



Titanium complexes containing new dianionic tetradentate [ONNO]-type ligands with benzyl substituents on bridging nitrogen atoms: Syntheses, X-ray structures, and catalytic activities in ring opening polymerization of lactide

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ARTICLE INFO

Article history:

Received 7 May 2009

Received in revised form 24 June 2009

Accepted 26 June 2009

Available online 1 July 2009

Dedicated to Professor Young Kook Shin in honor of his 65th birthday and on the occasion of his retirement.

Keywords:

Titanium
Tetradentate
Salan ligand
X-ray diffraction
Polylactide

ABSTRACT

Several titanium isopropoxides **1–8** have been prepared by the reaction of $\text{Ti}(\text{O-}i\text{-Pr})_4$ with a series of corresponding tetradentate Salan-type [ONNO] ligands with benzyl or methyl substituents on bridging nitrogen atoms. They have been characterized by ^1H NMR, $^{13}\text{C}\{^1\text{H}\}$ NMR, and elemental analysis. Solid state structures of compounds **2**, **4**, **6**, and **7** have been determined by X-ray crystallography. X-ray diffraction analysis and ^1H NMR confirmed that these titanium complexes were all monomeric species with a six-coordinated central titanium in their solid and solution structures. Complexes **2**, **4**, **6**, and **8** with benzyl substituents on bridging nitrogens gave PLA with higher molecular weight than compounds **1**, **3**, **5**, and **7** with methyl substituents did.

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1. Introduction

Polylactide (PLA) is a biodegradable and renewable polymeric material for the use as eco-friendly commodities such as controlled drug-release devices, absorbable sutures, medical implants for orthopedic use, disposable degradable plastic articles, and scaffolds for tissue engineering [1–5]. The ring opening polymerization (ROP) of lactide (LA) with a wide variety of catalytic systems based on tin, aluminum, zinc, magnesium, iron, lanthanide and lithium organometallic complexes containing initiating groups such as amides, carboxylates, and alkoxides has been intensively studied over the past few decades [6,7]. Despite the fact that some excellent initiators have been reported for the polymerization of LA in the literature [6,7], the search for new catalysts that generate well-defined PLA polymers are still important. Since 2002 several monomeric titanium precursors such as $\text{L}_m\text{Ti}(\text{OR})_n$ where m , $n = \text{integer}$; L = monodentate ligand [8–14]; L = bidentate ligand [14–22]; L = tridentate ligand [9,22–27]; L = tetradentate ligand

[8,9,28–37] have widely been explored in order to elucidate the relationship between structures of catalysts, catalytic activities, and the influence of their structure on physical properties of obtained PLA polymers. Among monomeric titanium complexes, titanium precursors with tetradentate ligands were most extensively studied [8–37].

Recently, titanium complexes **1** and **5** containing dianionic tetradentate Salan-type [ONNO] ligand with methyl substituents on two bridging nitrogens and methyl or *tert*-butyl substituents on two aryl-rings was used as an initiator both in solution and under the bulk ROP of LA in the literature [36,37]. Gendler et al. [36] reported that initiator **5** gave PLA with $M_n = 5400$ and $\text{PDI} = 1.11$ in the yield of 16% obtained under the bulk ROP condition of $[\text{l-LA}]/[\text{Ti}] = 300$. Independently, Chmura et al. [37] reported that poly(*rac*-lactide) with $M_n = 33\,000$ and $\text{PDI} = 1.64$ in the yield of 74% and with $M_n = 36\,000$ and $\text{PDI} = 1.51$ in the yield of 68% could be produced by **1** and **5**, respectively, under the bulk polymerization condition of $[\text{rac-LA}]/[\text{Ti}] = 300$. However, they found that **5** gave tetrameric oligomer with relatively low yield of 20% in the solution ROP condition of *l*-LA [37]. Also, Hormnirun et al. [38] reported that aluminum complexes containing **Lig²** and **Lig⁴** with benzyl substituents on bridging N atoms showed the improved activity and

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polymer properties when compared with aluminum counterparts containing **Lig¹** and **Lig³**. Although few examples of titanium isopropoxides with aryl-ring modified Salan ligands [36,37,39–41] and aluminum complexes [38,42] with ligands **Lig²** and **Lig⁴** have been reported in the literature, no examples in any electronic or steric modification of substituent on bridging N atoms in Salan–titanium complexes in order to improve the activity and polymer properties, have to our knowledge been reported.

In this regard, herein we report the synthesis and characterization of new complexes **2**, **4**, **6**, and **8** containing new tetradentate dianionic Salan-type [ONNO] ligands with benzyl groups on two bridging nitrogens and their very efficient catalytic behavior both under the bulk and in solution ROP condition of LA (see Fig. 1 and Scheme 1). Furthermore, we report here the catalytic performances for compounds **2**, **4**, **6**, and **8** have been compared with those for corresponding counterparts **1** [37,39], **3**, **5** [36,37,39,40], and **7**.

2. Results and discussion

Eight functionalized [ONNO]-type Salan ligand precursors such as **Lig¹H₂**–**Lig⁸H₂** were readily prepared by a one-pot Mannich reaction [42]. Mixing appropriate amount of substituted ethylenediamine, two equivalents of substituted phenol, and two equivalents of formaldehyde in methanol, and heating to reflux for several hours gave the desired products as a colorless precipitates

in good isolated yields. The ligands utilized in this study fall into two general types, featuring different substituents on both the bridging nitrogen atoms and the aromatic rings. One contains methyl (**Lig¹H₂**, **Lig³H₂**, **Lig⁵H₂**, and **Lig⁷H₂**) or benzyl substituents (**Lig²H₂**, **Lig⁴H₂**, **Lig⁶H₂**, and **Lig⁸H₂**) on the bridging nitrogen donor and the other has 3,5-dialkyl substituents (3,5-dimethyl, **Lig¹H** and **Lig³H**; 3-methyl-5-*tert*-butyl, **Lig³H** and **Lig⁴H**; 3,5-di-*tert*-butyl, **Lig⁵H** and **Lig⁶H**; 3-methoxy-5-methyl, **Lig⁷H** and **Lig⁸H**) on the two aryl-rings, allowing facile variation of steric factors and electronic effect (see Fig. 1).

These ligand precursors **Lig¹H₂**–**Lig⁸H₂** were complexed to titanium by reaction with Ti(O-*i*-Pr)₄ as outlined in Scheme 1. The treatment of Ti(O-*i*-Pr)₄ in toluene with the same equivalent of **Lig¹H₂**–**Lig⁸H₂** afforded, after workup, the monomeric titanium complexes **1**–**8**, respectively, as yellow crystals in good isolated yield. Complexes **1**–**8** obtained are soluble in common organic solvents such as methylene chloride, THF, chloroform, and toluene. They can be stored for months under an inert atmosphere without decomposition and remain air stable for some weeks in the solid state. The analytical composition fits well the proposed formulations.

All complexes were fully characterized by ¹H and ¹³C{¹H} NMR spectroscopy. The NMR characterization indicated that C₂-symmetric single isomers featuring aromatic rings, two different isopropoxide groups, and two AB spin system with a *J*-coupling of ca. 13 Hz for the two benzylic methylene groups with the

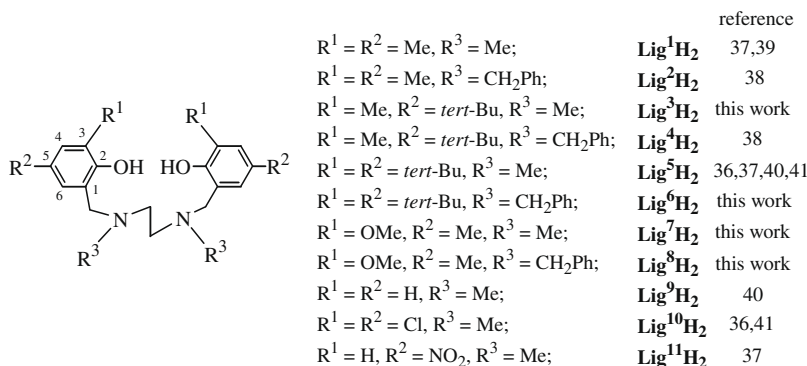
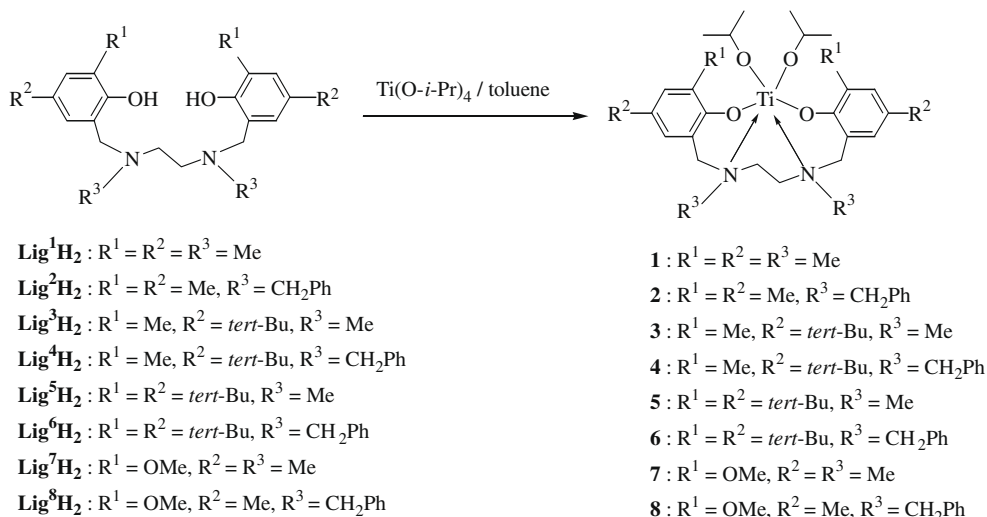


Fig. 1. Ligand structures employed for titanium complexes in this study and previous literatures. Atomic numberings on aryl carbons are included.



Scheme 1. Synthetic routes for **1**–**8** from **Lig¹H₂**–**Lig⁸H₂**.

phenolate group in a *trans* geometry had formed in all cases, and no signals that could be attributed to a non- C_2 -symmetric isomer were observed. On the NMR time scale, complexes **1–8** should have pseudo- C_2 symmetry, and therefore the NCH_2 -aryl methylene protons should not be equivalent. While the 1H NMR signals of the NCH_2 -aryl methylene protons for **Lig¹H₂**–**Lig⁸H₂** appear as singlet around at δ 3.6 ppm, these signals for **1–8** after complexation show two doublets evident from the AB spin systems. Indeed, the ca. 1.6 and 1.1 ppm chemical shift difference between two doublets of NCH_2 -aryl methylene protons for **1**, **3**, **5**, and **7** and for **2**, **4**, **6**, and **8**, respectively were observed in the room-temperature spectrum. Even at elevated temperature of 100 °C, the two resonances of NCH_2 -aryl methylene protons for **1–8** did not coalesce and still showed slightly broad but non-equivalent peaks on the NMR time scale. Furthermore, the characteristic peak of $Ti-OCHMe_2$ protons for **1–8** are observed around at δ 5.3 and 4.8 ppm. Similarly, the $^{13}C\{^1H\}$ NMR spectra of **1–8** exhibit resonances corresponding to non-equivalent *i*-Pr groups even at room temperature, owing to its pseudo- C_2 symmetry. In order to confirm the molecular structure and to elucidate the metal–ligand bonding in these complexes, we performed the single-crystal X-ray diffraction studies for the compounds **2**, **4**, **6**, and **7**.

Single crystals suitable for X-ray structural determination of **2**, **4**, **6**, and **7** were obtained as yellow crystals by cooling of a solution of toluene at -20 °C. Their X-ray crystal structures were drawn by DIAMOND Program ver. 2.1e. The selected bond lengths and angles are listed in Figs. 2–5 and Table 1. Both complexes **2** and **4** crystallize in space group $P1$, while **6** and **7** crystallize in Cc and $P2_1/c$, respectively. To check the non-centrosymmetric structure of complex **6**, Flack parameter was used [43]. Because Flack parameter value of 0.19(4) for complex **6** is near zero, the absolute structure given here in Fig. 4 by the structure refinement is almost certainly cor-

rect [43]. Like other known titanium complexes with Salan-type ligands [37,39–41], the structures reveal that complexes are certainly mononuclear.

All adopt the aryloxy oxygens O1 and O2 in **2**, **4**, **6**, and **7** are mutually *trans* with O1–Ti–O2 angles of 163.96(18), 161.23(7), 166.20(8), and 166.25(7)°, respectively, while the two isopropoxy groups are *cis*, as are the nitrogens with O3–Ti–O4 bond angles in **2**, **4**, **6**, and **7** of 106.88(10), 103.07(8), 105.07(9), and 105.42(7)° and N1–Ti–N2 bite angles of 76.10(8), 76.25(7), 74.23(7), and 76.27(7)°, respectively (see Table 1). Like other structurally characterized Salan–titanium complexes [37,39–41], the non-planar O1–N1–N2–O2 bonding fashion of fully deprotonated ligands [**Lig²**] $^{2-}$, [**Lig⁴**] $^{2-}$, [**Lig⁶**] $^{2-}$, and [**Lig⁷**] $^{2-}$ around the octahedral titanium center is in a *fac-fac* mode among the possibility of either *fac-fac*, *fac-mer*, *mer-fac*, or *mer-mer* geometry.

The Ti–O_{*i*-Pr} distances are within the expected range but all Ti–O_{*i*-Pr} bond lengths are shorter than Ti–O_{aryloxy}. Especially, the extremely short Ti–O4 bond lengths of 1.7794(17) Å and very wide Ti–O4–C20 bond angle of 161.7(3)° for **4** indicate the existence of strong π -donation from isopropoxy oxygen atom to titanium metal. Similar trends in bond length of 1.7923(14) Å and bond angle of 153.60(19)° are observed as for compound **5**. The average Ti–N bond distances range from 2.3491(19) to 2.417(5) Å. These distances are longer than those found in the previously reported Salan–titanium complexes of 2.317(2)–2.3449(16) Å [37,39–41]. The small difference between the two coordinative Ti–N bond lengths may indicate a weaker binding of the side arm nitrogen to the titanium center. The Ti–O_{aryloxy} distances in **2**, **4**, **6**, and **7**, which range from 1.893(4) to 1.936(2) Å, are longer than those in tetrahedral titanium phenoxide distances such as (ArO)₂TiX₂ (1.7–1.8 Å) [44–46] but similar to those in octahedral titanium complexes

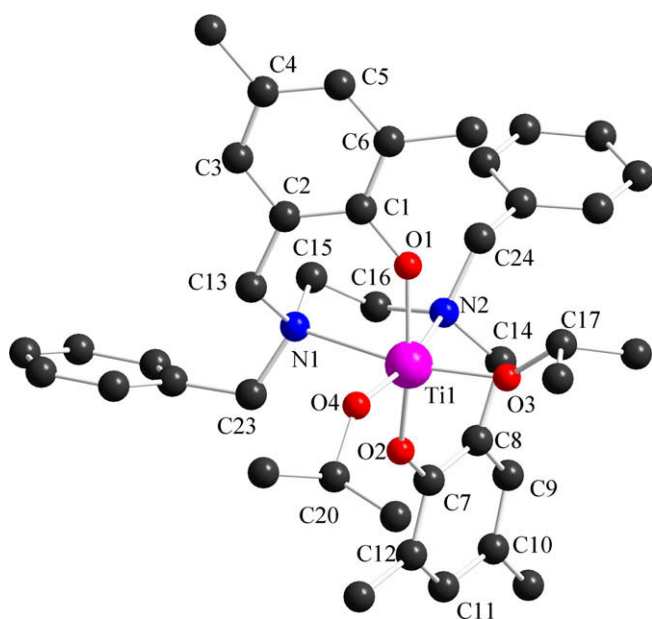


Fig. 2. Molecular drawing of compound **2** and atom labeling (H atoms were omitted for clarity). Selected bond distances (Å): Ti–O1 = 1.8952(19), Ti–O2 = 1.898(2), Ti–O3 = 1.820(2), Ti–O4 = 1.803(2), Ti–N1 = 2.363(2), Ti–N2 = 2.381(2). Selected bond angle (°): O1–Ti–O2 = 163.96(8), O1–Ti–O3 = 92.99(9), O1–Ti–O4 = 97.41(9), O2–Ti–O3 = 95.66(9), O2–Ti–O4 = 92.98(9), O3–Ti–O4 = 106.88(10), O1–Ti–N1 = 81.75(8), O2–Ti–N1 = 86.41(8), O3–Ti–N1 = 164.57(9), O4–Ti–N1 = 88.24(9), O1–Ti–N2 = 85.80(8), O2–Ti–N2 = 80.86(8), O3–Ti–N2 = 89.10(9), O4–Ti–N2 = 163.44(9), N1–Ti–N2 = 76.10(8), Ti–O1–C1 = 141.12(18), Ti–O2–C7 = 140.48(17), Ti–O3–C17 = 138.1(2), Ti–O4–C20 = 139.2(3), Ti–N1–C13 = 107.92(17), Ti–N1–C15 = 108.30(17), Ti–N1–C23 = 109.45(16), Ti–N2–C14 = 108.56(15), Ti–N2–C16 = 107.45(17), Ti–N2–C24 = 108.65(17).

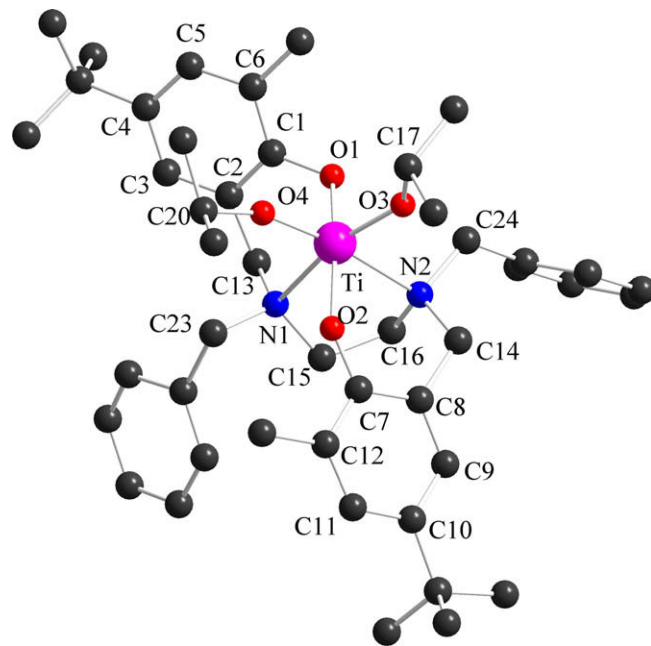


Fig. 3. Molecular drawing of compound **4** and atom labeling (H atoms were omitted for clarity). Selected bond distances (Å): Ti–O1 = 1.938(2), Ti–O2 = 1.934(2), Ti–O3 = 1.8174(16), Ti–O4 = 1.7794(17), Ti–N1 = 2.4246(18), Ti–N2 = 2.3347(18). Selected bond angle (°): O1–Ti–O2 = 161.23(7), O1–Ti–O3 = 95.97(9), O1–Ti–O4 = 94.57(9), O2–Ti–O3 = 98.90(9), O2–Ti–O4 = 93.16(9), O3–Ti–O4 = 103.07(8), O1–Ti–N1 = 79.54(7), O2–Ti–N1 = 82.70(8), O3–Ti–N1 = 161.05(7), O4–Ti–N1 = 95.66(7), O1–Ti–N2 = 86.86(8), O2–Ti–N2 = 83.06(8), O3–Ti–N2 = 85.17(8), O4–Ti–N2 = 171.42(7), N1–Ti–N2 = 76.25(7), Ti–O1–C1 = 118.63(15), Ti–O2–C7 = 140.35(15), Ti–O3–C17 = 135.80(16), Ti–O4–C20 = 161.7(3), Ti–N1–C13 = 113.61(13), Ti–N1–C15 = 105.46(12), Ti–N1–C23 = 108.33(13), Ti–N2–C14 = 109.29(14), Ti–N2–C16 = 110.69(12), Ti–N2–C24 = 107.13(12).

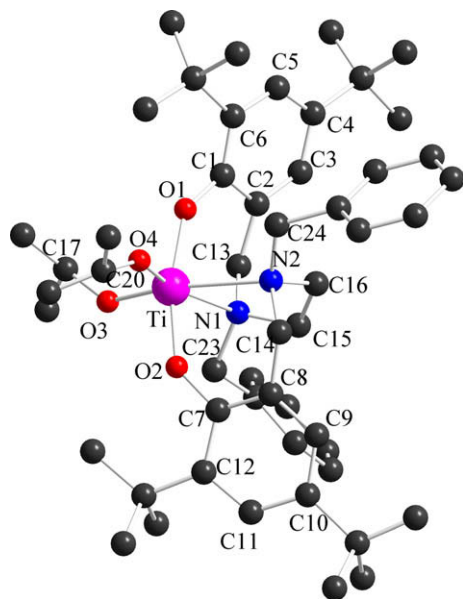


Fig. 4. Molecular drawing of compound **6** and atom labeling (H atoms were omitted for clarity). Selected bond distances (Å): Ti–O1 = 1.895(4), Ti–O2 = 1.890(4), Ti–O3 = 1.800(5), Ti–O4 = 1.818(4), Ti–N1 = 2.415(4), Ti–N2 = 2.419(5). Selected bond angle (°): O1–Ti–O2 = 166.20(8), O1–Ti–O3 = 95.5(2), O1–Ti–O4 = 93.74(17), O2–Ti–O3 = 93.33(19), O2–Ti–O4 = 94.18(18), O3–Ti–O4 = 105.07(9), O1–Ti–N1 = 81.57(17), O2–Ti–N1 = 87.84(17), O3–Ti–N1 = 90.10(18), O4–Ti–N1 = 164.52(18), O1–Ti–N2 = 85.63(18), O2–Ti–N2 = 82.98(18), O3–Ti–N2 = 163.99(17), O4–Ti–N2 = 90.76(17), N1–Ti–N2 = 74.23(7), Ti–O1–C1 = 145.5(4), Ti–O2–C7 = 141.1(4), Ti–O3–C17 = 138.3(4), Ti–O4–C20 = 148.9(5), Ti–N1–C13 = 110.5(3), Ti–N1–C15 = 110.1(3), Ti–N1–C23 = 108.0(3), Ti–N2–C14 = 108.6(4), Ti–N2–C16 = 109.9(4), Ti–N2–C24 = 109.0(3).

containing Salan ligand (1.900(2)–1.930(1) Å) [37,39–41]. The non-equivalency of the two benzylic methylene hydrogens is also apparent from the structure, one being approximately parallel to the aromatic ring and the other being perpendicular to it.

In order to evaluate the effect of ligand substituents of complexes **1–8** on the polymerization activity for the ROP of *l*-LA to isotactic PLA, the complexes **1–8** were pre-purified by recrystallization in toluene and then employed as single-site initiators. The bulk and solution ROP of LA initiated by **1–8** was carried out at 130 °C with the [LA]/[Ti] ratio fixed at 300, and the polymerization results are summarized in Table 2 in terms of the yield and M_n , M_w , and PDI, which were analyzed by GPC. Table 2 shows that the activities of these compounds were comparable to those of previously reported titanium alkoxides ROP catalysts [8–37].

Catalytic activities for complexes **1** and **5** under the bulk polymerization condition were similar to those reported previously by Chmura et al. [37] though *rac*-LA as a monomer was used instead of *l*-LA. Initiator **5**, which proved nearly inactive in the solution condition reported in the literature [37], was found to be active in slightly modified solution polymerization condition that a small amount of toluene (5 mL) and a lengthened polymerization time (6 h) were applied. Interestingly, **1** showed better activity than **5** in the reported literature [37]; however, we found **5** as a catalyst for ROP of *l*-LA was better than **1** under the bulk and in the solution polymerization. Under the bulk polymerization condition, complexes **1–8** gave PLA in a yield of 81.0–89.5%. In the solution polymerization condition, they produce PLA in a yield of 59.0–67.5%, which is more than 40% decreased ratio of yield compared with those under the bulk polymerization condition. Table 2 shows that compounds **3–6**, which have bulky *tert*-butyl substituents at 5 position of aryl-ring in common (see Fig. 1 for numbering), are the most active initiators both under the bulk and in the solution polymerization condition. Complexes **1** and **2** with the same substitu-

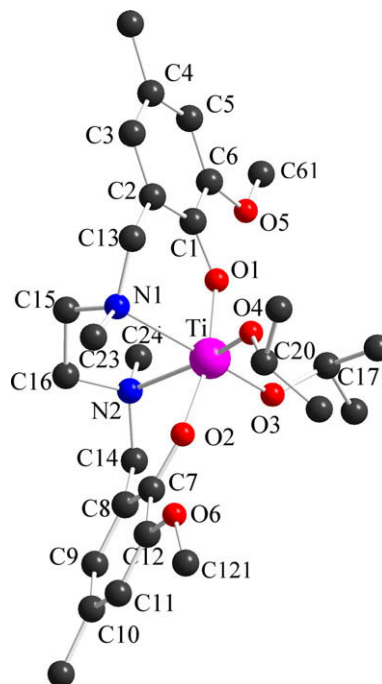


Fig. 5. Molecular drawing of compound **7** and atom labeling (H atoms and two CH₂Cl₂ solvents were omitted for clarity). Selected bond distances (Å): Ti–O1 = 1.9030(15), Ti–O2 = 1.8854(15), Ti–O3 = 1.8406(16), Ti–O4 = 1.8231(15), Ti–N1 = 2.3464(19), Ti–N2 = 2.3518(18). Selected bond angle (°): O1–Ti–O2 = 166.25(7), O1–Ti–O3 = 90.53(7), O1–Ti–O4 = 98.12(7), O2–Ti–O3 = 96.78(7), O2–Ti–O4 = 91.16(7), O3–Ti–O4 = 105.42(7), O1–Ti–N1 = 80.43(7), O2–Ti–N1 = 89.72(7), O3–Ti–N1 = 164.32(7), O4–Ti–N1 = 88.63(7), O1–Ti–N2 = 88.25(7), O2–Ti–N2 = 80.05(6), O3–Ti–N2 = 90.77(7), O4–Ti–N2 = 162.46(7), N1–Ti–N2 = 76.27(7), Ti–O1–C1 = 142.17(15), Ti–O2–C7 = 143.26(14), Ti–O3–C17 = 129.71(14), Ti–O4–C20 = 134.57(14), Ti–N1–C13 = 109.91(13), Ti–N1–C15 = 109.03(14), Ti–N1–C23 = 110.52(13), Ti–N2–C14 = 111.45(13), Ti–N2–C16 = 108.75(13), Ti–N2–C24 = 110.04(13), C6–O5–C61 = 117.02(19), C12–O6–C121 = 116.76(19).

ents at aryl-rings but the different groups on bridging nitrogens showed very similar activities both under the bulk and in the solution polymerization condition. The similar trends were observed as for the pairs **3** and **4**, **5** and **6**, **7** and **8**.

In contrast to the similar activity trends, a clear difference in molecular weight and PDI values was observed between the two pairs: the molecular weights of PLA obtained from **2** featuring the *N*-benzyl substituted Salan ligand both under the bulk and in the solution polymerization condition were much higher than those of **1** and so did the pairs **3** and **4**, **5** and **6**, **7** and **8**. In addition, the PDI values of PLA samples from the formers were broader except for complex pair **5** and **6** under the bulk polymerization condition, signifying a decrease in the controlling character of the

Table 1
Comparison of bond lengths and bond angles for **2**, **4**, **6**, and **7**.

	2	4	6	7
ave. Ti–O _{aryloxy} (Å)	1.897(2)	1.936(2)	1.893(4)	1.8942(15)
ave. Ti–O _{<i>i</i>-Pr} (Å)	1.812(2)	1.7984(17)	1.809(5)	1.8319(16)
ave. Ti–N (Å)	2.372(2)	2.3797(18)	2.417(5)	2.3491(19)
O1–Ti–O2 (°)	163.96(18)	161.23(7)	166.20(8)	166.25(7)
O3–Ti–O4 (°)	106.88(10)	103.07(8)	105.07(9)	105.42(7)
ave. <i>cis</i> O–Ti–O (°)	97.18(9)	97.13(9)	96.34(17)	96.40(7)
N1–Ti–N2 (°)	76.10(8)	76.25(7)	74.23(7)	76.27(7)
ave. <i>trans</i> N–Ti–O (°)	164.01(9)	166.24(7)	164.26(18)	163.39(7)
ave. <i>cis</i> N–Ti–O (°)	85.36(8)	85.50(8)	86.48(17)	86.31(7)
ave. Ti–N–C	108.39(17)	109.09(13)	109.4(3)	109.95(13)
ave. Ti–O–C	139.73(21)	139.12(19)	143.5(4)	137.43(17)

Table 2Ring opening polymerization data for *l*-lactide.

Catalyst	Bulk polymerization ^a					Solution polymerization ^b				
	g Polymer	Yield (%)	M_n	M_w	PDI	g Polymer	Yield (%)	M_n	M_w	PDI
1	1.60	80.0	15 800	26 900	1.71	1.18	59.0	6500	7700	1.17
2	1.69	84.5	20 300	35 100	1.72	1.17	58.5	9400	12 400	1.33
3	1.72	86.0	13 200	15 800	1.19	1.35	67.5	7100	8100	1.15
4	1.79	89.5	27 700	41 800	1.51	1.33	66.5	8600	11 100	1.30
5	1.74	87.0	10 000	12 900	1.30	1.34	67.0	6400	7600	1.18
6	1.78	89.0	18 100	22 100	1.22	1.30	65.0	7900	9700	1.22
7	1.62	81.0	15 400	20 800	1.35	1.25	62.5	9200	11 500	1.25
8	1.68	84.0	25 400	41 200	1.62	1.22	61.0	12 000	16 300	1.36

^a Polymerization conditions: 2 g of LA, [LA]/[Ti] = 300, polymerization temperature = 130 °C, polymerization time = 6 h.^b Polymerization conditions: 2 g of LA, [LA]/[Ti] = 300, polymerization temperature = 130 °C, polymerization time = 6 h, toluene = 5 mL.

polymerization process. Complexes **5** and **6** containing the most bulky substituents in two aryl-rings gave PLA with lowest molecular weight both under the bulk polymerization condition, which was consistent with the blocking of the metal center. Furthermore, PLA polymers obtained from the solution polymerization have much narrower PDI values but lower molecular weight than those from bulk polymerization. Both under the bulk and in solution polymerization condition, the relatively narrow PDI values support somewhat controlled polymerization catalysis. Interestingly, the actual M_n values obtained from both bulk and solution polymerization are always much smaller than expected M_n value of 36 000, which corresponds to the growth of one PLA polymer chain per Ti center. The end groups of PLA produced by **1–8** are the corresponding isopropoxy ester units as indicated by ¹H NMR spectroscopy. Thus, initiation occurs through the insertion of the isopropoxy group from the titanium catalyst into *l*-LA, consistent with a polymerization process that proceeds via a coordination–insertion mechanism. Homonuclear decoupled ¹H NMR spectroscopy support that ROP of *l*-LA using **1–8** gave isotactic PLA.

3. Experimental

3.1. General procedure

All reactions were carried out under dinitrogen atmosphere using standard Schlenk and glove box techniques [47,48]. All solvents were dried by distilling from sodium/benzophenone ketyl (toluene, tetrahydrofuran (THF), diethylether, and hexane) or CaH₂ (methylene chloride) under a dinitrogen atmosphere and stored over the activated molecular sieves 3A [49]. CDCl₃ was dried over activated molecular sieves (4A) and were used after vacuum transfer to a Schlenk tube equipped with J. Young valve.

3.2. Measurements

¹H and ¹³C{¹H} NMR spectra were recorded at ambient temperature on a Bruker DPX-300 NMR spectrometer or Varian VXR-400 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). Elemental analyses and mass data were performed by EA 1110-FISONS(CE) and ICP-MASS HP-4500, respectively. Molecular weights of PLA polymers were determined by gel permeation chromatography (GPC) calibrated with standard polystyrenes, which were obtained with Waters 2414 equipped with RI detectors and packing column (Waters Styragel HR 4E and 5E) using THF as an eluent at 40 °C.

3.3. Synthesis

All chemicals were purchased from Aldrich. The complexes **Lig¹**-Ti(O-*i*-Pr)₂ (**1**) [37,39] and **Lig⁵**-Ti(O-*i*-Pr)₂ (**5**) [36,37,39,40] were synthesized according to previously published procedures.

3.4. Synthesis of *N,N'*-dibenzyl-*N,N'*-bis[(3,5-dimethyl-2-hydroxyphenyl)methylene]-1,2-diaminoethane (**Lig²H₂**)

A mixture of *N,N'*-dibenzylethylenediamine (1.76 g, 7.31 mmol), 2,4-dimethylphenol (1.79 g, 14.6 mmol) and 37% aqueous formaldehyde (1.19 g, 14.6 mmol) was stirred in refluxing methanol for 4 h. The mixture was cooled to room temperature and the solid was filtered, and washed with methanol, yielding pure **Lig²H₂** in 91.2% (3.39 g).

¹H NMR (CDCl₃, 400.15 MHz, ppm): δ 10.38 (s, 2H, OH), 7.29–7.12 (m, 10H, Ph-*H*), 6.83 (s, 2H, aryl-*H*), 6.56 (s, 2H, aryl-*H*), 3.60 (s, 4H, aryl-CH₂N), 3.50 (s, 4H, PhCH₂N), 2.65 (s, 4H, NCH₂CH₂N), 2.19 (s, 6H, aryl-CH₃), 2.16 (s, 6H, aryl-CH₃).

¹³C{¹H} NMR (CDCl₃, 100.63 MHz, ppm): δ 153.04, 136.32, 130.65, 129.38, 128.55, 127.76, 127.61, 126.78, 124.56, 120.55 (aryl-C and Ph-C), 58.38 (PhCH₂N), 58.25 (aryl-CH₂N), 49.77 (NCH₂CH₂N), 20.44 (aryl-CH₃), 15.69 (aryl-CH₃).

EI-MS (% intensity): *m/z* calc.: 508 (22.68%, M⁺), 417 (100.00%, M⁺-CH₂Ph), 373 (55.42%, M⁺-[CH₂(3,5-dimethyl-2-hydroxyphenyl)]), 283 (33.58%, M⁺-CH₂Ph-[CH₂(3,5-dimethyl-2-hydroxyphenyl)]), 254 (87.93%, [CH₂NCH₂Ph{CH₂(3,5-dimethyl-2-hydroxyphenyl)}]⁺), 135 (59.44%, {CH₂(3,5-dimethyl-2-hydroxyphenyl)}⁺), 121 (17.92%, [3,5-dimethyl-2-hydroxyphenyl]⁺), 91 (74.11%, [CH₂Ph]⁺).

HRMS (EI) *m/z* Calc. 508.3090. Found: 508.3091.

3.5. Synthesis of *N,N'*-dimethyl-*N,N'*-bis[(3-methyl-5-*tert*-butyl-2-hydroxyphenyl)methylene]-1,2-diaminoethane (**Lig³H₂**)

The desired product **Lig³H₂** was prepared from *N,N'*-dimethylethylenediamine (8.82 g, 100 mmol), 2-methyl-4-*tert*-butylphenol (32.8 g, 200 mmol) and 37% aqueous formaldehyde (16.2 g, 200 mmol) in a yield of 87.6% (38.6 g) in a manner analogous to the procedure for **Lig²H₂**.

¹H NMR (CDCl₃, 400.15 MHz, ppm): δ 10.66 (br, 2H, OH), 7.04 (s, 2H, aryl-*H*), 6.78 (s, 2H, aryl-*H*), 3.66 (s, 4H, aryl-CH₂N), 2.67 (s, 4H, NCH₂CH₂N), 2.27 (s, 6H, NMe), 2.20 (s, 6H, aryl-CH₃), 1.26 (s, 18H, aryl-CMe₃).

¹³C{¹H} NMR (CDCl₃, 100.63 MHz, ppm): δ 153.33, 141.20, 126.89, 124.03, 122.79, 120.05 (aryl-C), 62.16 (aryl-CH₂N), 54.31 (NCH₂CH₂N), 41.76 (NMe), 33.85(aryl-CMe₃), 31.62 (aryl-CMe₃), 15.97 (aryl-CH₃).

EI-MS (% intensity): m/z calc.: 440 (22.73%, M^+), 220 (100.00%, $[\text{CH}_2\text{NMe}\{\text{CH}_2(3\text{-methyl-5-tert-butyl-2-hydroxyphenyl})\}]^+$), 177 (78.42%, $[\text{CH}_2(3\text{-methyl-5-tert-butyl-2-hydroxyphenyl})]^+$).

HRMS (EI) m/z Calc. 440.3403. Found: 440.3398.

3.6. Synthesis of *N,N'*-dibenzyl-*N,N'*-bis[(3-methyl-5-tert-butyl-2-hydroxyphenyl)methylene]-1,2-diaminoethane (**Lig⁴H₂**)

The desired product **Lig⁴H₂** was prepared from *N,N'*-dibenzylethylenediamine (8.83 g, 36.7 mmol), 2-methyl-4-*tert*-butylphenol (12.1 g, 73.5 mmol) and 37% aqueous formaldehyde (5.96 g, 73.5 mmol) in a yield of 84.5% (18.4 g) in a manner analogous to the procedure for **Lig²H₂**.

¹H NMR (CDCl_3 , 400.15 MHz, ppm): δ 10.48 (s, 2H, OH), 7.26–7.12 (m, 10H, Ph-*H*), 7.04 (s, 2H, aryl-*H*), 6.78 (s, 2H, aryl-*H*), 3.66 (s, 4H, aryl- CH_2N), 3.52 (s, 4H, PhCH_2N), 2.69 (s, 4H, $\text{NCH}_2\text{CH}_2\text{N}$), 2.21 (s, 6H, aryl- CH_3), 1.25 (s, 18H, aryl- CMe_3).

¹³C{¹H} NMR (CDCl_3 , 100.63 MHz, ppm): δ 153.06, 141.43, 136.28, 129.44, 128.52, 127.61, 126.99, 124.06, 123.09, 120.05 (aryl-C and Ph-C), 58.63 (aryl- CH_2N), 58.30 (PhCH_2N), 49.98 ($\text{NCH}_2\text{CH}_2\text{N}$), 33.85 (aryl- CMe_3), 31.60 (aryl- CMe_3), 16.06 (aryl- CH_3).

EI-MS (% intensity): m/z calc.: 592 (100.00%, M^+), 501 (16.37%, $M^+ - \text{CH}_2\text{Ph}$), 415 (20.42%, $M^+ - \text{CH}_2(3\text{-methyl-5-tert-butyl-2-hydroxyphenyl})$), 296 (65.54%, $\text{CH}_2\text{NCH}_2\text{Ph}\{\text{CH}_2(3\text{-methyl-5-tert-butyl-2-hydroxyphenyl})\}^+$), 177 (66.74%, $[\text{CH}_2(3\text{-methyl-5-tert-butyl-2-hydroxyphenyl})]^+$), 91 (87.17%, $[\text{CH}_2\text{Ph}]^+$).

HRMS (EI) m/z Calc. 592.4029. Found: 529.4025.

3.7. Synthesis of *N,N'*-dibenzyl-*N,N'*-bis[(3,5-di-*t*-butyl-2-hydroxyphenyl)methylene]-1,2-diaminoethane (**Lig⁶H₂**)

The desired product **Lig⁶H₂** was prepared from *N,N'*-dibenzylethylenediamine (0.75 g, 3.13 mmol), 2,4-di-*tert*-butylphenol (1.29 g, 6.27 mmol) and 37% aqueous formaldehyde (0.512 g, 6.27 mmol) in a yield of 90.1% (1.91 g) in a manner analogous to the procedure for **Lig²H₂**.

¹H NMR (CDCl_3 , 400.15 MHz, ppm): δ 10.60 (s, 2H, OH), 7.31–7.20 (m, 10H, Ph-*H*), 7.18 (s, 2H, aryl-*H*), 6.84 (s, 2H, aryl-*H*), 3.70 (s, 4H, aryl- CH_2N), 3.54 (s, 4H, PhCH_2N), 2.72 (s, 4H, $\text{NCH}_2\text{CH}_2\text{N}$), 1.46 (s, 18H, aryl- CMe_3), 1.31 (s, 18H, aryl- CMe_3).

¹³C{¹H} NMR (CDCl_3 , 100.63 MHz, ppm): δ 153.77, 140.64, 136.54, 135.62, 129.54, 128.46, 127.5, 123.63, 122.98, 121.01 (aryl-C and Ph-C), 59.15 (aryl- CH_2N), 58.04 (PhCH_2N), 49.97 ($\text{NCH}_2\text{CH}_2\text{N}$), 34.86 (aryl- CMe_3), 34.13 (aryl- CMe_3), 31.69 (aryl- CMe_3), 29.60 (aryl- CMe_3).

HRMS (EI) m/z Calc. 676.4968. Found: 676.4965.

3.8. Synthesis of *N,N'*-dimethyl-*N,N'*-bis[(3-methoxy-5-methyl-2-hydroxyphenyl)methylene]-1,2-diaminoethane (**Lig⁷H₂**)

The desired product **Lig⁷H₂** was prepared from *N,N'*-dimethylethylenediamine (0.882 g, 10.0 mmol), 2-methoxy-4-methylphenol (2.76 g, 20.0 mmol) and 37% aqueous formaldehyde (1.62 g, 20.0 mmol) in a yield of 87.3% (3.39 g) in a manner analogous to the procedure for **Lig²H₂**.

¹H NMR (CDCl_3 , 400.15 MHz, ppm): δ 10.61 (s, 2H, OH), 6.59 (s, 2H, aryl-*H*), 6.36 (s, 2H, aryl-*H*), 3.82 (s, 6H, OMe), 3.62 (s, 4H, aryl- CH_2N), 2.66 (s, 4H, $\text{NCH}_2\text{CH}_2\text{N}$), 2.27 (s, 6H, NMe), 2.22 (s, 6H, aryl- CH_3).

¹³C{¹H} NMR (CDCl_3 , 100.63 MHz, ppm): δ 147.52, 144.40, 128.07, 121.35, 120.76, 111.93 (aryl-C), 61.38 (aryl- CH_2N), 55.79 (OMe), 54.48 ($\text{NCH}_2\text{CH}_2\text{N}$), 41.94 (NMe), 20.95 (aryl- CH_3).

EI-MS (% intensity): m/z calc.: 388 (25.43%, M^+), 151 (100.00%, $[\text{CH}_2(3\text{-methoxy-5-methyl-2-hydroxyphenyl})]^+$), 137 (17.00%, $[\text{3-methoxy-5-methyl-2-hydroxyphenyl}]^+$).

HRMS (EI) m/z Calc. 388.2362. Found: 388.2364.

3.9. Synthesis of *N,N'*-dibenzyl-*N,N'*-bis[(3-methoxy-5-methyl-2-hydroxyphenyl)methylene]-1,2-diaminoethane (**Lig⁸H₂**)

The desired product **Lig⁸H₂** was prepared from *N,N'*-dibenzylethylenediamine (2.51 g, 10.4 mmol), 2-methoxy-4-methylphenol (2.88 g, 20.9 mmol) and 37% aqueous formaldehyde (1.69 g, 20.9 mmol) in a yield of 86.2% (4.85 g) in a manner analogous to the procedure for **Lig²H₂**.

¹H NMR (CDCl_3 , 400.15 MHz, ppm): δ 10.52 (s, 2H, OH), 7.26–7.12 (m, 10H, Ph-*H*), 6.61 (s, 2H, aryl-*H*), 6.34 (s, 2H, aryl-*H*), 3.85 (s, 6H, OMe), 3.62 (s, 4H, aryl- CH_2N), 3.52 (s, 4H, PhCH_2N), 2.68 (s, 4H, $\text{NCH}_2\text{CH}_2\text{N}$), 2.24 (s, 6H, aryl- CH_3).

¹³C{¹H} NMR (CDCl_3 , 100.63 MHz, ppm): δ 147.52, 144.15, 136.28, 129.36, 128.55, 128.21, 127.59, 121.41, 120.90, 111.87 (aryl-C and Ph-C), 58.63 (phenyl- CH_2N), 57.87 (OMe), 55.77 (aryl- CH_2N), 50.09 ($\text{NCH}_2\text{CH}_2\text{N}$), 20.99 (aryl- CH_3).

EI-MS (% intensity): m/z calc.: 540 (100.00%, M^+), 270 (71.09%, $[\text{CH}_2\text{NCH}_2\text{Ph}\{\text{CH}_2(3\text{-methoxy-5-methyl-2-hydroxyphenyl})\}]^+$), 373 (55.42%, $M^+ - [\text{CH}_2(3,5\text{-dimethyl-2-hydroxyphenyl})]$), 151 (69.43%, $[\text{CH}_2(3\text{-methoxy-5-methyl-2-hydroxyphenyl})]^+$), 91 (100.00%, $[\text{CH}_2\text{Ph}]^+$), 77 (60.14%, $[\text{Ph}]^+$).

HRMS (EI) m/z Calc. 540.2988. Found: 540.2983.

3.10. Synthesis of **Lig²Ti(O-*i*-Pr)₂ (2)**

To a stirred colorless solution of **Lig²H₂** (0.76 g, 1.5 mmol) in 30 mL toluene was added dropwise at room temperature a solution of $\text{Ti}(\text{O-}i\text{-Pr})_4$ (0.44 g, 1.5 mmol) in 20 mL toluene. The reaction mixture was allowed to warm to room temperature and stirred for overnight. The residue, obtained by removing the solvent under vacuum, was recrystallized in hexane. The desired product **2** was isolated as yellow crystals after the solution remained at -15°C in a refrigerator for a few days (0.90 g, 89.4%).

¹H NMR (CDCl_3 , 300.13 MHz, ppm): δ 7.30–7.06 (m, 10H, Ph-*H*), 6.84 (s, 2H, aryl-*H*), 6.48 (s, 2H, aryl-*H*), 5.25–5.17 (m, 2H, OCHMe_2), 4.45 (d, 2H, $J = 13$ Hz, aryl- CH_2N), 4.15 (s, 4H, PhCH_2N), 3.34 (d, 2H, $J = 13.08$ Hz, aryl- CH_2N), 2.67 (d, 2H, $J = 10.27$ Hz, $\text{NCH}_2\text{CH}_2\text{N}$), 2.40 (d, 2H, $J = 10.35$ Hz, $\text{NCH}_2\text{CH}_2\text{N}$), 2.21 (s, 6H, aryl- CH_3), 2.15 (s, 6H, aryl- CH_3), 1.33 (d, 6H, $J = 6.08$ Hz, OCHMe_2), 1.28 (d, 6H, $J = 6.13$ Hz, OCHMe_2).

¹³C{¹H} NMR (CDCl_3 , 300.13 MHz, ppm): δ 151.63, 147.74, 133.46, 132.35, 128.00, 127.79, 126.25, 125.26, 122.43, 114.25 (aryl-C and Ph-C), 78.02 (OCHMe_2), 59.63 (aryl- CH_2N), 57.79 (PhCH_2N), 56.5 ($\text{NCH}_2\text{CH}_2\text{N}$), 25.99 (OCHMe_2), 25.71 (OCHMe_2), 20.97 (aryl- CH_3), 20.75 (aryl- CH_3).

Elemental Anal. Calc. for $\text{C}_{40}\text{H}_{52}\text{N}_2\text{O}_4\text{Ti}$: C, 71.42; H, 7.79; N, 4.16. Found: C, 71.55; H, 8.03; N, 4.25%.

3.11. Synthesis of **Lig³Ti(O-*i*-Pr)₂ (3)**

The desired product **3** as yellow crystals in an isolated yield of 89.1% (0.81 g) in a manner analogous to the procedure for **1** using **Lig³H₂** (0.66 g, 1.5 mmol) and $\text{Ti}(\text{O-}i\text{-Pr})_4$ (0.44 g, 1.5 mmol).

¹H NMR (CDCl_3 , 400.15 MHz, ppm): δ 7.07 (s, 2H, aryl-*H*), 6.78 (s, 2H, aryl-*H*), 5.26–5.20 (m, 2H, OCHMe_2), 4.76 (d, 2H, $J = 13.28$ Hz, aryl- CH_2N), 3.12 (d, 2H, $J = 13.36$ Hz, aryl- CH_2N), 3.08 (d, 2H, $J = 9.16$ Hz, $\text{NCH}_2\text{CH}_2\text{N}$), 2.43 (s, 6H, NMe), 2.27 (s, 6H, aryl- CH_3), 1.77 (d, 2H, $J = 9.24$ Hz, $\text{NCH}_2\text{CH}_2\text{N}$), 1.31 (d, 6H, $J = 6.04$ Hz, OCHMe_2), 1.27 (s, 18H, aryl- CMe_3), 1.20 (d, 6H, $J = 6.2$ Hz, OCHMe_2).

¹³C{¹H} NMR (CDCl_3 , 100.63 MHz, ppm): δ 153.91, 139.48, 126.97, 124.05, 123.86, 123.16 (aryl-C), 77.09, 77.05 (OCHMe_2), 65.07 (aryl- CH_2N), 51.43 ($\text{NCH}_2\text{CH}_2\text{N}$), 47.06 (NMe), 33.79 (aryl- CMe_3), 31.71 (aryl- CMe_3), 26.23 (OCHMe_2), 25.90 (OCHMe_2), 17.64 (aryl- CH_3).

Elemental Anal. Calc. for $C_{34}H_{56}N_2O_4Ti$: C, 67.53; H, 9.33; N, 4.63. Found: C, 67.92; H, 9.16; N, 4.35%.

3.12. Synthesis of $Lig^4Ti(O-i-Pr)_2$ (**4**)

The desired product **4** as yellow crystals was prepared in an isolated yield of 96.0% (0.73 g) in a manner analogous to the procedure for **1** using Lig^4H_2 (0.59 g, 1.0 mmol) and $Ti(O-i-Pr)_4$ (0.29 g, 1.0 mmol).

1H NMR ($CDCl_3$, 400.15 MHz, ppm): δ 7.35–7.08 (m, 10H, Ph-H), 7.07 (s, 2H, aryl-H), 6.82 (s, 2H, aryl-H), 5.25–5.22 (m, 2H, $OCHMe_2$), 4.48 (d, 2H, $J = 12.93$ Hz, aryl- CH_2N), 4.20 (s, 4H, $PhCH_2N$), 3.40 (d, 2H, $J = 13$ Hz, aryl- CH_2N), 2.64 (d, 2H, $J = 10.24$ Hz, NCH_2CH_2N), 2.45 (d, 2H, $J = 10.44$ Hz, NCH_2CH_2N), 2.27 (s, 6H, aryl- CH_3), 1.36 (d, 6H, $J = 6.04$ Hz, $OCHMe_2$), 1.30 (d, 6H, $J = 6.04$ Hz, $OCHMe_2$), 1.25 (s, 18H, aryl- CMe_3).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.63 MHz, ppm): δ 158.76, 139.66, 132.99, 132.47, 128.11, 127.95, 127.33, 124.1, 124.03, 123.11 (aryl-C and Ph-C), 77.53 ($OCHMe_2$), 58.89 (aryl- CH_2N), 58.19 ($PhCH_2N$), 46.12 (NCH_2CH_2N), 33.83 (aryl- CMe_3), 31.72 (aryl- CMe_3), 26.30 ($OCHMe_2$), 26.08 ($OCHMe_2$), 17.57 (aryl- CH_3).

Elemental Anal. Calc. for $C_{46}H_{64}N_2O_4Ti$: C, 73.00; H, 8.52; N, 3.70. Found: C, 73.11; H, 8.48; N, 3.55%.

3.13. Synthesis of $Lig^6Ti(O-i-Pr)_2$ (**6**)

The desired product **6** as yellow crystals was prepared in an isolated yield of 89.2% (1.13 g) after recrystallization from the toluene solution in a manner analogous to the procedure for **1** using Lig^6H_2 (1.02 g, 1.5 mmol) and $Ti(O-i-Pr)_4$ (0.44 g, 1.5 mmol).

1H NMR ($CDCl_3$, 300.13 MHz, ppm): δ 7.36–7.28 (m, 6H, Ph-H), 7.20 (s, 2H, aryl-H), 7.08–7.01 (m, 4H, Ph-H), 6.65 (s, 2H, aryl-H),

5.10–4.90 (m, 2H, $OCHMe_2$), 4.28 (d, 2H, $J = 13.10$ Hz, aryl- CH_2N), 4.23 (s, 4H, $PhCH_2N$), 3.36 (d, 2H, $J = 13.15$ Hz, aryl- CH_2N), 2.81 (d, 2H, $J = 10.05$ Hz, NCH_2CH_2N), 2.43 (d, 2H, $J = 9.99$ Hz, NCH_2CH_2N), 1.50 (s, 18H, aryl- CMe_3), 1.28 (d, 6H, $J = 6.16$ Hz, $OCHMe_2$), 1.24 (s, 18H, aryl- CMe_3), 1.14 (d, 6H, $J = 6.02$ Hz, $OCHMe_2$).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 300.13 MHz, ppm): δ 159.62, 138.66, 135.58, 132.92, 132.46, 128.4, 128.09, 127.87, 124.2, 123.38 (aryl-C and Ph-C), 77.59 ($OCHMe_2$), 59.79 (aryl- CH_2N), 59.45 ($PhCH_2N$), 46.16 (NCH_2CH_2N), 35.10 (aryl- CMe_3), 34.11 (aryl- CMe_3), 31.78 (aryl- CMe_3), 30.36 (aryl- CMe_3), 26.68 ($OCHMe_2$), 26.3 ($OCHMe_2$).

Elemental Anal. Calc. for $C_{52}H_{76}N_2O_4Ti$: C, 74.26; H, 9.11; N, 3.33. Found: C, 74.57; H, 9.17; N, 3.15%.

3.14. Synthesis of $Lig^7Ti(O-i-Pr)_2$ (**7**)

The desired product **7** as yellow crystals was prepared in an isolated yield of 88.5% (0.73 g) in a manner analogous to the procedure for **1** using Lig^7H_2 (0.58 g, 1.5 mmol) and $Ti(O-i-Pr)_4$ (0.44 g, 1.5 mmol).

1H NMR ($CDCl_3$, 300.13 MHz, ppm): δ 6.62 (s, 2H, aryl-H), 6.38 (s, 2H, aryl-H), 5.20–5.12 (m, 2H, $OCHMe_2$), 4.61 (d, 2H, $J = 13.22$ Hz, aryl- CH_2N), 3.81 (s, 6H, OMe), 3.05 (d, 2H, $J = 13.36$ Hz, aryl- CH_2N), 2.98 (d, 2H, $J = 9.2$ Hz, NCH_2CH_2N), 2.40 (s, 6H, NMe), 2.22 (s, 6H, aryl- CH_3), 1.76 (d, 2H, $J = 9.23$ Hz, NCH_2CH_2N), 1.26 (d, 6H, $J = 6.11$ Hz, $OCHMe_2$), 1.05 (d, 6H, $J = 6.08$ Hz, $OCHMe_2$).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 300.13 MHz, ppm): δ 150.32, 147.95, 126.09, 124.98, 122.36, 114.59 (aryl-C), 77.43 ($OCHMe_2$), 64.26 (OMe), 56.93 (aryl- CH_2N), 51.87 (NCH_2CH_2N), 47.06 (NMe), 26.04 ($OCHMe_2$), 25.69 ($OCHMe_2$), 20.92 (aryl- CH_3).

Elemental Anal. Calc. for $C_{28}H_{44}N_2O_6Ti$: C, 60.87; H, 8.03; N, 5.07. Found: C, 60.72; H, 7.94; N, 5.12.

Table 3
Crystallographic data and parameters for **2**, **4**, **6** [54], and **7**.

	2	4	6	7
Empirical formula	$C_{40}H_{52}N_2O_4Ti$	$C_{46}H_{64}N_2O_4Ti$	$C_{52}H_{76}N_2O_4Ti$	$C_{30}H_{48}Cl_4N_2O_6Ti$
Formula weight	672.74	756.89	841.05	722.40
T (K)	296(2)	293(2)	293(2)	293(2)
Crystal system	triclinic	triclinic	monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	Cc	$P2_1/c$
<i>Unit cell dimensions</i>				
a (Å)	10.8577(7)	11.811(2)	18.934(4)	12.8334(12)
b (Å)	12.4264(8)	12.369(3)	10.025(2)	17.7190(16)
c (Å)	15.5284(10)	16.742(3)	26.592(6)	16.4111(15)
α (°)	96.163(4)	95.53(3)	90.00	90.00
β (°)	107.701(4)	99.18(3)	93.670(4)	107.154(2)
γ (°)	107.028(4)	114.40(3)	90.00	90.00
V (Å ³)	1863.5(2)	2162.8(8)	5037.3(18)	3565.8(6)
Z	2	2	4	4
D_{calc} (g cm ⁻³)	1.199	1.162	1.109	1.346
μ (mm ⁻¹) (absorption coefficient)	0.271	0.240	0.212	0.581
$F(000)$	720	816	1824	1520
θ Range for data collection (°)	1.41–27.45	1.32–29.56	2.16–27.9	1.66–27.91
Index ranges	$-14 \leq h \leq 14$ $-16 \leq k \leq 16$ $-19 \leq l \leq 20$	$-16 \leq h \leq 15$ $-21 \leq k \leq 14$ $-21 \leq l \leq 21$	$-24 \leq h \leq 23$ $-5 \leq k \leq 12$ $-19 \leq l \leq 34$	$-16 \leq h \leq 9$ $-23 \leq k \leq 12$ $-20 \leq l \leq 19$
Reflections collected	23 541	9027	14 309	15 121
Independent reflections	8355 [$R_{int} = 0.1542$]	9027 [$R_{int} = 0.0000$]	8838 [$R_{int} = 0.0339$]	7637 [$R_{int} = 0.0320$]
Data/restraints/parameters	8355/0/432	9027/0/546	8838/17/642	7637/0/426
Goodness-of-fit (GOF) on F^2	1.030	1.058	1.026	1.035
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0676$, $wR_2 = 0.1577$	$R_1 = 0.0711$, $wR_2 = 0.2101$	$R_1 = 0.0536$, $wR_2 = 0.1428$	$R_1 = 0.0499$, $wR_2 = 0.1321$
R indices (all data)	$R_1 = 0.1137$, $wR_2 = 0.1812$	$R_1 = 0.0749$, $wR_2 = 0.2189$	$R_1 = 0.0735$, $wR_2 = 0.1590$	$R_1 = 0.0643$, $wR_2 = 0.1435$
Largest difference in peak and hole (e Å ⁻³)	0.741 and -0.715	0.983 and -0.955	0.306 and -0.489	0.747 and -0.510

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

3.15. Synthesis of **Lig**⁸Ti(O-*i*-Pr)₂ (**8**)

The desired product **8** as yellow crystals was prepared in an isolated yield of 87.7% (0.93 g) after washed with *n*-hexane several times in a manner analogous to the procedure for **1** using **Lig**⁸H₂ (0.81 g, 1.5 mmol) and Ti(O-*i*-Pr)₄ (0.44 g, 1.5 mmol).

¹H NMR (CDCl₃, 300.13 MHz, ppm): δ 7.30–7.05 (m, 10H, Ph-*H*), 6.63 (s, 2H, aryl-*H*), 6.34 (s, 2H, aryl-*H*), 5.20–5.12 (m, 2H, OCHMe₂), 4.30–4.17 (m, 6H, aryl-CH₂N and PhCH₂N), 3.37 (s, 6H, OMe), 3.38 (d, 2H, *J* = 12.68 Hz, aryl-CH₂N), 2.56 (d, 2H, *J* = 9.70 Hz, NCH₂CH₂N), 2.30 (d, 2H, *J* = 10.08 Hz, NCH₂CH₂N), 2.21 (s, 6H, aryl-CH₃), 1.29 (d, 6H, *J* = 6.15 Hz, OCHMe₂), 1.27 (d, 6H, *J* = 6.12 Hz, OCHMe₂).

¹³C{¹H} NMR (CDCl₃, 300.13 MHz, ppm): δ 158.77, 132.82, 132.46, 130.98, 128.1, 128.01, 127.98, 125.98, 124.8, 123.51 (aryl-C and Ph-C), 77.57 (OCHMe₂), 58.46 (OMe), 57.89 (aryl-CH₂N), 56.43 (PhCH₂N), 45.50 (NCH₂CH₂N), 26.28 (OCHMe₂), 26.08 (OCHMe₂), 17.15 (aryl-CH₃).

Elemental Anal. Calc. for C₄₀H₅₂N₂O₆Ti: C, 68.17; H, 7.44; N, 3.98. Found: C, 68.54; H, 7.52; N, 3.95%.

3.16. X-ray structure determination for **2**, **4**, **6**, and **7**

The crystallographic measurements for **2**, **4**, **6**, and **7** were performed at ambient temperature using a Bruker Apex II-CCD area detector diffractometer with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. Single crystals of suitable size and quality were selected and mounted onto a glass capillary after coated with paratone oil, and centered in the X-ray beam by using a video camera. The hemisphere of reflection data were collected as ω scan frames with 0.3°/frame and an exposure time of 5 s/frame. Cell parameters were determined and refined by the SMART program [50]. Data reduction was performed using SAINT software [51]. The data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied using the SADABS program [52]. The structures of the compounds were solved by direct methods and refined by full matrix least-squares methods using the SHELXTL program package (version 5.1) with anisotropic thermal parameters for all non-hydrogen atoms [53]. Hydrogen atoms were placed at their geometrically calculated positions and refined riding on the corresponding carbon atoms with isotropic thermal parameters. Details for crystallographic data and parameters are listed in Table 3.

3.17. Polymerization procedure

Solution polymerizations of LA were carried out by charging a stirring bar and LA to a 10 mL vial in the glove box and then the flask was immersed at the oil bath of 130 °C. Polymerization began with the addition of 5 mL stock toluene solution of the titanium compound. After 6 h, the polymerization was terminated by the addition of 5 mL of MeOH. The reaction mixture was washed with excess methanol several times. The precipitated polymer was collected by filtration, washed with methanol (40 mL, washing for five times), and dried in a vacuum oven at 40 °C for 12 h. In the case of the bulk polymerization, no solvent was used and polymerization was carried out in a manner analogous to the solution polymerization except for the polymerization temperature of 130 °C.

4. Conclusion

We synthesized several types of titanium complexes containing various substituted Salan-type ligands. The [ONNO]-type ligands **Lig**¹–**Lig**⁸ bind to titanium in a tetrahedral fashion, leading to octahedral complexes **1**–**8** regardless of the steric bulkiness of the aryl-

ring substituents. The substituents on phenyl ring and Salan ligand backbone exerted significant influence upon the catalytic activity and molecular weight of PLA polymers obtained. Further living ROP studies of LA using complexes **1**–**8** and their zirconium congeners are now in progress.

5. Supplementary material

CCDC 716762, 716763, 716764 and 716765 contain the supplementary crystallographic data for compounds **2**, **4**, **6** and **7**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgment

This work was supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD, Basic Research Promotion Fund) (KRF-2008-314-D00079 and KRF-2007-313-C00396).

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