-O)$ (34). $Zr(N_3^{ArF}N)(NMe_2)$ (33) (0.100 g, 0.100 mmol) was slurried three times in "wet" diethyl ether (5 \times 15 mL) and dried in vacuo to yield 34 as a white solid. Yield: 0.12 g (61%). Crystals suitable for X-ray diffraction studies were obtained from slow evaporation of a concentrated diethyl ether solution at RT. ¹H NMR (C₆D₆, 499.9 MHz, 298 K): δ 8.79 (2H, s, 2-C₆H₃(CF₃)₂), 8.60 (2H, s, 2-C₆H₃(CF₃)₂), 8.38 (2H, s, 2-C₆H₃(CF₃)₂), 7.90 (1H, s, 4-C₆H₃(CF₃)₂), 7.82 (1H, s, 4-C₆H₃-(CF₃)₂), 7.56 (1H, s, 4-C₆H₃(CF₃)₂), 3.80 (1H, m, SNCH₂-CH₂N), 3.20 (2H, m, SNCH₂CH₂N), 2.77 (1H, m, SNCH₂CH₂-N), 2.67 (1H, m, SNCH₂CH₂N), 2.53 (1H, m, SNCH₂CH₂N), 2.28 (1H, m, SNCH₂CH₂N), 2.06 (1H, m, SNCH₂CH₂N), 1.87 (1H, m, SNCH₂CH₂N), 1.52 (1H, m, SNCH₂CH₂N), 1.36 (1H, m, SNCH₂CH₂N), 0.95 (1H, m, SNCH₂CH₂N) ppm. A satisfactory ¹³C NMR spectrum could not be obtained due to the insoluble nature of this compound. ¹⁹F NMR (C₆D₆, 125.8 MHz, 298 K): $\delta - 128.2$ (6F, s, CF₃), -128.1 (6F, s, CF₃), -127.9 (6F, s, CF₃) ppm. IR (KBr plates, Nujol mull cm⁻¹): 1281 (s), 1139 (s), 1006 (w), 992 (w), 966 (w), 905 (m), 844 (m), 808 (w), 722 (m), 698 (m), 682 (m), 648 (w). Anal. Found (calcd for C₆₀H₄₂F₃₆N₈O₁₃S₆Zr): C, 35.50 (35.14); H, 1.93 (2.06); N, 5.19 (5.46).

NMR Tube Scale Synthesis of $Zr(N_3^{Ts}N)(O^iPr)$ (35). To a solution of $Zr(N_3^{Ts}N)(CH_2SiMe_3)$ (30) (10.0 mg, 12.8 μ mol) in CD₂Cl₂ (0.2 mL) was added a solution of ¹PrOH (0.770 mg, 1.00 μ L, 12.8 μ mol) in CD₂Cl₂ (0.2 mL). After 1 h analysis by ¹H NMR indicated that 35 had been formed quantitatively. ¹H NMR (CD₂Cl₂, 299.9 MHz, 298 K): δ 9.97 (6H, d, ³J = 9.0 Hz, 2-C₆H₄Me), 7.29 (6H, d, ³J = 9.0 Hz, 3-C₆H₄Me), 4.40 (1H, sept., ³J = 6.0, OCHMe₂) 3.39 (6H, t, ³J = 5.8, TsNCH₂CH₂N), 2.89 (6H, t, ³J = 5.8, TsNCH₂CH₂N), 2.42 (9H, s, C₆H₄Me), 0.98 (1H, sept., ³J = 6.0, OCHMe₂) ppm.

NMR Tube Scale Synthesis of $Zr(N_3^{ArF}N)(O-2,6-C_6H_3Me_2)$ (36). To a solution of $Zr(N_3^{ArF}N)(NMe_2)$ (33) (10 mg, 8.7 μ mol) in CD₂Cl₂ (0.2 mL) was added a solution of 2,6-dimethylphenol (1.1 mg, 8.7 μ mol) in CD₂Cl₂ (0.2 mL). After 1 h, analysis by ¹H NMR indicated that **36** had been formed quantitatively. ¹H NMR (CD₂Cl₂, 299.9 MHz, 298 K): δ 8.34 (6H, s, 2-C₆H₃-(CF₃)₂), 7.51 (6H, s, 4-C₆H₃(CF₃)₂), 6.64 (2H, d, ³J = 9.0 Hz, 4-C₆H₃Me₂), 6.48 (2H, d, ³J = 9.0 Hz, 3-C₆H₃Me₂), 2.97 (6H, br s, SNCH₂CH₂N), 2.21 (6H, br s, SNCH₂CH₂N), 2.14 (2H, s, C₆H₃Me₂) ppm.

General Procedure for Polymerization of ε -CL. Parallel duplicate experiments were carried out in each of which a solution of ε -CL (6.6 mmol) in toluene (3.0 mL) was heated to 100 °C and added to a solution of initiator (0.066 mmol) in toluene (3.8 mL) also at 100 °C. For one sample aliquots were taken at the respective time. Upon completion, the reaction was quenched by addition of wet THF (10 mL) and the solution evaporated to dryness to give the crude polymer. Isolated yields were obtained from the parallel experiment for which the polymer was quenched by wet THF (10 mL) and precipitated by addition to ethanol (250 mL) with vigorous stirring, filtered, and dried to constant weight *in vacuo*.

Procedure for Polymerization of ε -CL in the Presence of Alcohol Co-initiators. Parallel duplicate experiments were carried out in each of which to initiator (0.066 mmol) was added a solution of HOR (0.066 mmol) in toluene (3.8 mL). This solution was stirred for 15 min at room temperature, then heated to 100 °C, and a solution of ε -CL (6.6 mmol) in toluene (3.0 mL) also at 100 °C was added. For one sample aliquots were taken at the respective time. Upon completion, the reaction was quenched by addition of wet THF (10 mL) and the solution evaporated to dryness to give the crude polymer. Isolated yields were obtained from the parallel experiment for which the polymer was quenched by wet THF (10 mL) and precipitated by addition to ethanol (250 mL) with vigorous stirring, filtered, and dried to constant weight *in vacuo*.

General Procedure for Solution Polymerization of *rac*-LA. *rac*-LA (6.00 mmol) and initiator (0.06 mmol) were added to a

Schlenk flask and heated to 70 °C. To this was added hot (70 °C) toluene (6.0 mL), rapidly dissolving both solids. The resultant solution was heated at 70 °C, and aliquots were taken at the respective time. Upon completion of the reaction, wet THF (10 mL) was added and the solution evaporated to dryness to give the poly(*rac*-LA). Conversions were determined by ¹H NMR integration of the OC<u>H</u>Me resonance relative intensities of the residual *rac*-LA and poly(*rac*-LA).

Procedure for Solution Polymerization of *rac*-LA in the Presence of Alcohol Co-initiators. *rac*-LA (6.00 mmol) and initiator (0.06 mmol) were added to a Schlenk flask and heated to 70 °C. To this was added a hot (70 °C) solution of HOR (0.06 mmol) in toluene (6.0 mL), rapidly dissolving both solids. The resultant solution was heated at 70 °C, and aliquots were taken at the respective time. Upon completion of the reaction, wet THF (10 mL) was added and the solution evaporated to dryness to give the poly(*rac*-LA). Conversions were determined by ¹H NMR integration of the OCHMe resonance relative intensities of the residual *rac*-LA and poly(*rac*-LA).

Crystal Structure Determinations of $H_2N_2^{Ms}N^{OMe}$ (12), $H_2CyN_2^{SO_2Mes}$ (17), $Ti(N_2^{Ts}N^{Ph})(NMe_2)_2$ (19), $Ti(N_2^{Ms}N^{OMe})$ -(OⁱPr)₂ (21), $Ti(N_2^{Ts}N^{Ph})(O^iPr)(NMe_2)$ (24), $Zr(N_3^{Ts}N)(CH_2-SiMe_3)$ (30), $Zr(N_3^{ArF}N)(CH_2SiMe_3)$ (32), $Zr(N_3^{ArF}N)(NMe_2)$ (33), and { $Zr(N_3^{ArF}N)_2(\mu-O)$ (34). X-ray data collection and processing parameters are given in the Supporting Information. Crystals were mounted on glass fibers using perfluoropolyether oil and cooled rapidly in a stream of cold N₂ using an Oxford Cryosystems Cryostream unit. Diffraction data were measured using an Enraf-Nonius KappaCCD diffractometer. As appropriate, absorption and decay corrections were applied to the data and equivalent reflections merged.¹¹² The structures were solved with SIR92¹¹³ or SHELXS-97,¹¹⁴ and further refinements and all other crystallographic calculations were performed using either the CRYSTALS program suite¹¹⁵ or SHELXS-97.¹¹⁶ Other details of the structure solution and refinements are given in the Supporting Information (CIF data). A full listing of atomic coordinates, bond lengths and angles, and displacement parameters for all the structures has been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors on the Web.

Acknowledgment. We thank the EPSRC for support to A.D.S. and Dr. A. L. Thompson for advice with regard to the crystallography. C.P. acknowledges MICINN (MAT2007-60997) for financial support and CAM and Universidad de Alcalá for fellow funding.

Supporting Information Available: X-ray crystallographic data in CIF format for the structure determinations of $H_2N_2^{Ms}N^{OMe}$ (12), $H_2CyN_2^{SO_2Mes}$ (17), $Ti(N_2^{Ts}N^{Ph})(NMe_2)_2$ (19), $Ti(N_2^{Ms}N^{OMe})(O^{P}r)_2$ (21), $Ti(N_2^{Ts}N^{Ph})(O^{P}r)(NMe_2)$ (24), $Zr(N_3^{Ts}N)(CH_2SiMe_3)$ (30), $Zr(N_3^{ArF}N)(CH_2SiMe_3)$ (32), $Zr-(N_3^{ArF}N)(NMe_2)$ (33), and $\{Zr(N_3^{ArF}N)\}_2(\mu$ -O) (34). Data concerning the ROP catalysis; X-ray data collection and processing parameters; additional crystallographic data (displacement ellipsoid plots, selected distances and angles, and discussion) for 12, 17, 32, and 34. This information is available free of charge via the Internet at http://pubs.acs.org.

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