

Polymerization of ethylene and propene promoted by binaphthyl-bridged Schiff base complexes of titanium

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Received 19 April 2006; accepted 17 May 2006

Available online 10 July 2006

Abstract

Three new binaphthyl-bridged Schiff base complexes featuring different phenolate substituents (*meta*-Me, *ortho,para*-di-Cl, *ortho,para*-di-Br) were synthesized. ¹H and ¹³C NMR analyses indicated that the *cis*-β isomers are preferentially formed in any case. These complexes were tested as precatalysts for ethylene and propene polymerization comparing their behaviour to that of related titanium and zirconium complexes previously reported.

The beneficial effect on polymerization activity of halogen atoms in the *ortho, para* positions of the phenolate rings was also demonstrated. © 2006 Elsevier B.V. All rights reserved.

Keywords: Binaphthyl-bridged Schiff base; Ti(IV) complexes; Catalyst; Polymerization; Polyethylene (PE)

1. Introduction

Schiff base ligands played an important role in the development of coordination chemistry and they have been employed throughout the transition metal series. Metal complexes of these ligands are characterized by their facile synthesis, the accessibility of diverse structural modifications and the availability of chiral versions [1].

Several studies, focusing on the alkylation of Schiff base Group 4 halide complexes to afford viable olefin polymerization catalysts, have demonstrated that alkyl complexes of these ligands have a limited lifetime (highly affected by the reaction conditions, namely the solvent, the temperature and the nature of the alkylating agent). This has been traced to the fact that the imine unit(s) readily undergo inter- or intra-molecular reduction, i.e. 1,2-migratory insertion (1,2-MI) with metal-bound alkyl ligands [2], the imine nitrogen is so transformed into an anionic donor which coordinates to the metal occupying a potential polymerization site.

Jordan [3] demonstrated that 1,2-MI process can be slowed by lowering the electrophilicity and increasing the crowding of the imine carbons.

C₂-symmetric Zr complexes of biaryl-bridged *salen*-type ligands displaying non-planar coordination of the Schiff base were also reported to be inactive in ethylene polymerization in the presence of methylalumoxane (MAO) cocatalyst [4a]. As a matter of fact, introduction of a methyl group at the *meta* position of the phenolate ring (shielding the imine functionality) afforded a modified Zr complex which, activated by MAO, is moderately active in the polymerization of ethylene at room temperature [4].

We recently demonstrated the importance of the cocatalyst choice for this type of complexes. In fact the activation of a binaphthyl-bridged Schiff base dichloro zirconium complex for α-olefin polymerization has been achieved by several combinations of aluminium alkyls and MAO or boron compounds, while MAO alone was not able to generate a catalytic active species. We concluded that some aluminium alkyls are able to reduce the imine bonds, *in situ*, generating catalytic active species which have a binaphthyl-amine ligand [5].

In this paper we report four titanium complexes based on binaphthyl-bridged Schiff base ligands as precatalysts for ethylene and propene polymerization highlighting the effect on olefin

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polymerization activity of imine steric protection and of the introduction of halogen substituents on the phenolate rings.

2. Experimental

2.1. General remarks

All manipulations of air- and/or water-sensitive compounds were carried out under a dry nitrogen atmosphere using a Braun Labmaster drybox or standard Schlenk line techniques.

All solvents, purchased from Carlo Erba, were purified and dried by refluxing over an appropriate agent before use them. Toluene and hexane were firstly dried over calcium chloride and then distilled over sodium-benzophenone. Dichloromethane and acetonitrile were distilled over calcium hydride.

(*R,S*)-2,2'-diamino-1,1'-binaphthyl was purchased from Strem Chemicals, TiCl_4 , NEt_3 , MgCl_2 , $\text{Al}(\text{i-Bu})_3$, 3,5-dichlorosalicylaldehyde, 3,5-dibromosalicylaldehyde were bought from Aldrich Inc., $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ is a Boulder SPA Company product. NEt_3 was distilled over calcium hydride and the TiCl_4 over metallic copper.

Methylaluminoxane (MAO, Euricen) was purchased as a 10 wt.% solution in toluene and used as received. An amount of MAO solution was distilled under reduced pressure to remove the solvent and residual trimethylaluminium, providing a solid white powder (dried MAO).

Dichloromethane- d_2 and chloroform- d were distilled over calcium hydride.

Polymerization grade ethylene and propene (SON 99%) were used without further purification.

Molecular weight and molar mass distribution of polymers were measured by gel permeation chromatography (GPC). GPC measurements were carried out at 140 °C, using 1,2,4-trichlorobenzene as solvent and narrow MWD polystyrene standards as reference. The measurements were performed on PL-GPC210 with PL-Gel Mixed A Columns, RALLS detector (Precision Detector, PD2040 at 800 nm), H502 Viscometer (Viscotek), refractive detector and DM400 datamanger (Viscotek). Every value is the average of the two independent measurements.

Differential scanning calorimetry (DSC) measurements were carried out with a DSC 2920 TA instrument in a nitrogen flow by using a heating and cooling rate of 10 °C min^{-1} .

The ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance spectrometer at 400 and 100.6 MHz, respectively. Chemical shifts (δ in ppm) are referenced versus tetramethylsilane (TMS). ^{13}C NMR polymer spectra were recorded on an AM Bruker 62.5 MHz spectrometer in 1,1,2,2-tetrachloroethane- d_2 ($\text{C}_2\text{D}_2\text{Cl}_4$ at 100 °C) and reported relative to hexamethyldisiloxane (HMDS).

2.2. Syntheses

2.2.1. Synthesis of

3-tert-butyl-6-methyl-2-hydroxybenzaldehyde

Following literature procedures [6] this compound was obtained in 26% yield.

^1H NMR (CDCl_3): δ 12.72 (s, 1H, ArOH), 10.29 (s, 1H, HC=O), 7.37 (d, 1H, ArH), 6.64 (dd, 1H, ArH), 2.55 (s, 3H, Me), 1.40 (s, 9H, CMe_3).

2.2.2. Synthesis of H_2L^{1-4}

The Schiff base pro-ligands H_2L^{1-4} were prepared following literature procedures [7] by condensation of rac-*N,N'*-binaphthyldiamine and the appropriate salicylaldehyde: respectively, 3-tert-butylsalicylaldehyde (H_2L^1 in 90% yield), 3-tert-butyl-6-methyl-2-hydroxybenzaldehyde (H_2L^2 in 54% yield), 3,5-dichlorosalicylaldehyde (H_2L^3 in 75% yield) and 3,5-dibromosalicylaldehyde (H_2L^4 in 70% yield).

2.2.3. Synthesis of L^1TiCl_2

According to literature procedures [8], L^1TiCl_2 was obtained in a yield of 76%.

^1H NMR (CD_2Cl_2): *cis*- β - L^1TiCl_2 : δ 8.47 (s, 1H, N=CH), 8.21 (s, 1H, N=CH), 8.08 (d, 1H, $J=8.3$ Hz), 8.01 (d, 1H, $J=8.3$ Hz), 7.804 (d, 1H, $J=8.3$ Hz), 7.798 (d, 1H, $J=8.3$ Hz), 7.68 (dd, 1H, $J=7.4$ Hz, $J=1.7$ Hz), 7.67 (d, 1H, $J=8.3$ Hz), 7.47 (m, 4H), 7.33 (t, 1H, $J=7.4$ Hz), 7.22 (t, 1H, $J=7.4$ Hz), 7.18 (d, 1H, $J=8.3$ Hz), 7.10 (dd, 1H, $J=7.4$ Hz, $J=1.7$ Hz), 7.06 (d, 1H, $J=7.4$ Hz), 6.98 (d, 1H, $J=9.1$ Hz), 6.85 (t, 1H, $J=7.4$ Hz), 1.51 (s, 9H, *t-Bu*), 1.40 (s, 9H, *t-Bu*). A minor symmetric isomer is identified by eleven further resonances, some of which (in the aromatic region of the spectrum) are hidden by the signals of the more abundant species: δ 8.58 (s, 2H, N=CH), 1.53 (s, 18H, *t-Bu*).

^{13}C NMR (CD_2Cl_2): *cis*- β - L^1TiCl_2 : δ 168.01 (C=N), 167.83 (C=N), 163.91 (q), 163.10 (q), 149.65 (q), 149.40 (q), 137.65 (q), 137.16 (q), 134.67, 134.49, 133.24, 133.02 (q), 132.97 (q), 132.89, 132.74 (q), 130.42, 129.68, 129.10, 128.70, 127.72, 127.37, 127.27, 127.16, 126.89 (q), 126.77, 126.48, 126.29 (q), 125.35 (q), 124.68, 124.50 (q), 124.16, 122.51, 122.27, 35.53 (CMe_3), 35.52 (CMe_3), 30.04 (CMe_3), 29.99 (CMe_3). The quaternary carbons (which are indicated with q) were identified comparing the DEPT 45 data with the ^{13}C NMR spectrum. Minor isomer: δ 169.93 (C=N), 36.04 (CMe_3), 30.32 (CMe_3).

2.2.4. Synthesis of L^2TiCl_2

This compound was synthesized in an analogous manner to L^1TiCl_2 to give a red solid which was crystallized from toluene/hexane (0.440 g, yield = 73%).

^1H NMR (CD_2Cl_2): *cis*- β - L^2TiCl_2 : δ 8.66 (s, 1H, N=CH), 8.43 (s, 1H, N=CH), 8.07 (d, 1H, $J=11.6$ Hz), 8.01 (d, 1H, $J=10.4$ Hz), 7.79 (t, 2H, $J=7.6$ Hz), 7.71 (d, 1H, $J=11.2$ Hz), 7.53–7.16 (m, 7H), 6.98 (t, 2H, $J=7.2$ Hz), 6.84 (d, 1H, $J=10.8$ Hz), 6.62 (d, 1H, $J=8.8$ Hz), 2.37 (d, 3H, $J=8$ Hz, Me), 2.14 (d, 3H, $J=8$ Hz, Me), 1.51 (s, 9H, *t-Bu*), 1.40 (s, 9H, *t-Bu*).

^{13}C NMR (CD_2Cl_2): *cis*- β - L^2TiCl_2 : δ 165.16 (C=N), 164.79 (C=N), 164.43 (q), 163.46 (q), 150.09 (q), 149.90 (q), 140.40 (q), 135.14 (q), 134.68 (q), 134.16, 134.00, 133.04 (q), 132.97 (q), 132.87 (q), 132.80 (q), 130.23, 129.51 (q), 129.38, 129.09, 128.68, 127.71, 127.36, 127.10, 127.02, 126.74, 126.40, 125.77 (q), 125.72 (q), 125.58 (q), 124.90, 124.48(2C), 124.31, 123.09 (q), 36.03 (CMe_3), 35.26 (CMe_3), 30.19 (CMe_3), 30.14 (CMe_3), 19.95 (Me), 19.43 (Me).

The quaternary carbons (which are indicated with q) were identified comparing the DEPT 45 data with the ^{13}C NMR spectrum.

MS (EI): $m/z = 713$ ($\text{M}^+ - \text{Cl}$).

2.2.5. Synthesis of L^3TiCl_2

H_2L^3 (0.6 g, 0.95 mmol) suspended in tetrahydrofuran (30 cm^3) was left to react with a toluene (5 cm^3) solution of TiCl_4 (0.95 mmol), cooling the reaction mixture to 0 °C. The final red suspension was stirred overnight. Volatiles were removed under reduced pressure to afford a red solid. Then the isolated solid was recrystallized from CH_2Cl_2 /hexane (0.60 g, 0.80 mmol, yield = 83%).

^1H NMR (CD_2Cl_2 , -20 °C): *cis*- β - L^3TiCl_2 : δ 8.43 (s, 1H, N=CH), 8.23 (s, 1H, N=CH), 8.10–7.95 (m, 3H), 7.89–7.84 (dd, 2H), 7.71–7.69 (dd, 1H), 7.64 (d, 1H), 7.56–7.11 (m, 7H), 7.02 (d, 1H, $J = 8.5$ Hz), 6.96 (d, 1H, $J = 8.5$ Hz). A minor symmetric isomer is identified by further resonances: δ 8.59 (s, 2H, N=CH), 8.10–7.95 (m, 2 H), 7.71–7.69 (dd, 2H), 7.56–7.11 (m, 10H), 6.88 (d, 2H, $J = 9.0$ Hz).

^{13}C NMR (CD_2Cl_2 , -20 °C): *cis*- β - L^3TiCl_2 : δ 166.34 (N=C), 158.81, 158.76, 148.35, 148.18, 136.23, 136.13, 132.65. Minor isomer: δ 168.13 (N=C), 157.8, 147.26, 136.15, 133.10. The further resonances attributable to both the isomers are mixed; this makes difficult to distinguish them but the total number of the spectrum signals is that predicted.

MS (EI): $m/z = 711$ ($\text{M}^+ - \text{Cl}$); 676 ($\text{M}^+ - 2\text{Cl}$).

2.2.6. Synthesis of L^4TiCl_2

This compound was synthesized in an analogous manner to L^3TiCl_2 to give a red solid which was crystallized from CH_2Cl_2 /hexane (1.12 g, 1.21 mmol, yield = 98%).

^1H NMR (CD_2Cl_2 , -20 °C): *cis*- β - L^4TiCl_2 : δ 8.42 (s, 1H, N=CH), 8.22 (s, 1H, N=CH), 8.10–7.95 (m, 3H), 7.89–7.84 (dd, 2H), 7.66–7.63 (m, 1H), 7.54–7.11 (m, 8H), 7.01 (d, 1H, $J = 8.5$ Hz), 6.95 (d, 1H, $J = 8.5$ Hz). A minor symmetric isomer is identified by further resonances: δ 8.59 (s, 2H, N=CH), 8.10–7.95 (m, 2H), 7.66–7.63 (m, 2H), 7.56–7.11 (m, 10H), 6.88 (d, 2H, $J = 8.6$ Hz).

^{13}C NMR (CD_2Cl_2 , -20 °C): *cis*- β - L^4TiCl_2 : δ 167.03 (N=C), 166.9 (N=C), 160.8, 160.7, 148.9, 148.81, 142.64, 142.30, 136.81, 136.40, 133.54, 133.44, 132.9, 132.77, 130.73, 130.43, 115.41, 115.11, 112.44, 112.27. Minor isomer: δ 168.73 (N=C), 159.82, 147.85, 142.25, 133.81, 133.31, 131.65, 129.9, 114.43, 111.28. The further resonances attributable to both the isomers are mixed; this makes difficult to distinguish them but the total number of the spectrum signals is that predicted.

MS (EI): $m/z = 650$ ($\text{M}^+ - 3\text{Br} - \text{Cl}$), 534 ($\text{M}^+ - 4\text{Br} - 2\text{Cl}$).

2.3. X-ray crystallography

A suitable crystal of L^2TiCl_2 (0.2 mm \times 0.3 mm \times 0.5 mm) was selected and sealed in a Lindemann capillary under nitrogen atmosphere. Diffraction measurements were performed at room temperature on a Rigaku AFC7S diffractometer (graphite monochromated Mo $\text{K}\alpha$ radiation, $\lambda = 0.71069$ Å).

Diffraction intensities were collected within $4^\circ < 2\theta < 55^\circ$, using $\omega - 2\theta$ scan method. Data reduction was performed with the crystallographic package CrystalStructure [9]. Intensity data were corrected for Lorentz and polarization, absorption correction was applied by means of psi scan measurement, no decay correction was applied.

The structure was solved by direct methods using SIR92 [10] and refined on F^2 using SHELXL97 [11]. From the beginning a Fourier difference map showed the presence of a disordered solvent site. NMR measurements, performed by dissolving the measured crystals in deuterated chloroform, show the presence of both pentane and methylene chloride molecule respectively in a ratio of 0.78 and 0.22 with the Ti complex molecule.

Any effort to consider two separate pentane and methylene chloride molecules with appropriate occupancy gave unsatisfactory results. The contribution of the solvent was subtracted from the observed structure factor according to the SQUEEZE [12] procedure as implemented in PLATON [13].

Hydrogen atoms were positioned geometrically and refined using a riding model.

Anisotropic thermal factors were used for all non-hydrogen atoms except those belonging to the solvent molecule. A total of 460 refinable parameters were finally considered. Maximum and minimum residual density were respectively, 0.29 and $-0.32 \text{ e}\text{\AA}^{-3}$. Final disagreement indices: $R_1 = 0.057$ for 2539 reflections with $F_0 > 4\sigma(F_0)$, $wR_2 = 0.073$ for all 5626 data.

The correctness of the absolute structure was checked and the Flack parameter for the present enantiomer was 0.13(5).

Atomic coordinates, thermal factors, bond lengths and angles are provided as Supplementary material. ORTEP drawings performed by means of the program ORTEP32 [14].

2.4. Crystallographic data

Formula: $\text{C}_{44}\text{H}_{42}\text{Cl}_2\text{N}_2\text{O}_2\text{Ti}$, 0.22 CH_2Cl_2 , 0.78 C_5H_{12} , system: orthorhombic, space group: $\text{P}2_12_12_1$, $Z = 4$, $a = 16.672(3)$ Å, $b = 17.246(5)$ Å, $c = 15.441(4)$ Å, $V = 4440(2)$ Å 3 .

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 604536.¹

2.5. Polymerization procedure

The polymerization runs were performed in a magnetically stirred glass reactor (100 cm^3) except for propene polymerizations which were carried out into a 500 mL Büchi glass autoclave. The reaction vessels were charged under nitrogen sequentially with toluene, MAO or the proper trialkylaluminium and a toluene solution of the precatalyst. The precatalyst was pre-treated with the aluminium alkyl compound (Al:Ti = 20) for 10 min at room temperature. The stirred mixture was ther-

¹ Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk].

mostated at the required polymerization temperature and the monomer gas feed was started, then the activator (either MAO or a boron ionizing agent) was added. After the prescribed time the polymerization mixture was poured into acidified ethanol. The precipitated polymer was recovered by filtration, dried (80 °C, vacuum oven, overnight) and weighed. The main polymerization conditions and results are reported in Tables 2 and 3.

2.6. Hydrolysis experiments

AlⁱBu₃ (20 equiv.) were poured into a stirred solution of complexes L^{1–4}TiCl₂ (15 μmol) in toluene (5 mL). The red mixture was stirred for 10 min then 5 mL of water were added. After extraction with methylene chloride, the organic fractions were collected together and dried over anhydrous Na₂SO₄. Volatiles were removed under reduced pressure to yield a white product.

NMR spectra interpretation supports the formation of *N,N'*-bis(2-hydroxy-3,5-diterbutylbenzyl)[1,1'-binaphthalene]-2,2'-diamine (amine ligand) as the only product for L¹TiCl₂, in the case of L^{2–4}TiCl₂ there are also NMR resonances attributable to the imine ligand.

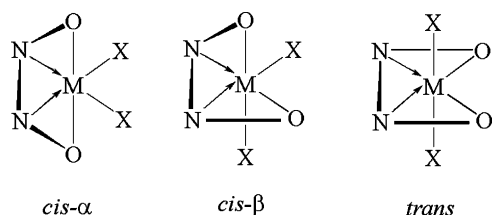
Analogous experiments were carried out using dried MAO (500 equiv.) instead of Al(*i*-Bu)₃. The predominant products were the imine ligand for all the complexes.

3. Results and discussion

3.1. Synthesis and characterization of the complexes

In this paper we report the synthesis of four binaphthyl-bridged titanium complexes and their catalytic behaviour in olefin polymerization. As previously reported, binaphthyl-based Schiff base ligands can wrap around an octahedron according to three different configurations (Scheme 1) and the presence of the binaphthyl bridge should be able to hamper the formation of the *trans* stereoisomer, which is not expected to afford a polymerization catalyst.

The pro-ligand *rac*-H₂L¹ was synthesized using a literature procedure by condensation of *rac*-*N,N'*-binaphthyl diamine and 3-*tert*-butyl-2-hydroxybenzaldehyde [7]. The direct reaction of TiCl₄ with this pro-ligand in toluene at 0 °C gave L¹TiCl₂ (Fig. 1), after the appropriate work up, as a red microcrystalline powder in 76% yield. As reported in a previous paper [8], L¹TiCl₂ exists in methylene chloride solution as a mixture of the *cis*-β and a symmetric isomer (*cis*-α or *trans*) in 9:1 molar ratio.



Scheme 1. Structural classes of quadridentate Schiff base octahedral complexes.

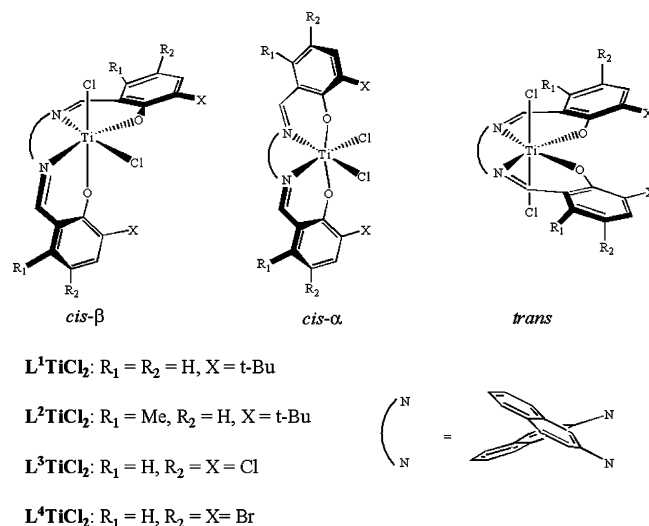


Fig. 1. Possible geometric isomers for complexes L^{1–4}TiCl₂.

Pro-ligand *rac*-H₂L² was synthesized similarly by condensation of 3-*tert*-butyl-6-methyl-2-hydroxybenzaldehyde [6] and the *rac*-*N,N'*-binaphthyl diamine. The corresponding titanium complex L²TiCl₂ (Fig. 1) was isolated in the same fashion as L¹TiCl₂ in 73% yield. ¹H and ¹³C NMR spectra support the presence of two isomers, the C₁-symmetric *cis*-β and either the C₂-symmetric *cis*-α or the C_{2v}-symmetric *trans*. The ¹H NMR spectrum of the mixture exhibits an asymmetric pattern for the more abundant *cis*-β isomer consisting of two singlets assignable to the two imine protons, four singlets in the aliphatic region for the two *tert*-butyl groups and the two methyl, and accordingly sixteen signals in the aromatic region. Simultaneously there is a symmetric pattern attributable either to the *cis*-α or to the *trans* isomer, it consists of one peak for each kind of proton. ¹³C NMR spectrum analysis led us to the same conclusions. The molar ratio for the different isomers is 20:1 (*cis*-β: *cis*-α or *trans*).

Single crystals suitable for X-ray analysis were obtained by crystallization from methylene chloride/pentane solution of L²TiCl₂. The molecular structures of compound L²TiCl₂ is shown in Fig. 2, selected bond lengths and angles are given in Table 1.

The coordination environment of the Ti atom is a distorted octahedral with two *cis* chlorine atoms and two nitrogen atoms

Table 1
Selected bond distances (Å) and angles (°) for L²TiCl₂ and L¹TiCl₂

	L ² TiCl ₂	L ¹ TiCl ₂
Ti–O1	1.811(4)	1.832(6)
Ti–O2	1.838(4)	1.840(5)
Ti–N2	2.161(5)	2.170(7)
Ti–N1	2.211(5)	2.206(7)
Ti–Cl1	2.307(2)	2.300(3)
Ti–Cl2	2.340(2)	2.336(3)
N1–C1	1.299(7)	1.312(10)
N2–C13/N2–C12	1.318(7)	1.276(9)
O1–Ti–O2	97.4(2)	101.0(2)
Cl1–Ti–Cl2	91.49(8)	91.56(11)
N1–Ti–N2	83.3(2)	81.8(3)

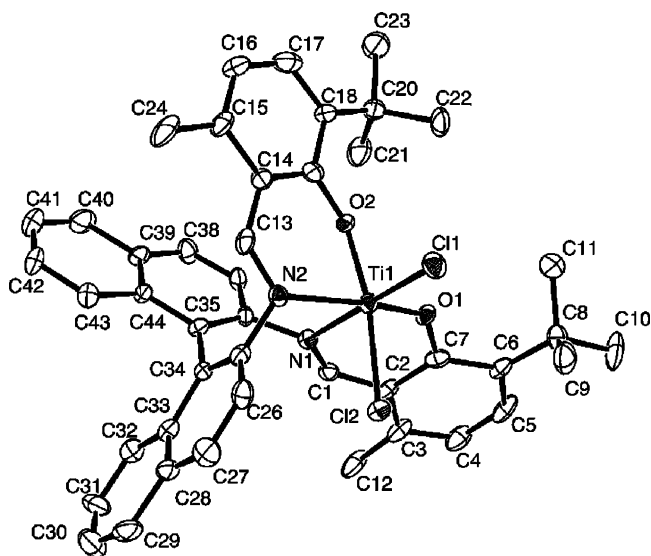


Fig. 2. Molecular structure of compound L^2TiCl_2 . Thermal ellipsoids are drawn at 20% probability level. Hydrogen atoms have been omitted for clarity.

in the equatorial plane, confirming that the asymmetric *cis*- β isomer is obtained by crystallization. The naphthyl rings result to be planar within a RMSD of 0.019 and 0.044 Å, respectively, the dihedral angle is 73.3(1)°. The two phenoxy rings (RMSD 0.011 and 0.020 Å) are *cis* to each other with a dihedral angle of 63.6(2)°.

The same configuration has been observed in the structure of L^1TiCl_2 [8]. Notably the binaphthyl moiety displays a certain degree of flexibility in forming complex with metal ions, comparing the present value with that obtained for L^1TiCl_2 (65.1(2)°).

L^3TiCl_2 and L^4TiCl_2 , bearing *ortho* halogen substituents on the phenoxy moiety, were obtained as red solids in high yields (see Section 2 for procedure details). 1H NMR spectra of complexes L^3TiCl_2 and L^4TiCl_2 , recorded at room temperature,

show broad signals for all the protons indicating a dynamic character of these complexes. The 1H and ^{13}C NMR spectra, recorded at 253 K, consisted of sharp resonances, indicating the presence of two isomers in methylene chloride solution (molar ratio for the different isomers is 3:1 β -*cis*: α -*cis* or *trans*) for both L^3TiCl_2 and L^4TiCl_2 .

3.2. Polymerization of ethylene and propene catalyzed by $L^{1-4}TiCl_2$

Complexes $L^{1-4}TiCl_2$ were tested as precatalysts for ethylene and propene polymerization.

Using L^1TiCl_2 and a 10 wt.% MAO solution in toluene or dried MAO (obtained by distilling off, under reduced pressure, a sample of MAO solution to remove the solvent and residual trimethylaluminum) as cocatalyst does not yield an active ethylene polymerization catalyst (see Table 2, runs 1 and 2), in agreement with previous results reported for similar biaryl-bridged *salen* titanium complexes [4]. In the same way, activation of L^2TiCl_2 with a 10 wt.% MAO solution in toluene (run 5) gave no ethylene polymerization activity while use of dried MAO resulted in a fair activity (run 6). Upon activation with dried MAO L^3TiCl_2 and L^4TiCl_2 showed a behaviour similar to L^1TiCl_2 (cf. runs 2, 9 and 13 in Table 2). As reported in the literature for similar complexes, L^1TiCl_2 , L^3TiCl_2 and L^4TiCl_2 in the presence of aluminum alkyls can easily undergo alkyl migration to the imine carbon resulting in poor or no catalytic activity. On the contrary L^2TiCl_2 exhibits some activity (run 6), owing to the imine steric protection of the methyl groups at the *meta* position of the phenolate rings.

In a previous study concerning a zirconium complex bearing the ligand L^1 we reported that the performances in olefin polymerization are significantly enhanced when an alkylating agent such as $Al(i-Bu)_3$ is used as cocatalyst together with either $Ph_3CB(C_6F_5)_4$ or MAO [5]. Keeping in mind these results we

Table 2
Ethylene polymerization conditions and results

Run No.	Precatalyst	Cocatalyst	Al/Ti	Time (min)	Yield (g)	T_m (°C)	$M_w/10^3$	M_w/M_n
1	L^1TiCl_2	MAO	500	120	–	–	–	–
2	L^1TiCl_2	MAO ^a	500	120	Trace	–	–	–
3	L^1TiCl_2	$Al(i-Bu)_3/Ph_3CB(C_6F_5)_4$	100	120	0.33	140.0	760	4.7
4	L^1TiCl_2	$Al(i-Bu)_3/MAO^{*a}$	600 ^b	120	0.08	–	450	7.5
5	L^2TiCl_2	MAO	500	120	–	–	–	–
6	L^2TiCl_2	MAO ^a	500	120	0.11	137.2	1010	4.2
7	L^2TiCl_2	$Al(i-Bu)_3/Ph_3CB(C_6F_5)_4$	100	120	0.14	140.0	1120	10.2
8	L^2TiCl_2	$Al(i-Bu)_3/MAO^{*a}$	600 ^b	120	0.08	136.4	1040	6.8
9	L^3TiCl_2	MAO ^a	500	10	Trace	–	–	–
10	L^3TiCl_2	$Al(i-Bu)_3/Ph_3CB(C_6F_5)_4$	100	10	0.15	–	n.e.	–
11	L^3TiCl_2	$Al(i-Bu)_3/MAO^{*a}$	600 ^b	10	0.09	–	n.e.	–
12	L^3TiCl_2	$Al(i-Bu)_3/Ph_3CB(C_6F_5)_4$	20	10	200.06	–	612	9.7
13	L^4TiCl_2	MAO ^a	500	10	Trace	–	–	–
14	L^4TiCl_2	$Al(i-Bu)_3/Ph_3CB(C_6F_5)_4$	100	10	0.35	–	n.e.	–
15	L^4TiCl_2	$Al(i-Bu)_3/MAO^{*a}$	600 ^b	10	0.2	–	n.e.	–
16	L^4TiCl_2	$Al(i-Bu)_3/Ph_3CB(C_6F_5)_4$	20	10	0.36	–	372	2.4

General polymerization conditions: precatalyst = 15 μ mol; toluene = 50 mL; $[B]/[Ti] = 2$; ethylene pressure = 1 atm; temperature = 25 °C.

^a Dried MAO obtained by distilling off the solvent by the commercial solution.

^b (Al in MAO)/Ti = 500.

tested complexes $L^{1-4}TiCl_2$ under the above mentioned activation conditions.

In these conditions, L^1TiCl_2 showed a productivity three times larger than that obtained with L^2TiCl_2 (runs 3 and 7). L^2TiCl_2 , instead, showed a similar activity with both dried MAO and $Al(i-Bu)_3/Ph_3CB(C_6F_5)_4$ as cocatalysts (runs 6 and 7).

Gratifyingly, under the same polymerization conditions, L^3TiCl_2 and above all L^4TiCl_2 afforded an enhanced polymerization activity, respectively, ~ 60 g PE (mmol Ti h atm) $^{-1}$ and ~ 140 g PE (mmol Ti h atm) $^{-1}$ versus 11 g PE (mmol Ti h atm) $^{-1}$ observed for L^1TiCl_2 , see Table 2 runs 10, 14 and 3.

This finding suggests that the presence of electron-withdrawing groups on the phenolate rings leads to an increase in ethylene polymerization activity, in agreement with results previously reported by Kol in the case of Group 4 complexes of diamine bis-(phenolate) ligands [15].

The cocatalytic system $Al(i-Bu)_3$ /dried MAO resulted in less activity than $Al(i-Bu)_3/Ph_3CB(C_6F_5)_4$ for all the complexes (runs 4, 8, 11 and 15 versus runs 3, 7, 10 and 14).

All ethylene polymerization runs yielded linear polyethylene which had melting points in the range 134–140 °C.

In all cases, polymers with a broad molecular weight distribution were produced, suggesting the possible formation of more than one catalytic active species, following the reduction *in situ* of the imine functionalities. L^2TiCl_2 gave polymer samples with

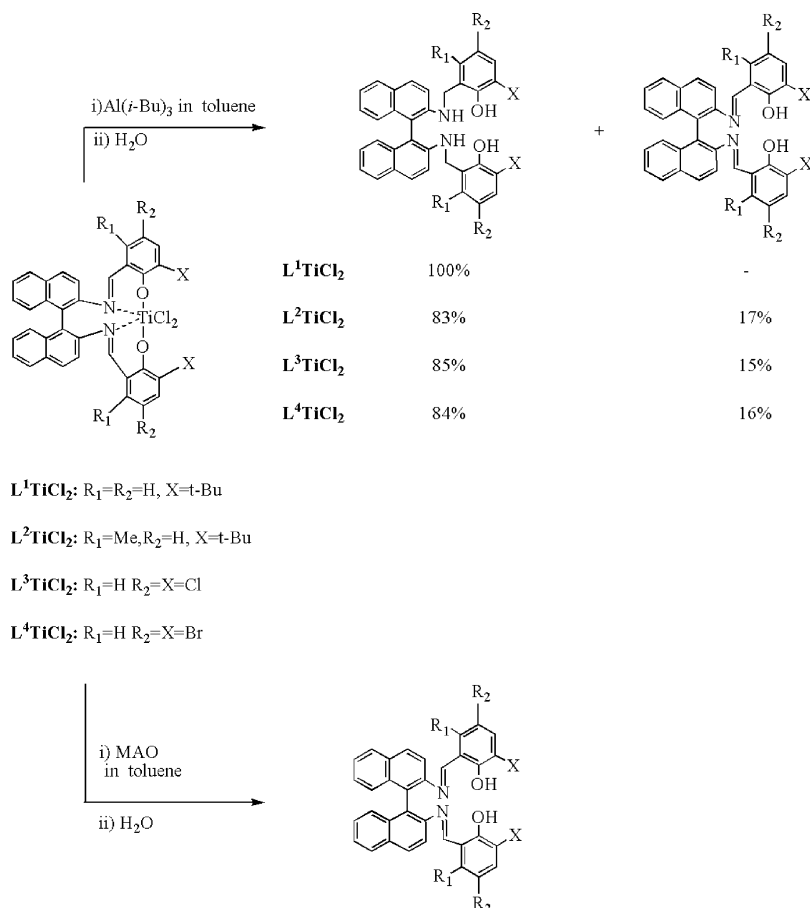
very high molecular weights and also higher than those obtained using L^1TiCl_2 . This could be due to a lower chain transfer rate for active species formed from L^2TiCl_2 owing to its increased encumbering.

Ethylene polymerization experiments were carried out at a lower Al/Ti ratio, considering the well known chain transfer ability of $Al(i-Bu)_3$. In these conditions both L^3TiCl_2 and L^4TiCl_2 , the most active precatalysts, provided polyethylenes with high molecular weight values ($M_w = 370,000$ – $610,000$) but still broad MWD's (Table 2 runs 12 and 16).

^{13}C NMR analyses indicated that the polyethylenes are linear with virtually no branching.

In order to gain further information on the different performance of $L^{1-4}TiCl_2$ as a result of using MAO and $Al(i-Bu)_3/Ph_3CB(C_6F_5)_4$ as cocatalysts, we carried out some hydrolysis experiments on the polymerization mixtures.

As we previously showed for a related zirconium complex [5] the imine functionality of this class of catalysts can be reduced *in situ* by $Al(i-Bu)_3$ to amine-donors leading to diamine bis-(phenolate) complexes while MAO is not able to perform the same reduction. The same observations were reported by Fujita in the case of phenoxyimine Group 4 catalysts [16]. Similar experiments were performed on the complexes $L^{1-4}TiCl_2$ (see Section 2 for further details). When L^1TiCl_2 was treated with $Al(i-Bu)_3$ in toluene, followed by the addition of water,



Scheme 2. Reaction with different cocatalysts and hydrolysis of $L^{1-4}TiCl_2$.

Table 3
Propene polymerization conditions and results

Run No.	Precatalyst	Cocatalyst	Al/Ti	Yield (g)	$M_w/10^3$	M_w/M_n
17	L^1TiCl_2	MAO* ^a	500	Trace	–	
18	L^1TiCl_2	Al(i-Bu) ₃ /Ph ₃ CB(C ₆ F ₅) ₄	100	0.04	n.e.	
19	L^1TiCl_2	Al(i-Bu) ₃ /MAO*	600 ^b	0.18	n.e.	
20	L^4TiCl_2	MAO* ^a	500	Trace	–	
21	L^4TiCl_2 ^c	Al(i-Bu) ₃ /Ph ₃ CB(C ₆ F ₅) ₄	20	0.20	446	36
22	L^4TiCl_2 ^{c,d}	Al(i-Bu) ₃ /Ph ₃ CB(C ₆ F ₅) ₄	20	0.40	450	68
23	L^2TiCl_2	MAO*	100	0.05	n.e.	
24	L^2TiCl_2	Al(i-Bu) ₃ /MAO*	600 ^b	0.06	n.e.	
25	L^2TiCl_2	Al(i-Bu) ₃ /Ph ₃ CB(C ₆ F ₅) ₄	100	Trace	–	

General conditions: toluene = 100 mL; precatalyst = 30 μ mol; [B]/[Ti] = 2; propene pressure = 6 atm; reaction time = 2 h; temperature = 25 °C.

^a Dried MAO obtained by distilling off the solvent by the commercial solution.

^b (Al in MAO)/Ti = 500.

^c Toluene = 75 mL; precatalyst = 50 μ mol; reaction time = 5 h.

^d T = 70 °C.

N,N'-bis(2-hydroxy-3-*tert*-butylbenzyl)[1,1'-binaphthalene]-2,2'-diamine (amine ligand) was exclusively obtained. In the case of L^2TiCl_2 the same experiment led to a mixture of imine and amine ligands (molar ratio amine:imine ligands = 5:1, calculated by NMR). In these conditions L^2TiCl_2 was not completely reduced probably due to a steric protection by methyl substituents at the *meta* position of the aromatic rings. L^3TiCl_2 and L^4TiCl_2 resulted in a behaviour very similar to L^2TiCl_2 , suggesting the hypothesis of an imine steric protection operated, in this case, by *para*-chloro or -bromo phenolate substituents.

Instead treatment of complexes $L^{1-4}TiCl_2$ with MAO, followed by addition of water, gave imine ligands as major products in all cases, no NMR resonances attributable to amine ligands were revealed (see Scheme 2).

$L^{1-4}TiCl_2$ were subsequently tested for propene polymerization using different cocatalytic systems.

As previously found for other salen type and phenoxyimine complexes, propene polymerization activity is lower than that of ethylene for all the synthesized complexes. As observed for ethylene polymerization, activation of $L^{1,4}TiCl_2$ with dried MAO yielded an inactive system (Table 3, runs 17 and 20), while use of either Al(i-Bu)₃/Ph₃CB(C₆F₅)₄ or Al(i-Bu)₃/dried MAO resulted in some activity (runs 18, 19 and 21). L^4TiCl_2 was found to be fairly active also at a temperature higher than room temperature (run 22).

L^2TiCl_2 demonstrated comparable activities both using dried MAO and Al(i-Bu)₃/dried MAO as activators, while it was found to be inactive upon activation with Al(i-Bu)₃/Ph₃CB(C₆F₅)₄ (runs 23, 24 and 25).

¹³C NMR analysis revealed that L^1TiCl_2 and L^4TiCl_2 gave very similar polymers ([*mm*]:[*mr*]:[*rr*] \approx 43:34:23, run 19 and [*mm*]:[*mr*]:[*rr*] \approx 34:39:27, run 21), however, in both cases a high content of *mmmm* sequences was observed (22%, run 19 and 17%, run 21). The raw polymers were fractionated by stirring in hexane at room temperature. The insoluble fractions (ca. 10 wt.%) were analyzed by ¹³C NMR showing a highly isotactic and regioregular microstructure ([*mm*] = 95%). The hexane soluble fractions (ca. 90 wt.%) resulted in highly stereo- and regio-irregular polypropylenes.

In the case of propene polymerization promoted by L^4TiCl_2 increasing the polymerization temperature slightly increases the yield (cf. runs 21 and 22), and the microstructure remains substantially unchanged ([*mm*]:[*mr*]:[*rr*] \approx 37:36:27). The crude polypropylene was fractionated by stirring in hexane at room temperature showing a composition very similar to that of the above discussed polypropylene (run 21).

On the contrary, L^2TiCl_2 activated by Al(i-Bu)₃/dried MAO produced an isotactic polymer (run 25, see the spectrum in Fig. 3), triad analysis of this sample is [*mm*]:[*mr*]:[*rr*] \approx 75:20:5 (the *rr* triad contents was evaluated by neglecting the regioinversions [17]) with \approx 10% of regioinversions. The methyl region showed only a single peak (*mmmm* pentad) at 19.74 ppm and three very weak resonances at 19.47, 18.94 and 17.70 ppm (*mmmr*, *mmrr* and *mrrm* pentads, respectively) from hexamethyldisiloxane (HMDS), in approximately 2:2:1 ratio. This microstructure is that expected of an *enantiomorphic-site* mechanism of steric control.

The different behaviour of $L^{1,4}TiCl_2$ and L^2TiCl_2 could be ascribed to the different reactivity of Al(i-Bu)₃ versus the imine moiety in the three complexes.

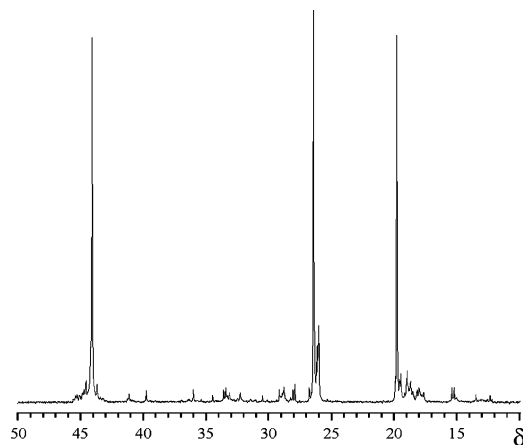


Fig. 3. The 62.5 MHz ¹³C NMR spectrum (C₂D₂Cl₄, 100 °C) of a polypropylene sample prepared with L^2TiCl_2 /Al(i-Bu)₃/dried MAO (run 24). δ in ppm from hexamethyldisiloxane.

One could hypothesize that the *salen* complexes are able to afford isotactic-specific polymerization, while the *salan* complexes are not stereospecific.

4. Conclusions

Three new binaphthyl-bridged Schiff base complexes of titanium ($L^{2-4}TiCl_2$) have been synthesized, characterized and tested as precatalysts for ethylene and propene polymerization.

As previously reported for a similar zirconium complex [4a], replacement of H atoms with Me groups in the *meta* position of the phenolate rings leads to an imine steric protection towards the alkyl migration from the metal to the imino carbon resulting in a catalytically active complex (L^2TiCl_2) for ethylene polymerization both using MAO and $Al(i-Bu)_3/Ph_3CB(C_6F_5)_4$ as activators.

On the other hand $L^{1,3,4}TiCl_2$, bearing H atoms in *meta* positions of the phenolate rings, need a pre-treatment with $Al(i-Bu)_3$ to result in reasonable polymerization activity. $Al(i-Bu)_3$ or aluminum hydride compounds, contaminants in $Al(i-Bu)_3$, work as reducing agent affording diamine bis-(phenolate) complexes which are the true catalytic species, as confirmed by hydrolysis experiments.

Moreover, a positive effect of *ortho,para*-phenolate halides on polymerization activity of the corresponding complexes $L^{3,4}TiCl_2$ has been demonstrated.

Polymerization of propene resulted in the production of an isotactic polymer in the case of L^2TiCl_2 , and of substantially atactic samples in the case of $L^{1,4}TiCl_2$ suggesting that *salen* complexes are able to afford isotactic-specific polymerization, while the *salan* complexes are not stereospecific.

Acknowledgement

This work was supported by the Italian Ministry of Education (MIUR), PRIN 2004.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2006.05.046.

References

- [1] (a) U. Knof, A. von Zelewsky, *Angew. Chem. Int. Ed.* 38 (1999) 302–322;
(b) P.D. Knight, P. Scott, *Coord. Chem. Rev.* 242 (2003) 125–143.
- [2] C. Floriani, E. Solari, F. Corazza, A. Chiesi-Villa, C. Guastini, *Angew. Chem. Int. Ed. Engl.* 28 (1) (1989) 64–66.
- [3] E.B. Tjaden, D.C. Swenson, R.F. Jordan, *Organometallics* 14 (1995) 371–386.
- [4] (a) P.D. Knight, A.J. Clarke, B.S. Kimberley, R.A. Jackson, P. Scott, *Chem. Commun.* (2002) 352–353;
(b) P.D. Knight, G. Clarkson, M.L. Hammond, B.S. Kimberley, P. Scott, *J. Organomet. Chem.* 690 (2005) 5125–5144.
- [5] M. Lamberti, M. Consolmagno, M. Mazzeo, C. Pellicchia, *Macromol. Rapid Commun.* 26 (2005) 1866–1871.
- [6] N.U. Hofsløkken, L. Skattebøl, *Acta Chem. Scand.* 53 (1999) 258–262.
- [7] (a) G. Zhou, J.-S. Huang, P.-H. Ko, K.-K. Cheung, C.-M. Che, *J. Chem. Soc., Dalton Trans.* (1999) 3303–3309;
(b) K. Da Silva Bernardo, A. Robert, F. Dahan, B. Meunier, *New J. Chem.* 19 (1995) 129–131.
- [8] A. Soriente, M. De Rosa, M. Lamberti, C. Tedesco, A. Scettri, C. Pellicchia, *J. Mol. Catal. A: Chem.* 235 (2005) 253–259.
- [9] Crystal Structure, Molecular Structure Corporation & Rigaku Corporation. (2001). Crystal-Structure. Version 2.00. MSC, 9009 New Trails Drive, The Woodlands, TX77381-5209, USA, and Rigaku Corporation, Akishima, Tokyo 196-8666, Japan.
- [10] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, *J. Appl. Cryst.* 27 (1994) 435–436.
- [11] G.M. Sheldrick, A Program for Refining Crystal Structures, University of Göttingen, Germany, 1997 (SHELXL97).
- [12] P. van der Sluis, A.L. Speck, *Acta Crystallogr. A* 46 (1990) 194–201.
- [13] A.L. Speck, *Acta Crystallogr. A* 46 (1990) C34.
- [14] L.J. Farrugia, *J. Appl. Cryst.* 30 (1997) 565–566.
- [15] S. Segal, I. Goldberg, M. Kol, *Organometallics* 24 (2005) 200–202.
- [16] S. Matsui, M. Mitani, J. Saito, Y. Tohi, H. Makio, N. Matsukawa, Y. Takagi, K. Tsuru, M. Nitabaru, T. Nakano, H. Tanaka, N. Kashiwa, T. Fujita, *J. Am. Chem. Soc.* 123 (2001) 6847–6856.
- [17] C. Pellicchia, A. Zambelli, M. Mazzeo, D. Pappalardo, *J. Mol. Catal. A: Chem.* 128 (1998) 229–237.