

Novel Titanatranes with Different Ring Sizes: Syntheses, Structures, and Lactide Polymerization Catalytic Capabilities

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The new titanatranes $\text{ArOTiO}(\text{o-Ar}'\text{CH}_2)_{3-x}\text{N}(\text{CH}_2\text{CH}_2\text{O})_x$ ($\text{Ar} = 2,6\text{-di-}i\text{-Pr-phenoxy}$; $\text{Ar}' = 2,4\text{-di-MeC}_6\text{H}_2$; $x = 0$, **5**; $x = 1$, **6**; $x = 2$, **7**; $x = 3$, **8**) featuring three six-membered chelating rings (**5**) to three five-membered chelating rings (**8**) in a stepwise fashion through **6** and **7** were synthesized from the corresponding trihydroxy chelating ligands **1–4**, respectively, using an equimolar mixture of $\text{Ti}(\text{O-}i\text{-Pr})_4$ and 2,6-di-*i*-Pr-phenol. The molecular structures of **5** and **6**, determined by X-ray means, revealed that in both of these complexes the transannular N–Ti bond lengths [2.305(2) Å, **5**; 2.287(4) Å, **6**] are at the short end of the range for titanatranes possessing three five-membered rings. These compounds show good catalytic activity for the bulk homopolymerization of *l*- and *rac*-lactide at 130 °C.

Introduction

Five-membered ring atranes synthesized from triethanolamine feature a wide variety of metallic and nonmetallic central atoms.¹ Many studies of these compounds have focused on main group elements such as silicon, phosphorus, aluminum, and tin.^{1,2} Among the transition metallic atranes, relatively few reports have appeared concerning titanatranes.³ Recently, Holmes et al. reported the synthesis of various silatranes containing three six-membered rings using ligand precursor **1**,⁴ whereas all previous work had centered on silatranes possessing five-membered rings arising from the use of the ligand precursor triethanolamine. The few examples of atranes having different ring sizes that have been reported in the literature contain a main group element

chelated by the trialkanolate ligand $(\text{OCH}_2\text{CH}_2)_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{O}^-$.⁵ Examples of titanatranes containing two different ring sizes have, to our knowledge, not been reported.

A wide variety of catalytic alkoxide systems based on tin,⁶ aluminum,⁷ zinc,⁸ magnesium,^{8b–e} iron,⁹ and lanthanide¹⁰ organometallic complexes have been reported to function as catalysts for the polymerization of lactide (LA). Despite the fact that excellent initiators have been found among these systems for the polymerization of LA, the search for new catalysts for generating well-defined polylactide (PLA) still remains of interest. In view of the well-known significant number of similarities in the chemistries of tin and titanium, we were

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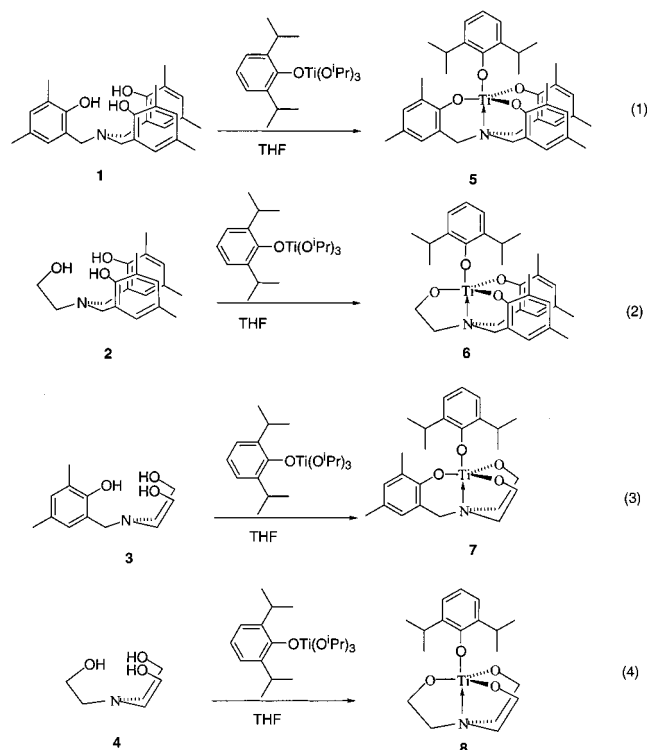
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somewhat surprised to find that no investigations of titanium alkoxides as potential catalysts in this polymerization reaction have been reported, although they are well-known to homogeneously catalyze olefin polymerization,¹¹ and some Ti complexes have been found to polymerize ϵ -caprolactone.¹²

Here we describe the synthesis, characterization, and catalytic ability for the bulk polymerization of LA, for four titanatranes possessing the ligands derived by deprotonation of the OH groups in tris(2-hydroxy-3,5-dimethylbenzyl)amine, **1**,^{4a} bis(2-hydroxy-3,5-dimethylbenzyl)ethanolamine, **2**,¹³ (2-hydroxy-3,5-dimethylbenzyl)diethanolamine, **3**,¹³ and triethanolamine, **4**, in reactions 1–4. The corresponding four titanatranes **5–8** all possess an axial anionic 2,6-di-*i*-Pr-phenolate ligand.



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(13) The syntheses of **2** and **3** were reported in the patent literature (Siegl, W. O.; Chattha, M. S. Eur. Pat. Appl. 276073, 1988), but no spectroscopic data were provided. **2**: ¹H NMR (CDCl₃, 400.147 MHz): δ 6.83 (s, 2H, aryl-*H*), 6.67 (s, 2H, aryl-*H*), 3.85 (t, *J* = 5.2 Hz, 2H, CH₂O), 3.71 (s, 4H, NCH₂-aryl), 2.67 (t, *J* = 5.2 Hz, 2H, NCH₂CH₂), 2.18 (d, *J* = 8.9 Hz, 12H, aryl-*Me*). ¹³C{¹H} NMR (CDCl₃, 100.626 MHz): δ 152.2, 131.4, 128.7, 128.4, 125.1, 121.7 (aryl), 60.92 (CH₂-OH), 57.07 (NCH₂-aryl), 53.58 (NCH₂CH₂), 20.61, 16.19 (aryl-*Me*). HRMS (EI) *m/z* calcd: 239.1521. Found: 239.1524. **3**: ¹H NMR (CDCl₃, 400.147 MHz): δ 6.83 (s, 1H, aryl-*H*), 6.61 (s, 1H, aryl-*H*), 3.77 (s, 2H, NCH₂-aryl), 3.73 (t, *J* = 6.8 Hz, 4H, CH₂O), 2.74 (t, *J* = 6.8 Hz, 4H, NCH₂CH₂), 2.19 (d, *J* = 8.5 Hz, 6H, aryl-*Me*). ¹³C{¹H} NMR (CDCl₃, 100.626 MHz): δ 152.9, 130.7, 127.9, 126.8, 124.8, 121.3 (aryl), 60.25 (CH₂OH), 59.45 (NCH₂CH₂), 56.10 (NCH₂-aryl), 20.38, 15.66 (aryl-*Me*). HRMS (EI) *m/z* calcd: 329.1991. Found: 329.1996.

Experimental Section

General Procedures. All reactions were carried out under an argon atmosphere using standard Schlenk and glovebox techniques.¹⁴ All chemicals were purchased from Aldrich and were used as supplied unless otherwise indicated. THF and toluene (Fischer HPLC grade) were dried and purified under a nitrogen atmosphere in a Grubbs-type nonhazardous two-column solvent purification system¹⁵ (Innovative Technologies) and were stored over activated 3 Å molecular sieves. All deuterium solvents were dried over activated molecular sieves (3 Å) and were used after vacuum transfer to a Schlenk tube equipped with a J. Young valve.

Measurements. ¹H and ¹³C{¹H} NMR spectra were recorded at ambient temperature on a Varian VXR-400, VXR-300, or Bruker AC200 NMR spectrometer using standard parameters. The chemical shifts are referenced to the residual peaks of CDCl₃ (7.24 ppm, ¹H NMR; 77.0 ppm, ¹³C{¹H} NMR) and C₆D₆ (7.15 ppm, ¹H NMR; 128 ppm, ¹³C{¹H} NMR). Elemental analyses were performed by Desert Analytics Laboratory. Molecular weights of polymers were determined by gel permeation chromatography (GPC), and the measurements were carried out at room temperature with THF as the eluent (1 mL/min) using a Waters 510 pump, a Waters 717 Plus Autosampler, four Polymer Laboratories PLgel columns (100, 500, 10⁴, 10⁵ Å) in series, and a Wyatt Optilab DSP interferometric refractometer as a detector. The columns were calibrated with polystyrene standards.

Syntheses. Compounds **6–8** were made by a procedure analogous to that given here for **5**. To a THF solution composed of 2,6-di-*i*-Pr-phenol (0.891 g, 5.00 mmol) in 10 mL of THF was added dropwise at room temperature a solution of Ti(O-*i*-Pr)₄ (1.42 g, 5.00 mmol) in 10 mL of THF. After 1 h, a solution of tris(2-hydroxy-3,5-dimethylbenzyl)amine (2.10 g, 5.00 mmol) in 10 mL of THF was added dropwise to the reaction vessel. The reaction mixture was stirred at room temperature overnight, and then the volatiles were evaporated under vacuum, leaving an orange-yellow solid, to which was added 15 mL of toluene. The orange solution was filtered, and the desired product **5** was isolated as orange-yellow crystals after the solution remained at -15 °C in a refrigerator for a few days (2.25 g, 70%). ¹H NMR (CDCl₃, 400.147 MHz): δ 7.18–6.73 (m, 9H, aryl-*H*), 4.11 (m, 5H, overlap of CHMe₂ with NCH₂-aryl), 2.97 (d, *J* = 13.4 Hz, 3H, NCH₂-aryl), 2.23 (d, *J* = 3.0 Hz, 9H, aryl-*Me*), 2.06 (d, *J* = 4.0 Hz, 9H, aryl-*Me*), 1.24 (s, 12H, CHMe₂). ¹H NMR (C₆D₆, 400.147 MHz): δ 7.28 (d, *J* = 7.6 Hz, 2H, aryl-*H*), 7.09 (m, 1H, aryl-*H*), 6.74 (s, 3H, aryl-*H*), 6.40 (s, 3H, aryl-*H*), 4.48 (m, 2H, CHMe₂), 3.95 (d, *J* = 13.8 Hz, 3H, NCH₂-aryl), 2.45 (d, *J* = 13.8 Hz, 3H, NCH₂-aryl), 2.20 (s, 9H, aryl-*Me*), 2.14 (s, 9H, aryl-*Me*), 1.45 (t, *J* = 7.2 Hz, 12H, overlapping pair of doublets for CHMe₂). ¹³C{¹H} NMR (CDCl₃, 100.626 MHz): δ 162.5, 159.7, 137.6, 130.8, 129.9, 127.3, 124.1, 123.3, 122.5, 121.3 (aryl), 58.56 (NCH₂), 26.67 (CHMe₂), 23.93 (CHMe₂), 23.73 (CHMe₂), 20.59 (aryl-*Me*), 15.85 (aryl-*Me*). Anal. Calcd for C₃₉H₄₇NO₄Ti·1/3 toluene: C, 73.83; H, 7.44; N, 2.08. Found: C, 74.10; H, 7.59; N, 2.16.

6: yield 62%. ¹H NMR (CDCl₃, 400.147 MHz): δ 7.27–6.80 (m, 7H, aryl-*H*), 4.53 (t, *J* = 5.6 Hz, 2H, CH₂O), 4.00 (m, 2H, CHMe₂), 3.91 (d, *J* = 13.4 Hz, 2H, NCH₂-aryl), 3.63 (d, *J* = 13.4 Hz, 2H, NCH₂-aryl), 3.00 (br s, 2H, NCH₂CH₂), 2.25 (s, 6H, aryl-*Me*), 2.15 (s, 6H, aryl-*Me*), 1.29 (d, *J* = 6.9 Hz, 12H, CHMe₂). ¹³C{¹H} NMR (CDCl₃, 100.626 MHz): δ 161.4, 159.1, 138.0, 131.1, 129.4, 127.6, 124.8, 122.9, 122.6, 121.0 (aryl), 72.00 (CH₂O), 57.18 (NCH₂-aryl), 56.85 (NCH₂CH₂), 26.76 (CHMe₂), 23.65 (CHMe₂), 20.55 (aryl-*Me*), 16.11 (aryl-*Me*). Anal. Calcd for C₃₂H₄₁NO₄Ti·1/3 toluene: C, 70.82; H, 7.56; N, 2.41. Found: C, 70.96; H, 7.83; N, 2.53.

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Table 1. Crystallographic Data and Parameters for 5 and 6

	5	6
formula	C ₄₁ H ₅₁ NO _{4.5} Ti	C ₃₄ H ₄₅ NO _{4.5} Ti
fw	677.73	585.59
cryst syst	monoclinic	triclinic
space group	<i>P2₁/n</i>	<i>P1</i>
<i>a</i> (Å)	14.890(4)	10.2280(19)
<i>b</i> (Å)	11.530(3)	11.448(2)
<i>c</i> (Å)	22.378(6)	15.344(3)
α (deg)	90	70.710(3)
β (deg)	105.533(4)	85.085(4)
γ (deg)	90	80.038(3)
<i>V</i> (Å ³)	3701.6(17)	1669.4(5)
<i>Z</i>	4	2
<i>d_c</i> (g/cm ³)	1.216	1.165
<i>F</i> (000)	1448	624
<i>T</i> (K)	173(2)	293(2)
abs coeff (mm ⁻¹)	0.273	0.293
θ range (deg)	1.89; 26.38	1.91; 20.82
no. of reflns collected	29 943	8305
no. of ind reflns	7539	3489
no. of params refined	429	388
<i>R</i> ₁ ^a	0.0586	0.0562
<i>wR</i> ₂ ^a	0.1772	0.1538
GOF	1.089	1.017
min. and max. dens (e Å ⁻³)	1.156, -0.426	0.476, -0.264

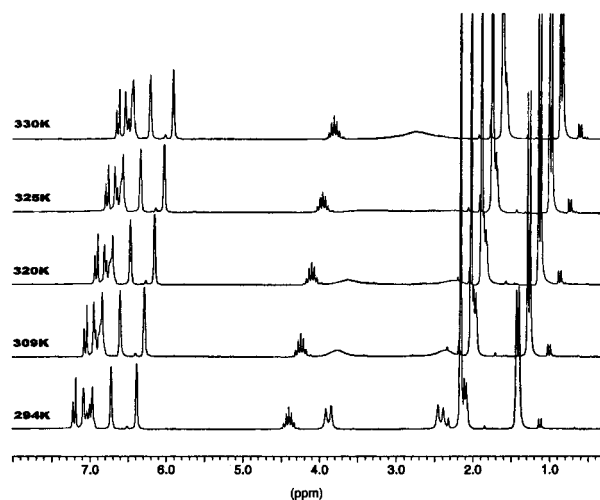
$$^a R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|} \text{ and } wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)]^2}{\sum [w(F_o^2)]^2} \right\}^{1/2}$$

7: yield 67%. ¹H NMR (CDCl₃, 400.147 MHz): δ 7.07–6.81 (m, 5H, aryl-*H*), 4.60 (t, *J* = 5.8 Hz, 2H, CH₂O), 4.45 (t, *J* = 5.6 Hz, 2H, CH₂O), 3.96 (s, 2H, NCH₂-aryl), 3.80 (t, *J* = 6.4 Hz, 2H, CHMe₂), 3.20 (t, *J* = 5.6 Hz, 2H, NCH₂CH₂), 3.13 (t, *J* = 5.8 Hz, 2H, NCH₂CH₂), 2.25 (s, 3H, aryl-*Me*), 2.16 (s, 3H, aryl-*Me*), 1.27 (d, *J* = 6.7 Hz, 12H, CHMe₂). ¹³C{¹H} NMR (CDCl₃, 100.626 MHz): δ 160.7, 158.9, 138.1, 133.5, 131.3, 128.9, 127.9, 125.4, 123.4, 122.6, 120.7, 120.5 (aryl), 71.56 (CH₂O), 56.34 (NCH₂-aryl), 26.80 (CHMe₂), 23.50 (CHMe₂), 22.75 (CHMe₂), 20.50 (aryl-*Me*), 16.67 (aryl-*Me*). Anal. Calcd for C₂₅H₃₅NO₄Ti: C, 65.08; H, 7.65; N, 3.04. Found: C, 64.60; H, 7.94; N, 3.11.

8: yield 76%. ¹H NMR (CDCl₃, 400.147 MHz): δ 7.02 (d, *J* = 7.6 Hz, 2H, aryl-*H*), 6.84 (t, *J* = 7.6 Hz, 1H, aryl-*H*), 4.54 (t, *J* = 5.6 Hz, 6H, CH₂O), 3.62 (m, 2H, CHMe₂), 3.29 (t, *J* = 5.5 Hz, 6H, NCH₂), 1.25 (d, *J* = 6.9 Hz, 12H, CHMe₂). ¹³C{¹H} NMR (CDCl₃, 100.626 MHz): δ 160.0, 137.9, 122.4, 120.4 (aryl), 71.17 (CH₂O), 56.78 (NCH₂), 26.84 (CHMe₂), 23.33 (CHMe₂). Anal. Calcd for C₁₈H₂₉NO₄Ti: C, 58.23; H, 7.87; N, 3.77. Found: C, 58.35; H, 8.12; N, 3.79.

X-ray Crystallography for 5 and 6. The crystallographic measurements were performed at 173 K for **5** or 293 K for **6** using a Bruker CCD-1000 diffractometer with Mo K α (λ = 0.71073 Å) radiation and a detector-to-crystal distance of 5.03 cm. Specimens of suitable quality and size (0.2 × 0.2 × 0.2 mm³) were selected and mounted onto glass fibers with silicon grease or epoxy glue. The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 30 frames collected at intervals of 0.3° in a 10° range about ω with the exposure time of 30 s per frame for **5** and 20 s per frame for **6**. All the intensity data were corrected for Lorentz and polarization effects. The structures were solved by the Patterson method and the direct method and were refined by full-matrix anisotropic approximation. All hydrogen atoms were placed at idealized positions in the structure factor calculation and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. Final refinement based on the reflections (*I* > 2.0 σ (*I*)) converged at *R*₁ = 0.0586, *wR*₂ = 0.1772, and GOF = 1.089 for **5** and at *R*₁ = 0.0562, *wR*₂ = 0.1538, and GOF = 1.017 for **6**. Further details are listed in Table 1.

Polymerization Procedure. LA polymerizations were carried out as follows: 2.00 g of LA and then the appropriate

**Figure 1.** Variable-temperature ¹H NMR spectra of **5**.

amount of catalyst precursor were charged to a 25 mL Schlenk flask. The flask was then immersed in an oil bath at 130 °C. After 24 h, the reaction was terminated by the addition of 5 mL of methanol. The polymers so obtained as precipitates were dissolved in a minimum amount of methylene chloride, and then excess methanol was added. The resulting reprecipitated polymers were collected, washed with 3 × 50 mL of methanol, and dried in vacuo at 50 °C for 12 h.

Results and Discussion

The treatment of Ti(O-*i*-Pr)₄ with 1 equiv of 2,6-di-*i*-Pr-phenol and 1 equiv of the ligand precursors **1–4** in THF gave, after workup, the novel titanatranes **5–8** as orange-yellow crystals in 62–76% isolated yield. These four products in the solid state were stable in air for a few weeks, and according to ¹H NMR spectroscopy, they decomposed slightly after a few days at room temperature in CDCl₃ solutions contained in capped NMR tubes. They are soluble in polar organic solvents and in toluene, but are insoluble in alkanes such as *n*-hexane.

The ¹H NMR spectra of **5–8** display well-defined resonances with their expected integrations. At 325K in toluene-*d*₈ solution, the two resonances for aryl methylene protons in **5** coalesce to a single resonance (Figure 1). On the NMR time scale, **5** should have pseudo-*C*₃ symmetry, and therefore the benzylic CH₂ protons should not be equivalent. Indeed, the proximity of these protons to aromatic rings may explain the ca. 1.4 ppm chemical shift difference displayed in the room-temperature spectrum shown in Figure 1. Upon heating, compound **5** assumes pseudo-*C*_{3v} symmetry on the NMR time scale and all six CH₂ protons become equivalent.

To estimate the barrier to inversion in **5**, ΔG^\ddagger (J/mol) = 19.14 *T_c*[9.97 + log(*T_c*/ $\delta\nu$)] was calculated from the coalescence temperature of the NCH₂C₆H₂ methylene protons in the ¹H NMR spectrum.¹⁶ ΔG^\ddagger for **5** (at *T_c* = 325 K with $\delta\nu$ = 292.66 Hz) is 62.3 kJ/mol. By contrast, the analogous benzylic protons of **6** cannot become equivalent upon ring inversion because the cage moiety of **6** is pseudo-*C*_s symmetric. The *C*₁-symmetric twisted solid-state structure for **6** suggested that four chemical shifts should be observed in the ¹H NMR spectrum, but

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Table 2. Comparison of ^1H Chemical Shifts for Compounds 1–8 Dissolved in CDCl_3

compound	peak assignment						
	aryl- <i>H</i>	<i>CH</i> 2O	<i>CH</i> Me ₂	NCH ₂ -aryl	NCH ₂ CH ₂	aryl-Me	<i>CH</i> Me ₂
1	6.83, 6.71			3.61		2.19	
2	6.83, 6.67	3.85		3.71	2.67	2.18	
3	6.83, 6.61	3.73		3.77	2.74	2.19	
4		3.69			2.43		
5	7.18–6.73		4.11 ^a	4.11, ^a 2.97		2.23, 2.06	1.24
6	7.27–6.80	4.53	4.00	3.91, 3.63	3.00	2.25, 2.15	1.29
7	7.07–6.81	4.60, 4.45	3.80	3.96	3.20, 3.13	2.25, 2.16	1.27
8	7.02, 6.84	4.54	3.62		3.29		1.25

^a The *CH*Me₂ and NCH₂-aryl proton resonances overlap.

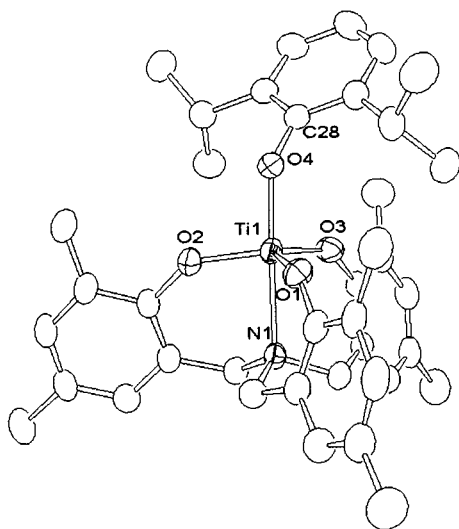


Figure 2. ORTEP drawing of **5** showing 50% probability thermal ellipsoids with H atoms and solvent omitted for clarity. Selected bond distances (Å): Ti1–O1 = 1.836(2), Ti1–O2 = 1.822(2), Ti1–O3 = 1.831(2), Ti1–O4 = 1.834(2), Ti1–N1 = 2.306(2). Selected bond angles (deg): C28–O4–Ti1 = 138.52(17), O4–Ti1–N1 = 174.89(8), O1–Ti1–O4 = 100.05(9), O2–Ti1–O4 = 97.96(9), O3–Ti1–O4 = 92.93(9).

only two were seen (Table 2). Similar considerations hold for the NCH₂ groups of **7**, for which two peaks were also observed in the ^1H NMR spectrum. (See Table 2) As observed in other five-membered titanatranes,³ the protons for both sets of methylene groups of **8** should be equivalent owing to the rate of ring inversion, which is rapid on the NMR time scale. Similarly, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **5** exhibits resonances corresponding to nonequivalent *i*-Pr groups even at room temperature, owing to its pseudo-*C*_s symmetry. In the ^1H NMR spectrum of **5**, the two *i*-Pr methyl groups displayed a somewhat broadened singlet, a doublet, and a triplet at room temperature in chloroform-*d*₁, toluene-*d*₈, and benzene-*d*₆, respectively. However, as the temperature of the benzene-*d*₆ solution decreased, the triplet gradually became two doublets, which is expected for two nonequivalent *i*-Pr groups whose CH₃ protons are equivalent owing to rapid rotation.

To elucidate the nature of the metal–ligand bonding in these titanatranes, we carried out single-crystal X-ray diffraction studies on **5** and **6**. ORTEP depictions,¹⁷ selected bond distances, and selected bond angles for **5** and **6** are shown in Figures 2 and 3, respectively. The

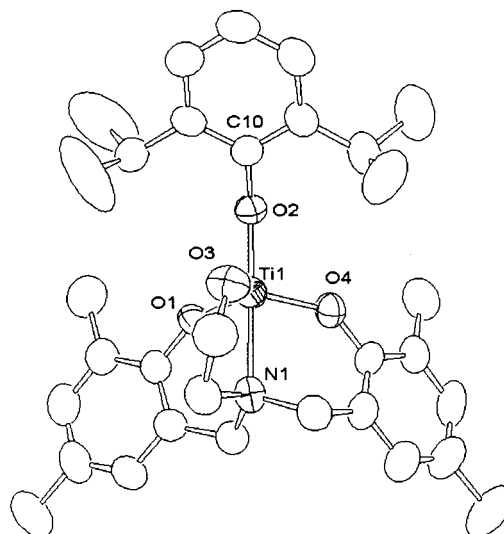
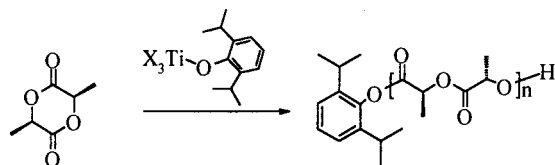


Figure 3. ORTEP drawing of **6** showing 50% probability thermal ellipsoids with H atoms and solvent omitted for clarity. Selected bond distances (Å): Ti1–O1 = 1.828(3), Ti1–O2 = 1.825(3), Ti1–O3 = 1.807(3), Ti1–O4 = 1.829(3), Ti1–N1 = 2.287. Selected bond angles (deg): C10–O2–Ti1 = 145.7(3), O1–Ti1–O2 = 102.43(13), O2–Ti1–O3 = 93.68(14), O2–Ti1–O4 = 99.66(14), O2–Ti1–N1 = 170.38(13).

X-ray analyses reveal that **5** and **6** have similar solid-state structures, and both possess 0.5 THF molecule of solvation. In contrast to oxygen-bridged dimeric structures frequently observed for titanatranes,^{3d,f} the molecular structures of **5** and **6** are monomeric (which is consistent with their NMR spectra) presumably because of the steric bulk of the axially located di-*i*-Pr-phenolate ligand.

The tricyclic cage moiety of **5** resembles a three-bladed turbine of *C*₃ symmetry, while that in **6** is similar (with an ethylene bridge replacing an aryl methylene group) resulting in *C*_s symmetry. In addition to the three anionic oxygens, the titanium atom in **5** and **6** is ligated via a transannular interaction stemming from the bridgehead amino nitrogen, giving a slightly distorted trigonal bipyramidal local geometry around the metal. The sum of the angles around the equatorial oxygens is 355.68(10)° and 353.54(15)° in **5** and **6**, respectively. As a result, the acute O_{eq}–Ti–N angles [*av* = 83.07(8)° for **5** and 81.59(14)° for **6**] and the obtuse O_{eq}–Ti–O_{ax} angles [*av* = 96.98(9)° for **5** and 98.59(14)° for **6**] reflect a displacement of the titanium atom toward the axial oxygen, which is larger for **6**. Furthermore, the N_{ax}–Ti–O_{ax} angle deviates from linearity by 5.11(8)° in **5** and by 9.62(13)° in **6**. These deviations are large compared with deviations of 0.20(8)–1.46(3)° reported

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Table 3. Data for *l*- and *rac*-Lactide Bulk Polymerizations Catalyzed by 5–8^a

catalyst	type of lactide	g polymer	yield (%)	M_w^b	M_n^b	PDI ^b
5	<i>l</i> -LA	1.38	69	29 300	19 400	1.51
	<i>rac</i> -LA	1.35	68	23 000	16 000	1.43
6	<i>l</i> -LA	1.50	75	30 700	18 700	1.64
	<i>rac</i> -LA	1.47	74	24 700	16 500	1.50
7	<i>l</i> -LA	1.82	91	30 800	20 000	1.56
	<i>rac</i> -LA	1.79	90	32 900	23 100	1.42
8	<i>l</i> -LA	1.98	99	44 500	25 400	1.75
	<i>rac</i> -LA	1.92	96	66 100	33 600	1.97

^a LA (2 g) LA/Ti = 300, polymerization temperature = 130 °C, polymerization time = 24 h. ^b The weight average molecular weight (M_w), the number average molecular weight (M_n), and the polydispersity index (PDI = M_w/M_n) were determined by GPC.

for other mononuclear titanatranes,^{3g–i,k,l} although values of 15.5(1)–51.05(8)° for this angle have been described for di- or multinuclear oxo-bridged titanatranes.^{3b,d–f,j} The average Ti–O bond distance for all four oxygens in each of **5** [1.831(2) Å] and **6** [1.822(3) Å] is similar to the average of this distance observed for other structurally characterized titanatranes.³ Interestingly, the transannular Ti–N bond distance in **5** [2.305(2) Å] and **6** [2.287(4) Å] falls near the short end of the range 2.264(3)–2.400(3) Å found in previously structurally characterized titanium trialkanolamine derivatives.³

Our preliminary results on the use of titanium alkoxide catalysts for the bulk polymerization of *l*-LA and *rac*-LA are summarized for **5–8** in Table 3. It appears that the initiating group is the highly bulky di-*i*-Pr-phenolate group, which was shown by ¹H NMR spectroscopy to be present in solutions of the isolated PLA samples. It is seen from Table 2 that the nature of the chelating tetradentate ligand significantly affects the molecular weight and the polydispersity indices (measured by GPC) and also the yield of the polymer. As the number of five-membered rings in the tetradentate ligand increases, there is a rough trend toward increasing polymerization activity and polydispersity index. Interestingly, catalysts **5–8** yield polymers with

somewhat large polydispersities and low molecular weights. This may be attributed to a rate of initiation that is slower than the rate of polymer propagation, thus allowing more time for the occurrence of transesterification reactions during propagation. As a consequence, bimodal and unimodal molecular weight distributions exhibiting a side tail or shoulder can be encountered, as was observed in the GPC trace of several of the polymers. However, despite this problem and the fact that the polymerizations were carried out at an elevated temperature, the PLA polydispersity indices are in an acceptable range (1.42–1.97 in Table 2).

A determination of the stereochemical microstructure of PLA can be achieved upon inspection of the methine region of homonuclear decoupled ¹H NMR spectra of PLA solutions.¹⁸ Such spectra of PLA derived from *rac*-LA display the typical five resonances predicted from a Bernoullian analysis of totally random (atactic) PLA, whereas spectra of PLA derived from *l*-LA exhibit only one peak, corresponding to the *mmm* tetrad for isotactic PLA. ¹H NMR spectra corresponding to these descriptions were also observed for our correspondingly derived polymers.

In summary, we have synthesized a novel series of four titanatranes featuring a stepwise change in ring size from five- to six-membered rings. These complexes function, with a trend in efficiency roughly paralleling the number of five-membered rings they possess, as single-site initiators for the polymerization of *l*-LA to isotactic PLA and *rac*-LA to atactic PLA.

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Supporting Information Available: Tables of crystal data, atomic coordinates, thermal parameters, bond distances, and bond angles for compounds **5** and **6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM0110686

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