A Series of Bis(thiophosphinic amido)yttrium Initiators for Lactide Ring-Opening Polymerization

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ABSTRACT: The syntheses of a series of bis(thiophosphinic amido) yttrium complexes are reported by the reaction of bis(thiophosphinic amine) ligands with $[Y(N(SiMe_3)_2)_3]$. The complexation reactions were monitored using NMR spectroscopy and one complex was characterized by single crystal X-ray crystallography. Two substitution sites on the ligand were varied, the phosphorus substituents were phenyl, isopropyl and ethoxy groups and the diamine backbones were ethylene, *trans*-cyclohexylene and 2,2-dimethylpropylene groups. All the new complexes were tested as initiators for the ring opening polymerization of *rac*-lactide. They exhibited good polymerization control, shown by the linear fits to plots of number-averaged molecular weight (M_n) versus the percentage conversion, the close agreement between the theoretical and observed degree of polymerization (DP) and the moderate polydispersity index (PDI) values. They also showed very high polymerization rates ($k_{app} = 2.2 \times 10^{-4}$ to 1.1×10^{-2} s^{-1} at $[lactide]_0 = 1$ M, $[initiator]_0 = 5$ mM). The phosphorus substituents had the greatest influence over the rate, with the order of decreasing rate being isopropyl > phenyl > ethoxy. The complexes with ethoxy phosphorus substituents exerted good stereocontrol; when *rac*-lactide was polymerized it formed predominantly heterotactic polylactide ($P_s = 0.69-0.79$).

Introduction

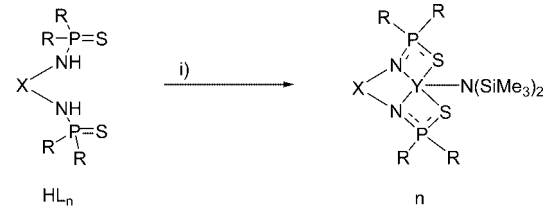
Polylactide (PLA) has attracted attention as a renewable and degradable alternative to petrochemicals and as a biocompatible polymer for applications in medicine.[1−4] It is synthesized by the ring opening polymerization of lactide; a process which can be initiated by a range of species from metal complexes to nucleophilic organocatalysts to enzymes.[5−7] Yttrium initiators are of particular interest due to their high rates, good control and low toxicity. The homoleptic yttrium alkoxides, first developed by Dupont, are still among the most active lactide polymerization initiators.[8−10] Single site complexes (i.e., complexes of the type LYX where L = ancillary ligand, X = amide/alkoxide initiating group) are useful as they have reproducible syntheses and maintain good control and rates.[11−33] The polymerization rate is affected by the ancillary ligand. 1,4,7-Triazacyclononane macrocycles, salen, guanidinate, 1,ω-dithiaalkanediyl bridged bis(phenolate), pyrrolide and tetraamide yttrium complexes show moderate activity (typically taking hours to reach completion at initiator loadings of approximately 1 mM).[11−16,18,19,26−29] In contrast, amidinate, bis(phenoxy)amine, bis(thio/oxophosphinic amide), bis(oxazolinate) and β-diiminate yttrium complexes were all very fast (typically taking minutes/seconds to reach completion at initiator loadings of approximately 1 mM).[17,21−25,31−33] The ancillary ligand has been used to control the stereochemistry; the bis(phenoxy)amine yttrium complexes show good-excellent heteroselectivity in the polymerization of *rac*-lactide ($P_s = 0.8-0.99$) and reasonable syndiotacticity in the polymerization of *meso*-lactide ($P_s = 0.7$).[17,19,21,29,32,33] However, despite their excellent potential, the chemistry of yttrium initiators is not as well developed as for Sn(II) or Zn(II). Furthermore, the development of novel single site yttrium complexes will enable structure−activity studies which may help elucidate the important steps in the reaction mechanism.

We have been investigating the preparation of single site yttrium amido complexes using bis(thio/oxophosphinic amine) ancillary ligands.[23,25] The motivation to study this ligand class derived from results indicating that ancillary ligands with weakly coordinating donor groups, such as amides, ethers and thioethers, enable excellent catalytic activity while maintaining high degrees of polymerization control.[16−21,23−25,29,32,33] Recently, we isolated [(bis(*P*,*P*′-diisopropylthiophosphinic)-2,2-dimethylpropylene diamido)(bis(trimethylsilyl)amido)yttrium], **1**, (Scheme 1) and discovered it was a highly active polymerization initiator.[23] The bis(oxophosphinic amido) yttrium analogue complexes were also very active but showed double the expected M_n for the polylactide.[25] In fact, these species were dimers in solution; the M_n data were rationalized by initiation occurring from only one of the two possible amide groups. Thus, the bis(thiophosphinic amido)yttrium complexes are of significant interest due to their high rates and enhanced control vs the oxo-analogue compounds. Here, we report a series of bis(thiophosphinic amido) yttrium initiators and study the influence of ligand substitution on the initiator's rate and control.

Results and Discussion

Synthesis and NMR Characterization. A series of bis(thiophosphinic) diamine ligands ($H_2L_1-H_2L_8$, Scheme 1) were synthesized by a novel method involving the reaction of two

Scheme 1. Synthesis of Initiators 1−8[a]



n=**1** X=2,2-dimethylpropylene, R=*iso*-propyl
n=**2** X=ethylene, R=*iso*-propyl
n=**3** X=*trans*-1,2-cyclohexylene, R=*iso*-propyl
n=**4** X=2,2-dimethylpropylene, R=phenyl
n=**5** X=ethylene R=phenyl
n=**6** X=*trans*-1,2-cyclohexylene, R=phenyl
n=**7** X=ethylene, R=ethoxy
n=**8** X=*trans*-1,2-cyclohexylene, R=ethoxy

[a] Reagents and conditions: (i) $[Y(N(SiMe_3)_2)_3]$, THF, room temperature, 2−10 days.

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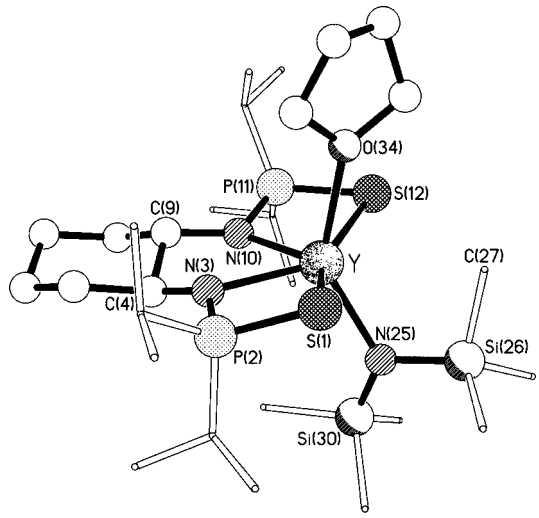

Figure 1. The molecular structure of [**3**·**THF**].

equivalents of di(isopropyl/phenyl/ethoxy)thiophosphinic chloride with the appropriate diamine (see Supporting Information). The Y(III) initiators, **1**−**8**, were prepared *in situ* by an amine metathesis route, i.e., by reaction between the ligand (H_2L_1−H_2L_8) and [$Y(N(SiMe_3)_2)_3$] in THF (Scheme 1).

The reactions were slow, typically taking 2−10 days to reach complete conversion, but the P atoms in the ligand enabled straightforward, *in situ* monitoring of the reaction progress by NMR spectroscopy. The strong coupling between ^{31}P and ^{89}Y for this ligand class has already been established,[23,25,34] here the coupling is useful as it enables *in situ* monitoring of the complexation reaction by $^{31}P\{^1H\}$ NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectra showed the disappearance of the free ligand signals and the conversion to a doublet(s), due to coupling with the ^{89}Y, at higher field. The complexes with isopropyl/ethoxy phosphorus substituents (**1**−**3** and **7**) each showed a single doublet indicating formation of a coordination complex in which both P atoms are equivalent (on the NMR time scale). The complexes were monomeric in solution, as established by the close agreement between the solution hydrodynamic radius, determined by PGSE NMR experiments, and that calculated from the X-ray crystal structure of **1**.[25] The complexes with phenyl substituents (**4**−**6**) showed several doublets, these were assigned to isomers arising due to slow rotations about the Y−N bond and/or chelate ring isomerization. It was not possible to uncover further information about the isomerization processes as the signals did not change in VT-NMR experiments. However, the complex purity was firmly established by isolating the complexes—they showed elemental analyses in excellent agreement with those calculated. Complex **8**, with an ethoxy substituent on the phosphorus, showed two broadened signals indicating that the two P atoms were inequivalent, this was expected due to the difference between the axial and equatorial substituents on the cyclohexylene ring.

X-ray Crystallography. Crystals of **3** suitable for X-ray analysis were isolated from a THF solution. The solid state structure revealed a highly distorted octahedral coordination geometry at the yttrium center where the tetradentate *S*,*N*,*N*′,*S*′ ligand occupies the equatorial sites, and the axial sites are filled by bis(trimethylsilyl)-amido and THF ligands (Figure 1). It should be noted that although THF coordination is observed here, the crystal was grown from a THF solution. When complexes **1**[23] and **4**−**6** were isolated they showed no evidence, by ^1H NMR spectroscopy, for THF coordination to the yttrium center.

The Y−N and Y−S bond lengths in **3** (Table 1) are *ca.* 0.03 and 0.09 Å respectively longer than their counterparts in **1**.[23]

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 3

	bond length (Å)		bond length (Å)
Y−S(1)	2.8881(8)	Y−N(3)	2.319(3)
Y−N(10)	2.326(2)	Y−S(12)	2.8570(9)
Y−N(25)	2.265(2)	Y−O(34)	2.425(2)
	bond angle (deg)		**bond angle (deg)**
S(1)−Y−N(3)	65.66(6)	S(1)−Y−N(10)	134.35(7)
S(1)−Y−S(12)	154.90(3)	S(1)−Y−N(25)	91.20(7)
S(1)−Y−O(34)	80.86(6)	N(3)−Y−N(10)	69.57(9)
N(3)−Y−S(12)	135.58(7)	N(3)−Y−N(25)	111.16(9)
N(3)−Y−O(34)	102.10(8)	N(10)−Y−S(12)	66.36(6)
N(10)−Y−N(25)	113.15(9)	N(10)−Y−O(34)	100.50(8)
S(12)−Y−N(25)	91.16(7)	S(12)−Y−O(34)	80.98(5)
N(25)−Y−O(34)	138.87(8)		

Table 2. Lactide Polymerization Rates and Control Using Initiators 1−8[a]

initiator	% conversion[b]	time/s	k_{app}[c] × 10^{-3}/s^{-1}	M_n(SEC)[d] (DP)	PDI
1	96	410	9.50	32 100 (223)	1.52
2	96	305	7.82	29 900 (207)	1.35
3	96	220	10.70	31 800 (220)	1.47
4	91	2460	1.57	24 000 (166)	1.53
5	99	5440	0.83	30 800 (213)	1.66
6	91	1500	1.95	28 300 (196)	1.57
7	96	3945	0.36	30 200 (210)	1.54
7(THF)	95	5400	0.53	32 600 (226)	1.57
8	96	12 619	0.078	27 936 (194)	1.56

[a] The polymerization conditions: [LA]$_0$=1 M, [**2**-**8**]$_0$=5 mM, CH_2Cl_2, 298 K. [b] Determined by integration of the methyne signals in the ^1H NMR spectrum. [c] Determined from the gradients in Figure 2. [d] Determined by SEC, in THF vs. polystyrene standards and using a correction factor of 0.58 according to the literature.[40]

This reflects the increased coordination number in **3** [the Y−N(SiMe$_3$)$_2$ distance in **3** is *ca.* 0.02 Å longer than in **1**], and the effect of the shorter carbon chain between the two nitrogen centers [the N−Y−N bite angle in **3** is 69.57(9)° cf. 77.72(6)° in **1**].[23] The equatorial nitrogen and sulfur atoms in **3** are coplanar to within *ca.* 0.03 Å with the metal lying *ca.* 0.26 Å out of this plane in the direction of N(25). The five-membered *N*, *N*′ chelate ring has a twist conformation, C(4) and C(9) lying *ca.* 0.33 and 0.29 Å "below" [toward N(25)] and "above" the plane respectively (in the structure shown in Figure 1 the ring has a δ-twist, but the crystal contains an equal number of molecules with a λ-twist).

Lactide Ring-Opening Polymerization. Although yttrium initiators are known to be very active for lactide polymerization, they can be difficult to isolate and handle. The lactide polymerization rate and control using isolated crystals of **1** or the complex generated *in situ* (by reaction between H_2L_1 and [$Y(N(SiMe_3)_3]$) were identical.[23] Therefore, all the polymerizations using **1**−**8** were carried out using complexes generated *in situ*.

Polymerization Kinetics. Complex **1** had previously shown very high activity for lactide polymerization (k_p = 0.19 s^{-1} M^{-1}). The rate constant, k_p, was the same order of magnitude as the Dupont homoleptic alkoxide initiators and among the highest yet reported.[23] Furthermore, the rate law was second order, with a dependence on both the concentration of lactide and of the initiator. The pseudo first order rate constants, k_{app}, were compared for complexes **2**−**8** (Table 2, Figure 2).

The polymerizations were all very fast, reaching greater than 90% conversion, at a lactide-to-yttrium ratio of 200, in minutes/hours depending on the ancillary ligand. The diamine backbone groups do not exert a significant influence on the rate. Instead, the phosphorus substituents exert the greatest influence over the polymerization rate. Complexes with isopropyl substituents (**1**−**3**) were significantly faster than those with phenyl substituents (**4**−**6**) which were, in turn, faster than those with ethoxy

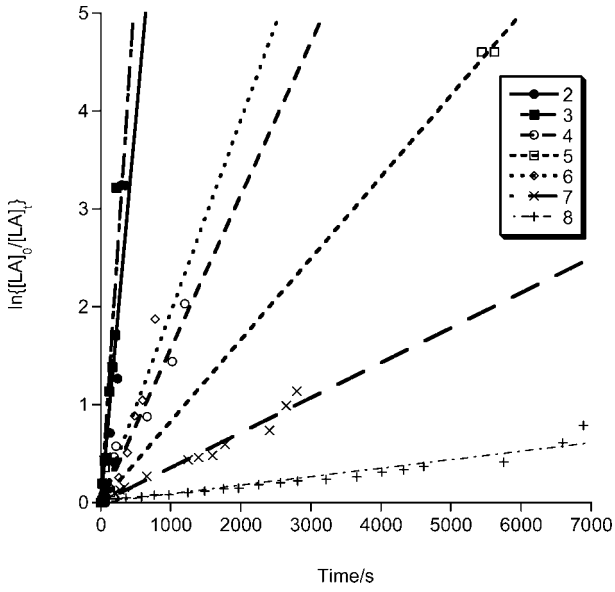

Figure 2. Plot of $\ln\{[LA]_0/[LA]_t\}$ versus time (s) for initiators **2**−**8**. The k_{app} values are the gradients of the fits: **2** = 0.00782 (R = 0.92), **3** = 0.01070 (R = 0.91), **4** = 0.00157 (R = 0.98), **5** = 0.00083 (R = 0.99), **6** = 0.00195 (R = 0.96), **7** = 0.00036 (R = 0.98), **8** = 0.00008 (R = 0.97).

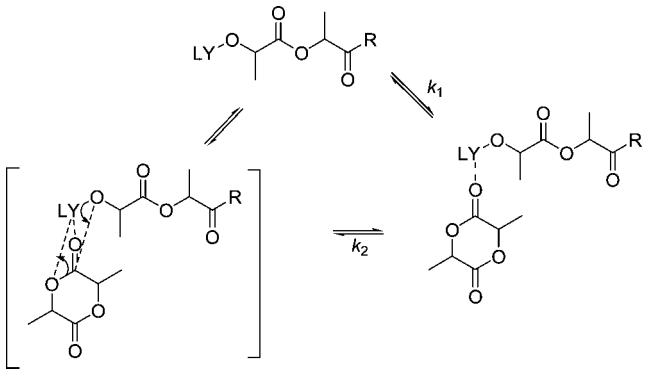

Figure 3. The coordination-insertion mechanism for lactide ring-opening polymerization. L = ligand structures illustrated in Scheme 1. (N.B. the attack at the carbonyl carbon by the metal bound alkoxide and the lactide acyl bond cleavage are not necessarily occurring concertedly).

substituents (**7**−**8**). The relative rates are probably due to the electronic influence, as the steric hindrance of an isopropyl and phenyl group are not sufficiently different to account for an order of magnitude difference in rate. The rates can be rationalized using the proposed coordination-insertion mechanism (Figure 3) which has two potential rate determining steps: the coordination (k_1) or the insertion (k_2) of the lactide monomer at the yttrium center. It is proposed that the electron withdrawing phenyl and ethoxy groups will increase the Lewis acidity of the yttrium center and thereby increase k_1. However, an increase in Lewis acidity at the yttrium center will also increase the polarity/strength of the putative yttrium alkoxide bond and thereby decrease k_2. The lower rates observed with phenyl/ethoxy substituents suggest that k_2 is rate determining for these yttrium complexes. The insertion step (k_2) has also been found to be rate determining for zinc and magnesium trispyrazolylborate/β-diiminate complexes, on the other hand, bimetallic zinc phenolate complexes have rates controlled by the coordination of lactide (k_1).[35−37] It is clear that a subtle balance between k_2 and k_1 affects the overall rate; the fundamental rules governing which is rate determining are not yet uncovered.

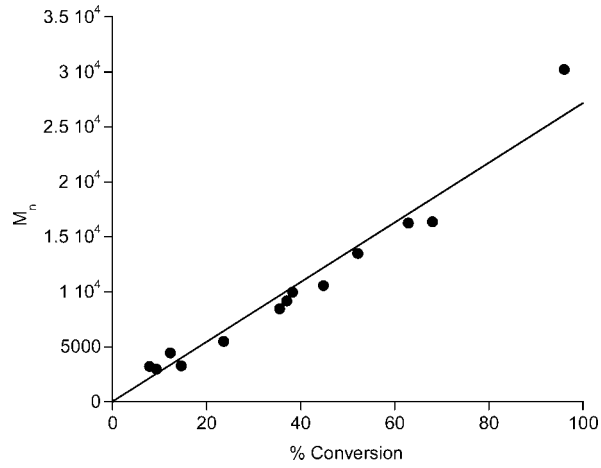

Figure 4. Plot showing M_n, determined by SEC versus the percentage conversion, determined by ^{1}H NMR for **7**. Polymerization conditions: $[LA]_0$ = 1 M, $[7]_0$ = 5 mM, CH_2Cl_2, and 298 K.

Polymerization Control. The initiators all controlled the polymerization effectively; in each case there was a good correlation between the degree of polymerization (DP) predicted on the basis of the initiator loadings used (200) and the experimentally observed DPs (166−223). The polymerization control is further illustrated by the linear fit of a plot of M_n versus the percentage conversion using **7** (Figure 4). The polydispersity indices (PDI) were quite high (1.35−1.66) which is likely due to transesterification side reactions and/or to a relatively low ratio of $k_{initiation}/k_{propagation}$. MALDI−TOF spectra were obtained for the PLA produced using all the initiators (a representative example using initiator **6** is illustrated in Figure S2, Supporting Information). The spectrum shows the expected linear chains with bis(trimethylsilyl)amido and hydroxyl end groups as the major species present. However, the repeat unit corresponds to 72 amu (the mass of lactic acid or lactide/2) which indicates that significant intermolecular transesterification occurs. There is also a low intensity population of cyclic species, formed by intramolecular/back biting transesterification reactions.

Stereocontrol. Stereochemical control in the ring-opening polymerization of *rac*-lactide is an attractive method to tune the polymer's properties (e.g., T_m/crystallinity) and is also an intriguing academic challenge. First, it was established that the initiators did not epimerize *S*-lactide; its polymerization yielded only isotactic, poly(*S*-lactide) as confirmed by homonuclear decoupled ^{1}H NMR spectroscopy. In polymerizations using *rac*-lactide, complexes **1**-**6** showed no stereocontrol and gave rise to atactic PLA. Complexes **7** and **8**, however, showed a distinct heterotactic bias with P_s values (probability of syndiotactic enchainment of lactide units) of 0.68 and 0.79 respectively (Supporting Information, Figures S3 and S4).[38] There are only a few examples of stereocontrolled yttrium initiators, the degree of control exhibited by these initiators is comparable to the bis(phenoxy)amine yttrium complexes.[17,19,21,29,32,33] It is notable that these initiators also require a coordinating ether group in the ligand backbone and/or the use of a coordinating reaction solvent (THF) to display good hetereoselectivity.[17,19,21,29,32,33] A polymerization was conducted in THF using complex **7** (Table 2), it showed very similar kinetics (Figure S5, Supporting Information) and a slightly lower P_s (0.63, Figure S6, Supporting Information) compared to the polymerization in methylene chloride. It seems likely that the ability of the phosphorus ether substituents to form labile, coordination bonds to yttrium enables binding/rebinding to occur throughout the catalytic cycle. Therefore, it is proposed that such hemilabile binding controls the coordination environment at the active propagating center and thereby leads to stereocontrolled polymerization. It is worth noting that the polylactide

produced using complexes **7** and **8** shows significant intermolecular transesterification had occurred (peaks in the MALDI−TOF spectrum are separated by 72 amu), such transesterification is likely to scramble the stereochemistry of the PLA produced. This finding suggests that the initiator could be capable of exerting even higher levels of polymerization control if the transesterification side reactions could be reduced.

Conclusions

In conclusion, the preparation and use of a series of bis(thiophosphinic amido) yttrium complexes for lactide polymerization has been described. The complexes were synthesized *in situ* by an amine elimination route from [Y(N(SiMe$_3$)$_3$] and characterized by ^{31}P(^{1}H) NMR spectroscopy. The complexes were active and controlled initiators of lactide ring-opening polymerization. The nature of the substituents on the phosphorus atom exerted a significant effect on the polymerization rate with the order of decreasing rate being isopropyl > phenyl > ethoxy. It is proposed that the rate determining step involves the insertion of the lactide monomer into the yttrium alkoxide bond and that the phosphorus substituents control the rate by influencing the strength of the yttrium alkoxide bond. Complexes with ethoxy substituents also showed a heterotactic bias in the polymerization of *rac*-lactide. These yttrium complexes are an important new type of initiator as they can be generated easily and cleanly in solution and display very high rates, good control and in some cases stereocontrol in lactide ring-opening polymerization.

Experimental Section

Materials and Methods. All reactions were conducted under nitrogen, using either standard anaerobic techniques or in a nitrogen filled glovebox. All solvents and reagents were obtained from commercial sources and dried. *rac*-Lactide and *S*-lactide were generously donated by Purac. The lactide was recrystallized from anhydrous ethyl acetate and sublimed three times under vacuum. Tetrahydrofuran was distilled from sodium and stored under nitrogen. Chloroform-*d* was dried using calcium hydride. [Y{N(SiMe$_3$)$_2$}$_3$] was prepared according to literature procedures.[39] The ligand syntheses (H_2L_1−H_2L_8) and characterization are included in the Supporting Information.

Measurements. NMR spectra were performed on a Bruker AV-400 instrument. Elemental analyses were determined by Mr. Stephen Boyer, London Metropolitan University, North Campus, Holloway Road, London, N7. SEC data was collected using a Polymer laboratories PCL-50 using THF as the eluent at a flow rate of 1 mLmin^{-1}. Two Polymer laboratories Mixed D columns were used in series and the M_n were calibrated against narrow M_n polystyrene standards (Easical standards A and B). A correction factor of 0.58 was applied to the M_n obtained vs polystyrene, according to the literature.[40]

Crystal Data for 3. 3: $C_{28}H_{64}N_3OP_2S_2Si_2Y$, M = 729.97, monoclinic, $P2_1/c$ (no. 14), a = 18.0407(6) Å, b = 10.6500(4) Å, c = 20.3838(8) Å, β = 100.558(3)°, V = 3850.1(2) Å^3, Z = 4, D_c = 1.259 g cm^{-3}, μ(Mo Kα) = 1.793 mm^{-1}, T = 173 K, colorless prisms, Oxford Diffraction Xcalibur X3 diffractometer; 13288 independent measured reflections, F^2 refinement, R_1 = 0.056, wR_2 = 0.133, 8434 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 66°], 403 parameters. CCDC 638408.

General Procedure for Initiator Synthesis. The appropriate diamine (0.25 mmol) and [Y{N(SiMe$_3$)$_2$}$_3$] (143 mg, 0.25 mmol) were dissolved in THF (3 mL). The reaction was stirred until the ligand peak had disappeared from the ^{31}P{^{1}H} NMR (2−10 days). The same procedure was used for all the complexations.

1.[23] ^{31}P{^{1}H} NMR (161.9 MHz, THF-CDCl$_3$ probe) δ, ppm: 71.9 (d, $^2J_{P-Y}$ = 6.64 Hz). ^{1}H NMR (400 MHz, C_5D_8O) δ, ppm: 2.88 (m, 4H, CH_2) 2.33−2.04 (m, 4H, CH(CH$_3$)$_2$), 1.09−1.28 (m, 24H, 4 × CH(CH_3)$_2$, 2 × CH_3), 0.04 (s, 18H, Si(CH_3)$_3$).

2. ^{31}P{^{1}H} NMR (161.9 MHz, THF-CDCl$_3$ probe) δ, ppm: 71.7 (d, $^2J_{P-Y}$ = 5.02 Hz).

3. ^{31}P{^{1}H} NMR (109.3 MHz, THF-CDCl$_3$ probe) δ, ppm: 72.1 (d, $^2J_{P-Y}$ = 5.35 Hz).

4. ^{31}P{^{1}H} NMR (161.9 MHz, C_7D_8) δ, ppm: 48.7 (d, $^2J_{P-Y}$ = 5.80 Hz, 2P), 44.5 (d, $^2J_{P-Y}$ =6.48 Hz, 1P), 42.5 (d, $^2J_{P-Y}$ = 6.96 Hz, 1P). ^{1}H NMR (400 MHz, C_7D_8) δ, ppm: 8.25−6.95 (m, 20H, *ArH*), 2.90−2.82 (m, 2H, NCH_2C), 2.14−2.07 (m, 2H, NCH_2C), 0.76 (s, 3H, C(CH_3)$_2$), 0.52 (s, 3H, C(CH_3)$_2$), 0.29 (s, 9H, Si(CH_3)$_2$), 0.07 (s, 9H, Si(CH_3)$_2$). Anal. Calcd for $C_{35}H_{48}N_3P_2S_2Si_2Y$: C, 53.76, H, 6.19, N, 5.37, Found: C, 53.78, 6.08, 5.60.

5. ^{31}P{^{1}H} NMR (161.9 MHz, C_7D_8) δ, ppm: 42.9 (d, $^2J_{Y-P}$ = 5.34 Hz). ^{1}H NMR (400 MHz, C_7D_8) δ, ppm: 7.65−6.92 (m, 20H, Ar*H*), 3.90 (m, 1H, NCH_2CH_2N), 3.17 (m, 2H, NCH_2CH_2N), 2.37−2.05 (m, 10H, NCH_2CH_2N, Si(CH_3)$_2$), 0.41 (s, 9H, Si(CH_3)$_3$). Anal. Calcd for $C_{32}H_{42}N_3P_2S_2Si_2Y$: C, 51.95, H, 5.72, N, 5.68, Found: C, 52.03, 5.88; 5.66.

6. ^{31}P{^{1}H} NMR (161.9 MHz, C_7D_8) δ, ppm: 43.2 (d, $^2J_{P-Y}$ = 4.43 Hz, 6 P), 40.6 (d, $^2J_{P-Y}$ = 4.10 Hz, 1P), 40.1 (d, $^2J_{P-Y}$ = 5.25 Hz, 1P), 37.6 (d, $^2J_{P-Y}$ = 5.58 Hz, 4P), 36.5 (d, $^2J_{P-Y}$ = 5.58 Hz, 4P). Anal. Calcd for $C_{36}H_{48}N_3P_2S_2Si_2Y$: C, 54.46, H, 6.09, N, 5.29, Found: C, 54.55, H, 5.88, N, 5.66.

7. ^{31}P{^{1}H} NMR (161.9 MHz, THF−CDCl$_3$ probe) δ, ppm: 58.0 (d, $^2J_{P-Y}$ = 2.42 Hz).

8. ^{31}P{^{1}H} NMR (161.9 MHz, THF−CDCl$_3$ probe) δ: 54.7 (bs), 54.6 (bs).

General Polymerization Procedure. All glassware was treated with Me_2SiCl_2 (1 M solution in CH_2Cl_2) and oven-dried for 4 h prior to use. The lactide was dissolved in CH_2Cl_2. The initiator stock solution in THF was 3.8 mM. A portion of the initiator stock solution was added to the solution of *rac*-lactide in CH_2Cl_2, so that the initial lactide concentration was always 1 M. The polymerization was monitored by removal of aliquots at regular intervals, these were quenched by addition to wet hexane solutions and the crude product dried *in vacuo*.

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Supporting Information Available: A cif file with crystallographic data and text giving complete experimental protocols, characterization data for H_2L_1-H_2L_8, and the X-ray crystallographic procedure for **3**·THF and figures showing the molecular structure of **1**, a representative MALDI−TOF spectrum, the ^{1}H NMR spectra (decoupled) for the PLA produced using initiators **7** and **8**, the semilogarithmic plot for initiator **7** in THF, and and the ^{1}H NMR spectrum (decoupled) for the polylactide produced using initiator **7** in THF.This material is available free of charge via the Internet at http://pubs.acs.org.

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