



Synthesis, structure, and catalytic activity of titanium complexes with new chiral 11,12-diamino-9,10-dihydro-9,10-ethanoanthracene-based ligands

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ABSTRACT

A new series of organo-titanium complexes have been prepared from the reaction between $\text{Ti}(\text{NMe}_2)_4$ and C_2 -symmetric ligands, (*R,R*)-11,12-bis(pyrrol-2-ylmethyleneamino)-9,10-dihydro-9,10-ethanoanthracene (**1H₂**), and (*R,R*)-bis(diphenylthiophosphoramino)-9,10-dihydro-9,10-ethanoanthracene (**2H₂**), (*R,R*)-11,12-bis(mesitylenesulphonylamino)-9,10-dihydro-9,10-ethanoanthracene (**3H₂**) and (*R,R*)-bis(diphenylthiophosphoramino)-1,2-cyclohexane (**4H₂**). Treatment of $\text{Ti}(\text{NMe}_2)_4$ with 1 equiv of **1H₂** gives, after recrystallization from a benzene solution, the binuclear double helicate titanium amide (**1**)₂[Ti(NMe₂)₂]₂ (**5**) in 71% yield. While under similar reaction conditions, reaction of $\text{Ti}(\text{NMe}_2)_4$ with 1 equiv of **2H₂**, **3H₂** or **4H₂** gives, after recrystallization from a toluene or benzene solution, the mononuclear single helicate titanium amides (**2**)Ti(NMe₂)₂ (**6**), (**3**)Ti(NMe₂)₂ (**7**) and (**4**)Ti(NMe₂)₂ (**8**), respectively, in good yields. All new compounds have been characterized by various spectroscopic techniques, and elemental analyses. The solid-state structures of complexes **5–8** have further been confirmed by X-ray diffraction analyses. The titanium amides are active catalysts for the polymerization of *rac*-lactide, leading to the isotactic-rich polylactides.

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1. Introduction

In recent years, chiral titanium complexes have been designed and prepared to give variants which bear appropriate structural and electronic features for intended specific reactions [1–17], and these complexes have been shown good to excellent enantioselectivities in a number of asymmetric reactions such as epoxidation reaction [1,2], allylation reaction [3], cyanation reaction [4,5], Strecker reactions [6,7], Aldol reaction [8,9], Diels–Alder reactions [10–13], and other transformations [14–17]. Although a variety of chiral titanium complexes have been studied, the development of new chiral titanium complexes for asymmetric transformations is still a desirable goal.

Ligand modification plays a key role in developing new catalyst precursors for asymmetric synthesis. In recent years, we have therefore developed a series of chiral nitrogen-containing multidentate ligands, and their Ir(I), Rh(I), Ti(IV), Ag(I), Cu(II), Zr(IV) and lanthanide complexes are useful catalysts for a wide range of transformations [18–39]. In our endeavors to further explore the chiral nitrogen-containing ligand system, we have recently extended

our research work to (*R,R*)-11,12-diamino-9,10-dihydro-9,10-ethanoanthracene derivatives, including C_2 -symmetric (*R,R*)-11,12-bis(pyrrol-2-ylmethyleneamino)-9,10-dihydro-9,10-ethanoanthracene (**1H₂**), (*R,R*)-bis(diphenylthiophosphoramino)-9,10-dihydro-9,10-ethanoanthracene (**2H₂**), and (*R,R*)-11,12-bis(mesitylenesulphonylamino)-9,10-dihydro-9,10-ethanoanthracene (**3H₂**). We report herein the synthesis and properties of the chiral ligands, their use in the coordination chemistry of titanium(IV), and the applications of the resulting complexes as catalysts for the polymerization of *rac*-lactide. For comparison, the titanium complex derived from ligand (*R,R*)-bis(diphenylthiophosphoramino)-1,2-cyclohexane (**4H₂**) will be also included in this contribution.

2. Experimental section

2.1. General methods

Titanium complexes and catalytic reactions were performed under an atmosphere of dry dinitrogen with rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glovebox. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. (*R,R*)-11,12-Diamino-9,10-dihydro-9,10-ethanoanthracene [40] and (*R,R*)-bis(dipheny

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lthiophosphoramino)-1,2-cyclohexane (**4H₂**) [41] were prepared according to the literature methods. All chemicals were purchased from Aldrich Chemical Co. and Beijing Chemical Co., and used as received unless otherwise noted. Infrared spectra were obtained from KBr pellets on an Avatar 360 Fourier transform spectrometer. Molecular weights of the polymer were estimated by gel permeation chromatography (GPC) using a PL-GPC 50 apparatus. ¹H and ¹³C NMR spectra were recorded on a Bruker AV 400 spectrometer at 400 and 100 MHz, respectively. All chemical shifts are reported in δ units with reference to the residual protons of the deuterated solvents for proton and carbon chemical shifts. Melting points were measured on an X-6 melting point apparatus and were uncorrected. Elemental analyses were performed on a Vario EL elemental analyzer.

2.2. Preparation of (R,R)-11,12-bis(pyrrol-2-ylmethyleneamino)-9,10-dihydro-9,10-ethanoanthracene (**1H₂**)

Pyrrole-2-carboxaldehyde (0.95 g, 10.0 mmol) was mixed with (R,R)-11,12-diamino-9,10-dihydro-9,10-ethanoanthracene (1.18 g, 5.0 mmol) in dry toluene (25 mL). A few 4-Å molecular sieves were added, and the solution was warmed up to 70 °C and kept for two days at this temperature. The solution was filtered and the solvent was removed under reduced pressure. The resulting pale yellow residue was washed with cold *n*-hexane (30 mL \times 3) to give **1H₂** as a pale yellow solid. Yield: 1.50 g (77%). M.p.: 228–230 °C. ¹H NMR (CDCl₃): δ 9.01 (br, s, 2H, NH), 7.86 (s, 2H, CH=N), 7.24 (m, 4H, aryl), 7.09 (m, 4H, aryl), 6.67 (s, 2H, aryl), 6.30 (d, *J* = 3.4 Hz, 2H, aryl), 6.01 (t, *J* = 3.2 Hz, 2H, aryl), 4.11 (s, 2H, CHN), 3.33 (s, 2H, CH). ¹³C NMR (CDCl₃): δ 150.9, 142.0, 141.0, 130.1, 126.0, 125.8, 123.7, 121.5, 114.1, 111.2, 109.7, 77.2, 52.2. IR (KBr, cm⁻¹): ν 3431 (s), 2953 (m), 2854 (m), 1626 (vs), 1547 (s), 1417 (s), 1369 (s), 1213 (s), 1032 (s), 879 (s), 746 (s). Anal. Calcd for C₂₆H₂₂N₄: C, 79.97; H, 5.68; N, 14.35. Found: C, 80.03; H, 5.73; N, 14.18.

2.3. Preparation of (R,R)-bis(diphenylthiophosphoramino)-9,10-dihydro-9,10-ethanoanthracene (**2H₂**)

Diphenylthiophosphinic chloride (2.52 g, 10.0 mmol) was mixed with (R,R)-11,12-diamino-9,10-dihydro-9,10-ethanoanthracene

(1.18 g, 5.0 mmol) in dry toluene (30 mL). Pyridine (2 mL, 25.3 mmol) was added, and the solution was refluxed for two days. The solvent was removed and the residue was decomposed with H₂O (20 mL) and extracted with ethyl acetate (20 mL \times 3) and washed with brine (20 mL). The combined organic layers were dried with anhydrous Na₂SO₄ and the solvent was removed under reduced pressure to give a pale yellow solid, which was further purified by flash column chromatography (*n*-hexane/ethyl acetate = 20:1) to give **2H₂** as a pale yellow solid. Yield: 2.74 g, (82%). M.p.: 218–220 °C. ¹H NMR (CDCl₃): δ 7.88 (m, 4H, aryl), 7.80 (m, 4H, aryl), 7.44 (m, 6H, aryl), 7.32 (m, 2H, aryl), 7.25 (m, 4H, aryl), 7.14 (m, 2H, aryl), 7.00 (m, 6H, aryl), 4.35 (s, 2H, NH), 3.49 (t, *J* = 10.6 Hz, 2H, CHN), 2.27 (s, 2H, CH). ¹³C NMR (CDCl₃): δ 138.4, 135.6, 134.6, 133.5, 131.8, 131.6, 128.6, 128.4, 126.6, 124.7, 61.4, 50.7. IR (KBr, cm⁻¹): ν 3310 (s), 3047 (m), 2854 (m), 1477 (s), 1430 (s), 1412 (s), 1218 (s), 1098 (s), 849 (s), 723 (s). Anal. Calcd for C₄₀H₃₄N₂P₂S₂: C, 71.84; H, 5.12; N, 4.19. Found: C, 71.76; H, 5.03; N, 4.18.

2.4. Preparation of (R,R)-11,12-bis(mesitylenesulphonylamino)-9,10-dihydro-9,10-ethanoanthracene (**3H₂**)

This compound was prepared as a pale yellow solid from the reaction of mesitylenesulphonyl chloride (2.19 g, 10.0 mmol) with (R,R)-11,12-diamino-9,10-dihydro-9,10-ethanoanthracene (1.18 g, 5.0 mmol) in the presence of pyridine (2 mL, 25.3 mmol) in dry toluene (30 mL) at reflux and purification by flash column chromatography (*n*-hexane/ethyl acetate = 6:1) using a similar procedure as in the synthesis of **2H₂**. Yield: 2.37 g, (79%). M.p.: 98–100 °C. ¹H NMR (CDCl₃): δ 7.08 (m, 6H, aryl H), 6.98 (m, 2H, aryl H), 6.91 (s, 4H, aryl H), 4.07 (s, 2H, NH), 4.04 (s, 2H, CHN), 3.08 (s, 2H, CH), 2.47 (s, 12H, CH₃), 2.27 (s, 6H, CH₃). ¹³C NMR (CDCl₃): δ 142.7, 140.4, 139.3, 137.5, 134.1, 132.1, 127.2, 127.0, 126.4, 124.5, 61.3, 49.3, 23.0, 21.0. IR (KBr, cm⁻¹): ν 3299 (s), 2937 (m), 1603 (s), 1458 (s), 1332 (s), 1155 (s), 1056 (s), 850 (s), 762 (s). Anal. Calcd for C₃₄H₃₆N₂S₂O₄: C, 67.97; H, 6.04; N, 4.66. Found: C, 67.89; H, 6.08; N, 4.73.

2.5. Preparation of (1)₂[Ti(NMe₂)₂]₂(5)

A toluene solution (10 mL) of **1H₂** (0.20 g, 0.5 mmol) was slowly added to a toluene solution (10 mL) of Ti(NMe₂)₄ (0.11 g,

Table 1
Crystal data and experimental parameters for compounds **5–8**

Compound	5 ·2C ₆ H ₆	6 ·2C ₇ H ₈	7 ·2C ₆ H ₆	8
Formula	C ₇₂ H ₇₆ N ₁₂ Ti ₂	C ₅₈ H ₆₀ N ₄ P ₂ S ₂ Ti	C ₅₀ H ₅₈ N ₄ O ₄ S ₂ Ti	C ₃₄ H ₄₂ N ₄ P ₂ S ₂ Ti
Formula weight	1205.25	987.06	891.02	680.68
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Triclinic
Space group	P12 ₁ 1	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁	P(-1)
<i>a</i> (Å)	12.426(1)	8.892(1)	8.570(1)	8.542(4)
<i>b</i> (Å)	15.273(2)	20.970(1)	21.353(1)	13.933(6)
<i>c</i> (Å)	16.817(2)	27.055(1)	25.452(1)	15.759(7)
α (deg)	90	90	90	106.09(1)
β (deg)	97.76(1)	90	90	94.39(1)
γ (deg)	90	90	90	106.24(1)
<i>V</i> (Å ³)	3162.6(6)	5044.9(3)	4657.7(3)	1705.9(13)
<i>Z</i>	2	4	4	2
<i>D</i> _{calc.} (g/cm ³)	1.266	1.300	1.271	1.325
Size (mm)	0.22 \times 0.14 \times 0.12	0.22 \times 0.12 \times 0.08	0.40 \times 0.22 \times 0.20	0.12 \times 0.10 \times 0.08
<i>F</i> (000)	1272	2080	1888	716
2 θ range (deg)	3.30–55.68	3.58–55.72	3.20–55.76	3.50–55.90
No. of reflections collected	39083	50410	33023	21847
No. of unique reflections [<i>R</i> _(int)]	14861 (0.0486)	11987 (0.0621)	11063 (0.0401)	8147 (0.0654)
No. of observed reflections	12832	11151	10085	6731
Absorbed corrections (<i>T</i> _{max} , <i>T</i> _{min})	0.96, 0.94	0.97, 0.93	0.94, 0.88	0.96, 0.94
<i>R</i>	0.047	0.043	0.039	0.091
<i>R</i> _w	0.099	0.090	0.084	0.176
<i>wR</i> ₂ (all data)	0.106	0.093	0.087	0.182
GO _F	1.03	1.06	1.04	1.20

Table 2
Selected bond distances (Å) and bond angles (deg) for compounds **5–8**

Compound	5	6	7	8
Ti–N (av.)	Ti(1): 2.113(2) Ti(2): 2.113(2)	1.993(2)	1.965(2)	1.969(4)
Ti–N (NMe ₂)	N(9): 1.924(2) N(10): 1.913(2) N(11): 1.918(2) N(12): 1.914(2)	N(3): 1.884(2) N(4): 1.878(2)	N(3): 1.880(2) N(4): 1.865(2)	N(5): 1.881(4) N(6): 1.872(4)
Ti–X		S(1): 2.632(1) P(2): 2.958(1)	O(1): 1.931(1) O(3): 2.111(1) S(2): 2.758(1)	S(1): 2.590(2) P(1): 2.949(2)
Sum angles of N (TiNMe ₂)	N(9): 359.7(2) N(10): 359.9(2) N(11): 359.9(2) N(12): 360.0(2)	N(3): 359.0(2) N(4): 359.6(2)	N(3): 359.9(2) N(4): 359.9(2)	N(5): 358.7(4) N(6): 359.4(4)

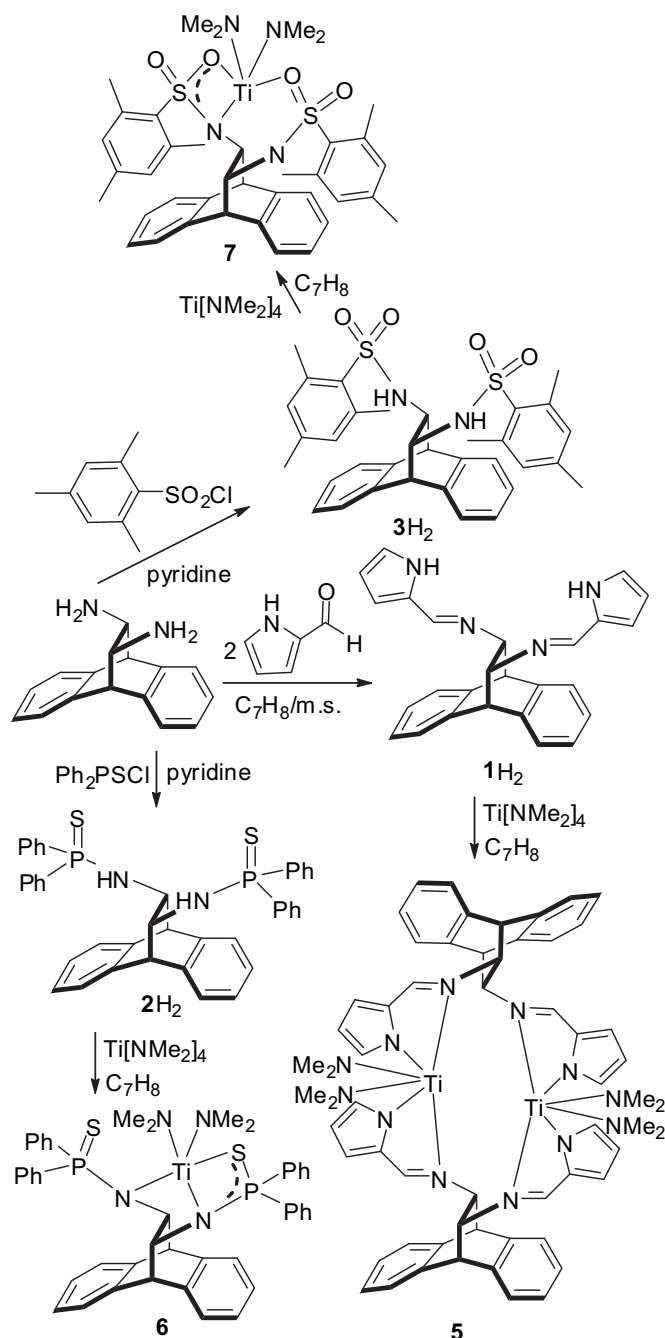
0.5 mmol) with stirring at room temperature. After this mixture was stirred at room temperature for one day, the solution was filtered and the solvent was removed under reduced pressure. The resulting red solid was recrystallized from a benzene solution to give **5** as red microcrystals. Yield: 0.19 g (71%). M.p. 288–290 °C (dec.). ¹H NMR (C₆D₆): δ 7.49 (s, 4H, CH=N), 7.20 (m, 4H, aryl), 7.07 (m, 12H, aryl), 6.94 (m, 4H, aryl), 6.47 (m, 4H, aryl), 6.44 (m, 4H, aryl), 3.93 (s, 4H, CHN), 3.53 (s, 24H, TiNMe₂), 3.11 (s, 4H, CH). ¹³C NMR (C₆D₆): δ 156.5, 142.6, 137.7, 137.0, 134.3, 129.1, 126.1, 125.4, 124.4, 116.8, 111.6, 64.8, 50.6, 47.7. IR (KBr, cm⁻¹): ν 2961 (w), 2762 (w), 1577 (s), 1434 (s), 1393 (s), 1260 (s), 1098 (s), 1023 (s), 799 (s). Anal. Calcd for C₆₀H₆₄N₁₂Ti₂: C, 68.70; H, 6.15; N, 16.02. Found: C, 68.73; H, 6.08; N, 16.13. Few red crystals suitable for X-ray diffraction analysis were picked up from the mixture, which was identified as **5**·2C₆H₆.

2.6. Preparation of (2)Ti(NMe₂)₂ (**6**)

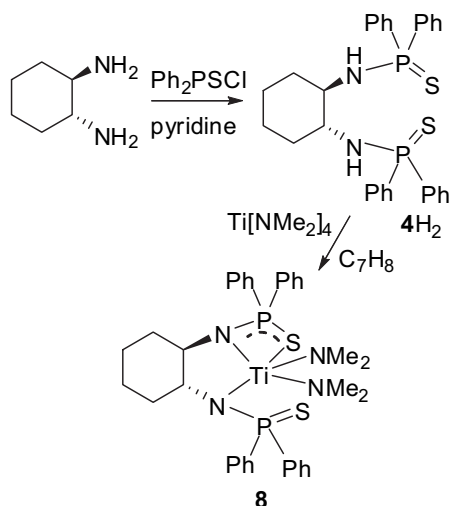
This compound was prepared as red microcrystals from the reaction of **2**H₂ (0.34 g, 0.5 mmol) with Ti(NMe₂)₄ (0.11 g, 0.5 mmol) in toluene (20 mL) and recrystallization from a toluene solution by a similar procedure as in the synthesis of **5**. Yield: 0.29 g (73%). M.p.: 238–240 °C (dec.). ¹H NMR (C₆D₆): δ 8.20 (m, 4H, aryl), 7.92 (m, 4H, aryl), 7.24–6.75 (m, 20H, aryl), 4.57 (s, 2H, CHN), 4.32 (s, 2H, CH), 2.77 (s, 12H, TiNMe₂). ¹³C NMR (C₆D₆): δ 139.2, 137.7, 132.4, 131.8, 130.8, 129.1, 125.7, 125.4, 123.2, 121.9, 71.7, 50.4, 44.5. IR (KBr, cm⁻¹): ν 2968 (m), 2853 (m), 1476 (s), 1456 (s), 1434 (s), 1209 (s), 1157 (s), 1098 (s), 1048 (s), 931 (s), 890 (s), 840 (s). Anal. Calcd for C₄₄H₄₄N₄P₂S₂Ti: C, 65.83; H, 5.52; N, 6.98. Found: C, 65.85; H, 5.50; N, 6.85. Few red crystals suitable for X-ray diffraction analysis were picked up from the mixture, which was identified as **6**·2C₇H₈.

2.7. Preparation of (3)Ti(NMe₂)₂ (**7**)

This compound was prepared as red microcrystals from the reaction of **3**H₂ (0.30 g, 0.5 mmol) with Ti(NMe₂)₄ (0.11 g, 0.5 mmol) in toluene (20 mL) and recrystallization from a benzene solution by a similar procedure as in the synthesis of **5**. Yield: 0.30 g (82%). M.p.: 178–180 °C (dec.). ¹H NMR (C₆D₆): δ 7.16 (s, 2H, aryl), 7.06 (m, 4H, aryl), 6.88 (s, 2H, aryl), 6.69 (s, 4H, aryl), 4.44 (s, 2H, CHN), 4.31 (s, 2H, CH), 3.24 (s, 12H, TiNMe₂), 2.74 (s, 12H, CH₃), 1.98 (s, 6H, CH₃). ¹³C NMR (C₆D₆): δ 144.6, 141.7, 139.8, 139.6, 131.8, 129.3, 126.2, 126.0, 125.7, 123.4, 65.5, 51.6, 46.8, 22.9, 20.7. IR (KBr, cm⁻¹): ν 3024 (w), 2957 (m), 1599 (s), 1454 (s), 1415 (s), 1257 (s), 1229 (s), 1119 (s), 1012 (s), 934 (s), 885 (s). Anal. Calcd for C₃₈H₄₆N₄O₄S₂Ti: C, 62.11; H, 6.31; N, 7.62. Found: C, 62.08; H, 6.35; N, 7.60. Few red crystals suitable for X-ray diffraction analysis were picked up from the mixture, which was identified as **7**·2C₆H₆.



Scheme 1.



Scheme 2.

2.8. Preparation of (4)Ti(NMe₂)₂ (8)

This compound was prepared as red microcrystals from the reaction of **4H₂** (0.27 g, 0.5 mmol) with Ti(NMe₂)₄ (0.11 g, 0.5 mmol) in toluene (20 mL) and recrystallization from a benzene solution by a similar procedure as in the synthesis of **5**. Yield: 0.30 g (87%). M.p.: 168–170 °C (dec.). ¹H NMR (C₆D₆): δ 8.26 (m, 4H, aryl), 8.00 (m, 4H, aryl), 7.08 (m, 12H, aryl), 4.10 (s, 2H, CHN), 3.12 (s, 12H, TiNMe₂), 1.51 (m, 4H, CH₂), 1.10 (m, 4H, CH₂). ¹³C NMR (C₆D₆): δ 132.0, 131.8, 130.5, 125.4, 69.4, 44.4, 20.6, 11.4. IR (KBr, cm⁻¹): ν 3038 (m), 2963 (m), 2916 (s), 1455 (s), 1434 (s), 1303 (s), 1248 (s), 1092 (s), 1068 (s), 936 (s), 797 (s). Anal. Calcd for C₃₄H₄₂N₄P₂S₂Ti: C, 59.99; H, 6.22; N, 8.23. Found: C, 59.89; H, 6.18; N, 8.20. Few red crystals suitable for X-ray diffraction analysis were picked up from the mixture.

2.9. General procedure for polymerization of *rac*-lactide

In a glovebox, a Schlenk flask was charged with a solution of the complex (typically 0.01 mmol) in toluene or THF (0.2 mL). To this solution was added rapidly a toluene or THF solution (5.0 mL) of *rac*-lactide (2.5 mmol), and the reaction mixture was vigorously stirred for 24 h at 70 °C. The polymerization was quenched by the addition of acidified methanol. The resulting precipitated polylactide was collected, washed with methanol several times, and dried in vacuum at 50 °C overnight.

2.10. X-ray crystallography

Single-crystal X-ray diffraction measurements were carried out on a Rigaku Saturn CCD diffractometer at 113(2) K using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). An empirical absorption correction was applied using the SADABS program [42]. All structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXL-97 program package [43]. All the hydrogen atoms were geometrically fixed using the riding model. The crystal data and experimental data for complexes **5–8** are summarized in Table 1. Selected bond lengths and angles are listed in Table 2.

3. Results and discussion

3.1. Synthesis and characterization of ligands

The C₂-symmetric Schiff base ligand, (*R,R*)-11,12-bis(pyrrol-2-ylmethyleneamino)-9,10-dihydro-9,10-ethanoanthracene (**1H₂**), is

readily prepared in 77% yield by condensation of (*R,R*)-11,12-diamino-9,10-dihydro-9,10-ethanoanthracene with 2 equiv of pyrrole-2-carboxaldehyde in the presence of molecular sieves in toluene at 70 °C (Scheme 1). Of course, the C₂-symmetric ligands, (*R,R*)-11,12-bis(diphenylthiophosphoramino)-9,10-dihydro-9,10-ethanoanthracene (**2H₂**) and (*R,R*)-11,12-bis(mesitylenesulfonylamino)-9,10-dihydro-9,10-ethanoanthracene (**3H₂**), are also readily prepared in good yields by treatment of the starting material (*R,R*)-11,12-diamino-9,10-dihydro-9,10-ethanoanthracene with 2 equiv of diphenylthiophosphinic chloride or mesitylenesulfonyl chloride, respectively, in the presence of an excess of pyridine in toluene at reflux, followed by purification with flash column chromatography (Schemes 1).

All new ligands are air-stable, and are soluble in CH₂Cl₂, CHCl₃, toluene and benzene, and slightly soluble in *n*-hexane. They have been fully characterized by various spectroscopic techniques, and elemental analyses. The ¹H and ¹³C NMR spectra of them indicate

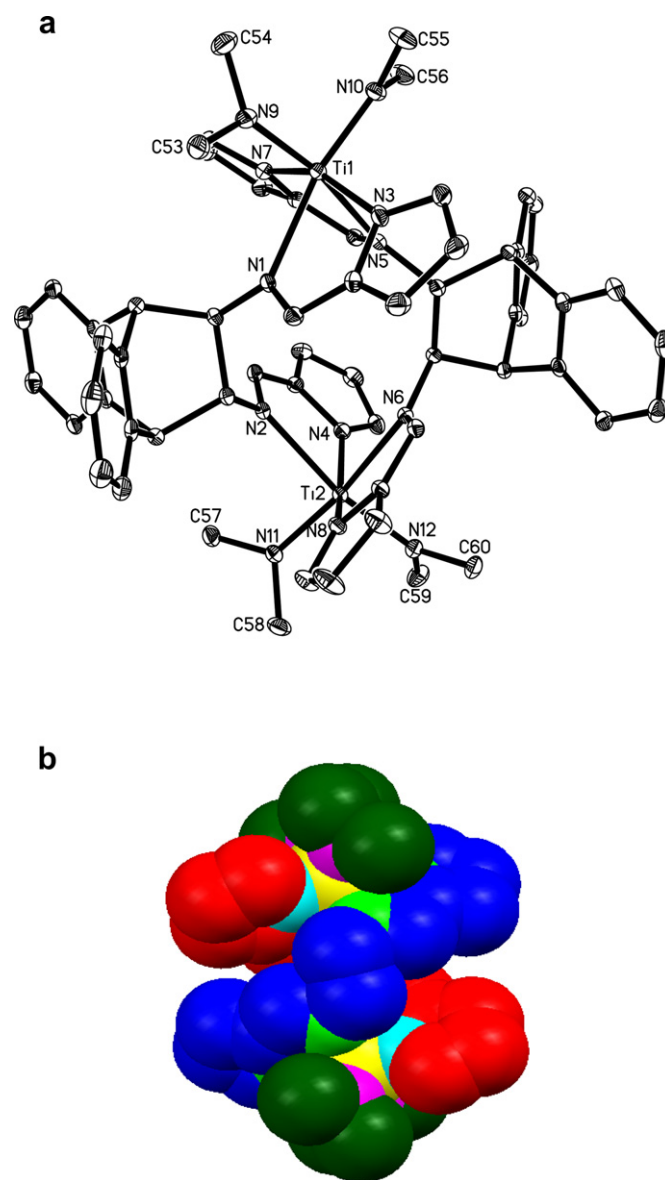


Fig. 1. (a) Molecular structure of **5** (thermal ellipsoids drawn at the 35% probability level). (b) Space-filling diagram of **5** (9,10-dihydro-9,10-anthracenyl groups omitted for clarity).

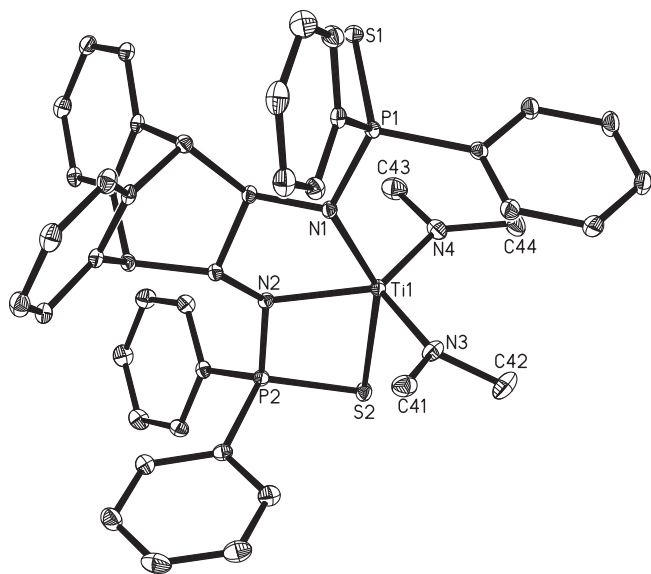


Fig. 2. Molecular structure of **6** (thermal ellipsoids drawn at the 35% probability level).

that they are symmetrical on the NMR timescale, which are consistent with their C_2 -symmetric structures. The infrared spectra of these compounds exhibit peaks corresponding to aromatic stretches in addition to N-H stretches at about 3300 cm^{-1} , and strong C=N stretches at 1626 cm^{-1} for **1H₂**.

3.2. Synthesis and characterization of complexes

Titanium amide complexes can be efficiently prepared via amine elimination reaction between $\text{Ti}(\text{NMe}_2)_4$ and protic reagents. For example, treatment of $\text{Ti}(\text{NMe}_2)_4$ with 1 equiv of (*R,R*)-11,12-bis(pyrrol-2-ylmethyleneamino)-9,10-dihydro-9,10-ethanoanthracene (**1H₂**) gives, after recrystallization from a benzene solution, the binuclear double helicate titanium amide $(\mathbf{1})_2[\text{Ti}(\text{NMe}_2)_2]_2$ (**5**) in 71% yield (Scheme 1). While under similar reaction conditions, treatment of $\text{Ti}(\text{NMe}_2)_4$ with 1 equiv of bis(diphenylthiophosphoramino)-9,10-dihydro-9,10-ethanoanthracene (**2H₂**), (*R,R*)-11,12-bis(mesitylenesulfonylamino)-9,10-dihydro-9,10-ethanoanthracene (**3H₂**) or (*R,R*)-bis(diphenylthiophosphoramino)-1,2-cyclohexane (**4H₂**) gives, after recrystallization from a toluene or benzene solution, the mononuclear single helicate titanium amides $(\mathbf{2})\text{Ti}(\text{NMe}_2)_2$ (**6**), $(\mathbf{3})\text{Ti}(\text{NMe}_2)_2$ (**7**) and $(\mathbf{4})\text{Ti}(\text{NMe}_2)_2$ (**8**), respectively, in good yields (Schemes 1 and 2).

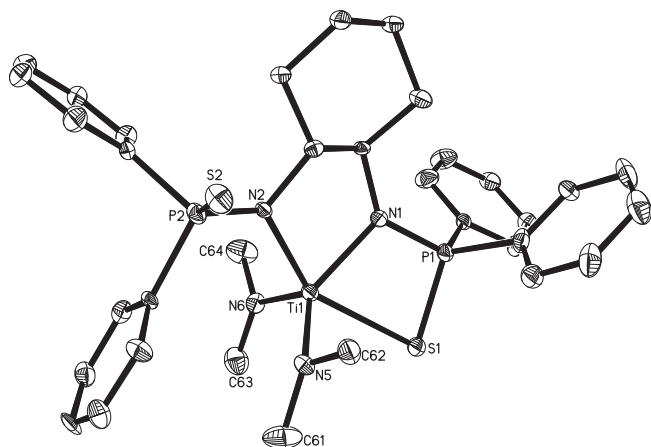


Fig. 3. Molecular structure of **8** (thermal ellipsoids drawn at the 35% probability level).

These complexes are stable in dry nitrogen atmosphere, while they are very sensitive to moisture. They are soluble in organic solvents such as THF, DME, pyridine, toluene, and benzene, and only slightly soluble in *n*-hexane. They have been characterized by various spectroscopic techniques and elemental analyses. The ^1H NMR spectra of **5–8** support that the ratio of amino group NMe_2 and ligand anion **1**, **2**, **3**, or **4** is 2:1. Their solid-state structures have been further confirmed by X-ray diffraction analyses.

The single-crystal X-ray diffraction analysis show that there is one molecule $(\mathbf{1})_2[\text{Ti}(\text{NMe}_2)_2]_2$ (**5**) and two solvated benzene molecules in the lattice. The molecule $(\mathbf{1})_2[\text{Ti}(\text{NMe}_2)_2]_2$ is a binuclear double helicate (Fig. 1a), the coordination of two **1** ligands around two Ti^{4+} ions results in the formation of a *P* double helix (Fig. 1b). Each Ti^{4+} ion is σ -bound to four nitrogen atoms from the two ligands **1** and two nitrogen atoms from amino groups NMe_2 in a distorted-octahedron geometry (Fig. 1a) with the average distance of Ti-N is $2.113(2)\text{ \AA}$. The short distances of Ti-NMe₂ $1.924(2)$ and $1.913(2)\text{ \AA}$ for Ti(1), and $1.918(2)$ and $1.914(2)\text{ \AA}$ for Ti(2), respectively, and the planar geometry around the nitrogen atoms of NMe_2 groups indicate that the nitrogen atoms (TiNMe_2) with sp^2 hybridization are engaged in $\text{N}(\text{p}\pi) \rightarrow \text{Ti}(\text{d}\pi)$ interactions. These structural data are close to those found in $[(R)-1,1'-(\text{C}_{10}\text{H}_6)_2-2,2'-(\text{NCHC}_4\text{H}_3\text{N})_2]\text{Ti}(\text{NMe}_2)_2$ [34] and $[(R)-1,1'-(6\text{-MeC}_6\text{H}_3)_2-2,2'-(\text{NCHC}_4\text{H}_3\text{N})_2]\text{Ti}(\text{NMe}_2)_2$ [36]. The two titanium centers within the helical dication are separated by $6.757(2)\text{ \AA}$.

The single-crystal X-ray diffraction analyses show that there is one molecule $(\mathbf{2})\text{Ti}(\text{NMe}_2)_2$ (**6**) and two solvated toluene molecules in the lattice. In each molecule of $(\mathbf{2})\text{Ti}(\text{NMe}_2)_2$ (**6**) or $(\mathbf{4})\text{Ti}(\text{NMe}_2)_2$ (**8**), the Ti^{4+} is σ -bound to two nitrogen atoms and one sulfur atom from the

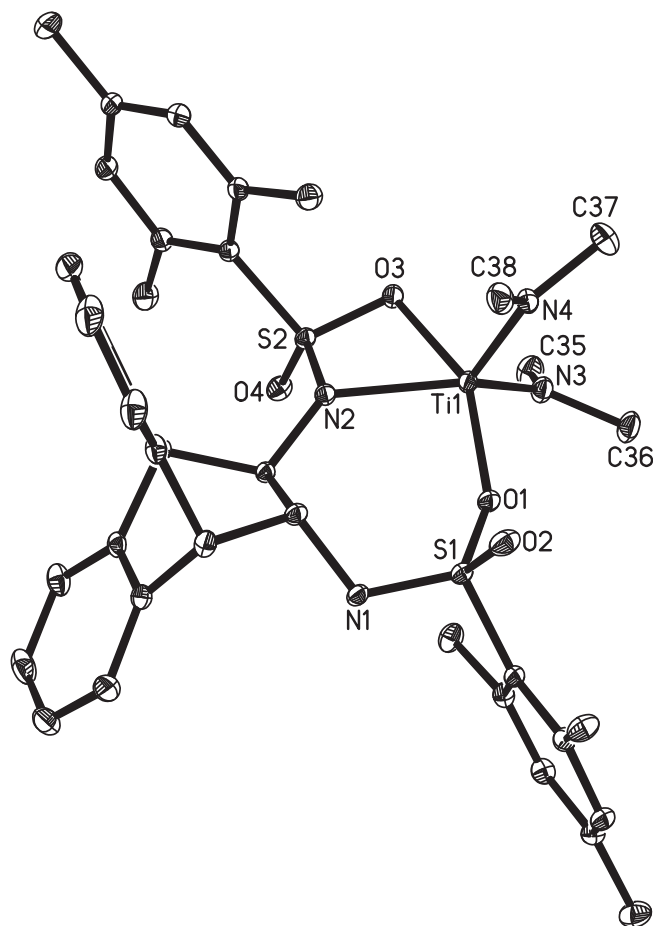
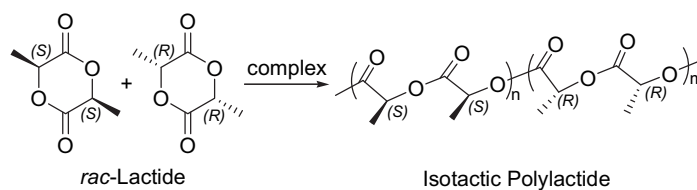


Fig. 4. Molecular structure of **7** (thermal ellipsoids drawn at the 35% probability level).

Table 3
Polymerization of *rac*-lactide catalyzed by chiral organo-titanium amides **5–8**^a



Entry	Complex	Solvent	Conv. (%)	M_n^b (kg/mol)	M_w/M_n^b	P_m^c (%)
1	5	Toluene	78	29.1	1.39	72
2	6	Toluene	96	32.2	1.31	70
3	7	Toluene	100	34.3	1.23	71
4	8	Toluene	100	36.5	1.36	68
5	5	THF	80	26.2	1.22	69
6	6	THF	100	33.0	1.33	70
7	7	THF	100	32.3	1.23	72
8	8	THF	98	31.5	1.35	65

^a Conditions: 70 °C, precat./LA (mol/mol) = 1/250; pre-catalyst (0.01 mmol, based on Ti(NMe₂)₂ group); polymerization time, 24 h; solvent, 5 mL; [LA] = 0.5 mol/L.

^b Measured by GPC (using polystyrene standards in THF).

^c P_m is the probability of *meso* linkages between monomer units and is determined from the methine region of the homonuclear decoupling ¹H NMR spectrum in CDCl₃ at 25 °C.

ligand **2** or **4** and two nitrogen atoms from amino groups NMe₂ in a distorted-trigonal-bipyramidal geometry (Figs. 2 and 3) with the average distance of Ti–N is 1.993(2) Å for **6**, and 1.969(4) Å for **8**, respectively. The distance of Ti–S is 2.632(1) Å for **6**, and 2.590(2) Å for **8**, respectively. The short distances of Ti–NMe₂ 1.884(2) and 1.878(2) Å for **6**, and 1.881(4) and 1.872(4) Å for **8**, respectively, and the planar geometry around the nitrogen atoms of NMe₂ groups indicate that both nitrogen atoms with sp² hybridization are engaged in N(p_π)→Zr(d_π) interactions. These structural data are close to those found in [(R)-1,1'-(C₁₀H₁₀)₂-2,2'-(NP(S)Ph₂)₂]Ti(NMe₂)₂ [37].

The single-crystal X-ray diffraction analysis shows that there is one molecule of (3)Ti(NMe₂)₂ (**7**) and two solvated benzene molecules in the lattice. In the molecule of (3)Ti(NMe₂)₂, the Ti⁴⁺ is σ-bound to two oxygen atoms and one nitrogen atom from the ligand **3** and two nitrogen atoms from amino groups NMe₂ in a distorted-trigonal-bipyramidal geometry (Fig. 4) with the average distance of Ti–N (1.965(2) Å) and the average distance of Ti–O (2.021(1) Å). The short distances of Ti–NMe₂ (1.880(2) and 1.865(2) Å) and the planar geometry around the nitrogen atom of NMe₂ indicate that the nitrogen atoms with sp² hybridization are engaged in N(p_π)→Ti(d_π) interactions. These structural data are comparable to those found in [(R)-1,1'-(C₁₀H₆)₂-2,2'-(NSO₂(*p*-tolyl))₂]Ti(NMe₂)₂ [38] and [(R)-1,1'-(C₁₀H₁₀)₂-2,2'-(NSO₂(2,4,6-Me₃C₆H₂))₂]Ti(NMe₂)₂ [38].

3.3. Polymerization of racemic-lactide

The results clearly show that the titanium complexes **5–8** are active catalysts for the ring opening polymerization (ROP) of *racemic*-lactide under the conditions given in Table 3. Titanium complex **7** allows the complete conversion of 250 equiv of lactide within 24 h at 70 °C in toluene or THF at [rac-LA] = 0.5 mol L⁻¹ (Table 3, entries 3 and 7), while polymerizations with the double helicate titanium initiator/catalyst **5** proceed much more slowly (Table 3, entries 1 and 5). The reason for the different catalytic activity between the double helicate catalyst **5** and the single helicate titanium complexes **6** and **7**, is not clear at this time, however, the sterically encumbered environment around the metal center seems to be a major reason for this difference. Their catalytic activities are similar in both THF and toluene solutions, and the resulting poly-lactides are all isotactic rich under the conditions examined. Molecular weights and polydispersities of the polymers produced

ranged from 26.2 to 36.5 kg mol⁻¹ and 1.22 to 1.39, respectively. Our results show that the catalytic activities of **5–8** resemble that of [(C₅H₄O)(C₅H₄CH=N-2,6-*i*-Pr₂C₆H₃)Fe]₂Ti(O^{*i*}Pr)₂ [44], while the microstructure of the resulting poly(MMA)s are similar to those initiated by [(S)-2-MeO-C₂₀H₂₀-2'-(NCHC₄H₃N)]₂YN(SiMe₃)₂ [33].

4. Conclusions

A new series of titanium complexes have been prepared from the reactions between Ti(NMe₂)₄ and chiral ligands **1H₂**, **2H₂**, **3H₂** and **4H₂**. The organo-titanium amides can initiate the ring-opening polymerization of *rac*-lactide, leading to the isotactic-rich poly-lactides. When a change is made from pyrrol-2-ylmethyleneamino group to mesitylenesulphonylamino or diphenylthiophosphoramino group, the ligands (R,R)-11,12-bis(pyrrol-2-ylmethyleneamino)-9,10-dihydro-9,10-ethanoanthracene (**1H₂**), and bis(diphenylthiophosphoramino)-9,10-dihydro-9,10-ethanoanthracene (**2H₂**) or (R,R)-11,12-bis(mesitylenesulphonylamino)-9,10-dihydro-9,10-ethanoanthracene (**3H₂**) exhibit different reactivity patterns. For example, reaction of Ti(NMe₂)₄ and **1H₂** gives the binuclear double helicate titanium amide (**1**)₂[Ti(NMe₂)₂]₂ (**5**), while reaction of Ti(NMe₂)₄ and **2H₂** or **3H₂** affords the mononuclear single helicate titanium amides (**2**)Ti(NMe₂)₂ (**6**) and (**3**)Ti(NMe₂)₂ (**7**), respectively. The single helicate titanium amides **6** and **7** have shown good catalytic activity for the polymerization of *rac*-lactide, while the double helicate titanium amide **5** has not. Further efforts will focus on the application of these chiral titanium complexes toward asymmetric reactions and the exploration of new group 4 complexes based on chiral ligands.

Acknowledgements

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Appendix A. Supplementary materials

CCDC 768355, 768356, 768357, and 768358 contain the supplementary crystallographic data for **5**, **6**, **7**, and **8**. These data

can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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