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

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## Abstract

Three new binaphthyl-bridged Schiff base complexes featuring different phenolate substituents (*meta*-Me, *ortho*,*para*-di-Cl, *ortho*,*para*-di-Br) were synthesized. $^{1}$H and $^{13}$C 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.

*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.

$C_2$-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. Dichlorometane and acetonitrile were distilled over calcium hydride.

(*R*,*S*)-2,2′-diamino-1,1′-binaphthyl was purchased from Strem Chemicals, $TiCl_4$, $NEt_3$, $MgCl_2$, $Al(i\text{-}Bu)_3$, 3,5-dichlorosalicylaldehyde, 3,5-dibromosalicylaldehyde were bought from Aldrich Inc., $Ph_3CB(C_6F_5)_4$ 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).

Dichlorometane-$d_2$ 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 ($\delta$ 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-$d_2$ ($C_2D_2Cl_4$ 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 ($CDCl_3$): $\delta$ 12.72 (s, 1H, ArO*H*), 10.29 (s, 1H, *H*C=O), 7.37 (d, 1H, Ar*H*), 6.64 (dd, 1H, Ar*H*), 2.55 (s, 3H, *Me*), 1.40 (s, 9H, C*Me*$_3$).

#### 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-$L^1TiCl_2$: $\delta$ 8.47 (s, 1H, N=C*H*), 8.21 (s, 1H, N=C*H*), 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: $\delta$ 8.58 (s, 2H, N=C*H*), 1.53 (s, 18H, *t-Bu*).

$^{13}C$ NMR ($CD_2Cl_2$): *cis*-β-$L^1TiCl_2$: $\delta$ 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 (*C*Me$_3$), 35.52 (*C*Me$_3$), 30.04 (C*Me*$_3$), 29.99 (C*Me*$_3$). The quaternary carbons (which are indicated with q) were identified comparing the DEPT 45 data with the $^{13}C$ NMR spectrum. Minor isomer: $\delta$ 169.93 (C=N), 36.04 (*C*Me$_3$), 30.32 (C*Me*$_3$).

#### 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-$L^2TiCl_2$: $\delta$ 8.66 (s, 1H, N=C*H*), 8.43 (s, 1H, N=C*H*), 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-$L^2TiCl_2$: $\delta$ 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 (*C*Me$_3$), 35.26 (*C*Me$_3$), 30.19 (C*Me*$_3$), 30.14 (C*Me*$_3$), 19.95 (*Me*), 19.43 (*Me*).