



Synthesis and olefin polymerization activity of (quinolin-8-ylamino)phenolate and (quinolin-8-ylamido)phenolate Group 4 metal complexes

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ABSTRACT

New Zr and Hf complexes bearing either a tridentate monoanionic 2-*tert*-butyl-6-[(quinolin-8-ylamino)methyl]phenolate [N,N,O⁻] or a dianionic 2-*tert*-butyl-6-[(quinolin-8-ylamido)methyl]phenolate [N,N⁻,O⁻] ligand have been synthesized and characterized. The geometries of the zirconium complexes have been studied using DFT methods. The complexes were tested as catalysts in the polymerization of ethylene and α -olefins after activation with methylalumoxane, resulting in the production, with moderate activities, of high molecular weight linear polyethylene and prevalently isotactic polypropylene, poly(1-butene), poly(1-pentene) and poly(1-hexene). The content of isotactic pentads of these poly(α -olefins) increases while the size of the monomer increases, ranging between 50% for polypropylene and 99% for poly(1-hexene).

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1. Introduction

Group 4 metallocenes are highly successful catalysts for homogeneous olefin polymerization [1]. In the last years, however, research has been directed also toward the synthesis of new monocyclopentadienyl (CGC) and cyclopentadienyl-free derivatives [2]. The design of new non-metallocene catalysts thus remains a topic of interest in both academic and industrial research. In particular, in the last years a large variety of polydentate ligands with nitrogen and/or oxygen donors has been explored, including amidinate [3], α -diimine [4], phenoxyimine [5], pyrrolidimine [6], heteroscorpionates [7], diaminebis(phenolate) [8], amino-iminobis(phenolate) [9], iminopyridine [10] and pyridylamido ligands [11].

In this framework, we have recently reported the synthesis of Group 4 metal complexes bearing monoanionic (quinolinylimino)methylphenolate [N,N,O⁻] [12] or dianionic anilidomethylpyridylpyrrolide [N,N,N⁻] [13] tridentate ligands. While the former were octahedral complexes of formula [N,N,O]MX₃ and afforded poorly active and poorly stereospecific catalysts for the polymerization of α -olefins, the latter were pentacoordinate square-pyramidal complexes of formula [N,N,N]MX₂

and afforded highly active and highly stereospecific catalysts, e.g. producing polypropylenes with up to 95% mmmm pentad content and MW's up to 1 million da.

With the aim to investigate the catalytic performance of related pentacoordinate [N,N,O]MX₂ complexes, we have synthesized the tridentate monoanionic 2-*tert*-butyl-6-[(quinolin-8-ylamino)methyl]phenolate ligand and the dianionic 2-*tert*-butyl-6-[(quinolin-8-ylamido)methyl]phenolate ligand and the corresponding [N,N,O]MCl₃ and [N,N,O]MCl₂ (M = Zr, Hf) complexes. We report here the results concerning the characterization and the performance of these complexes in the polymerization of ethylene and α -olefins.

2. Experimental

2.1. Materials and methods

All inorganic manipulations were carried out under oxygen- and moisture-free atmosphere in a Braun MB 200 G-II glove-box. All reaction solvents were thoroughly deoxygenated and dehydrated following common procedures [14], while NMR solvents (Euriso-Top products) were kept in the dark over molecular sieves. 1-pentene and 1-hexene (Aldrich) were distilled over calcium hydride. ZrCl₄(THF)₂ and HfCl₄(THF)₂, 8-aminoquinoline, 3-*tert*-butyl-2-hydroxybenzaldehyde, potassium *tert*-butoxide, lithium aluminium hydride (1M solution in THF), AlⁱBu₃ and butyllithium (1.6M solution in hexanes) (Aldrich products) were

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used as received. $B(C_6F_5)_3$ is a Boulder SPA Company product. 2-*tert*-butyl-6-[(quinolin-8-ylimino)methyl]phenol (qimph^H) was prepared on the basis of a reported procedure [12], by reacting 8-aminoquinoline and 3-*tert*-butyl-2-hydroxybenzaldehyde in methanol in the presence of anhydrous Na_2SO_4 and molecular sieves. 2-*tert*-butyl-6-[(quinolin-8-ylamino)methyl]phenol (qamph^H) was synthesized as reported in a previous paper [15], by reacting qimph^H with $LiAlH_4$ in THF at low temperature.

Polymerization grade ethylene, propene and 1-butene (SON 99%) were used without further purification.

Microanalyses were performed at the Istituto di Chimica Inorganica e delle Superfici, CNR, Padova. 1H NMR, ^{13}C { 1H } NMR, COSY, NOESY and HSQC spectra were recorded at 298 K on a Bruker Avance 300 spectrometer operating at 300 MHz (1H) and 75 MHz (^{13}C) and referred to internal tetramethylsilane. ^{13}C NMR polymer spectra were recorded on a Bruker Avance 300 spectrometer at 75 MHz in 1,1,2,2-tetrachloroethane- d_2 ($C_2D_2Cl_4$, TCDE) at 90 °C and referenced against hexamethyldisiloxane (HMDS).

Methylaluminoxane (MAO, Euricen) was purchased as a 10 wt% solution in toluene. The solvent and residual trimethylaluminium of the commercial MAO solution were removed under reduced pressure to provide a solid white powder (MAO(s)).

The molecular weight and molar mass distribution of polymers were measured by gel permeation chromatography (GPC) at 135 °C by a Waters instrument GPCV 2000 equipped with refractive index and viscometer detectors, using a set consisting of four PSS columns: 10^5 , 10^4 , 10^3 , 10^2 Å (pore size) with 10 mm (particle size). *o*-Dichlorobenzene was the carrier solvent used with a flow rate of $1.0 mL \cdot min^{-1}$. The calibration curve was established with polystyrene standards.

2.2. Synthesis of $[ZrCl_3(qamph)]$ (**1**) ($C_{20}H_{21}Cl_3N_2OZr$, $M_W = 502.98$) and $[HfCl_3(qamph)]$ (**2**) ($C_{20}H_{21}Cl_3HfN_2O$, $M_W = 590.24$)

To a solution of the ligand qamph^H (0.460 g, 1.5 mmol) in THF (25 mL) a stoichiometric amount of solid potassium *tert*-butoxide (0.168 g, 1.5 mmol) was slowly added at room temperature. After 15 min under magnetic stirring the resulting solution was added drop by drop to a solution containing 1.5 mmol of $ZrCl_4(THF)_2$ (0.566 g) or $HfCl_4(THF)_2$ (0.698 g) in 10 mL of THF. The reaction mixture was allowed to react overnight at room temperature. After elimination by centrifugation of the KCl formed, the solution was concentrated to ca. 2 mL under reduced pressure. By addition of diethylether (25 mL) a yellow–pink microcrystalline precipitate slowly separated out, which was filtered, washed with diethylether and dried under vacuum. Yield = 0.641 g (85%) for **1**, 0.770 g, (87%) for **2**.

2.2.1. Characterization of $[ZrCl_3(qamph)]$ (**1**)

Elemental analysis: found (%): C 47.8, H 4.20, N 5.60, Cl 21.1. Calcd. for $C_{20}H_{21}Cl_3N_2OZr$, $M_W = 502.98$ (%): C 47.76, H 4.21, N 5.57, Cl 21.15.

1H NMR ($CDCl_3$, 298 K; refer to Scheme 1 for the numeration of aromatic H atoms): 9.42 (d, 1H, $^3J_{HH} = 5.0$ Hz, H₁); 8.43 (d, 1H, $^3J_{HH} = 8.0$ Hz, H₃); 8.04 (d, 1H, $^3J_{HH} = 7.8$ Hz, H₆); 7.88 (d, 1H, $^3J_{HH} = 7.8$ Hz, H₄); 7.77 (t, 1H, $^3J_{HH} = 7.8$ Hz, H₅); 7.65 (dd, 1H, $^3J_{HH} = 5.0$ Hz, $^3J_{HH} = 8.0$ Hz, H₃); 7.07 (d, 1H, $^3J_{HH} = 7.5$ Hz, H₉); 6.75 (d, 1H, $^3J_{HH} = 7.5$ Hz, H₇); 6.60 (t, 1H, $^3J_{HH} = 7.5$ Hz, H₈); 5.93 (s, slightly br, 1H, NH); 5.23 (d, 1H, $^2J_{HH} = 13.6$ Hz, CH₂); 4.54 (dd, 1H, $^2J_{HH} = 13.6$ Hz, $^3J_{HH} = 4.3$ Hz, CH₂); 1.36 (s, 9H, ^tBu).

^{13}C { 1H } NMR ($CDCl_3$, 298 K; refer to Scheme 1 for the numeration of aromatic C atoms): 152.6 C₁; 140.9 C₃; 128.4–127.7 C₆, C₄, C₅, C₉, C₇, 122.4 C₃, 121.0 C₉, 54.0 CH₂, 34.6 quaternary ^tBu; 29.7 ^tBu.

2.2.2. Characterization of $[HfCl_3(qamph)]$ (**2**)

Elemental analysis: found (%): C 40.7, H 3.60, N 4.75, Cl 18.0. Calcd. for $C_{20}H_{21}Cl_3HfN_2O$, $M_W = 590.24$ (%): C 40.70, H 3.59, N 4.75, Cl 18.02.

1H NMR (CD_2Cl_2 , 298 K; refer to Scheme 1 for the numeration of aromatic H atoms): 9.40 (d, 1H, $^3J_{HH} = 5.1$ Hz, H₁); 8.51 (d, 1H, $^3J_{HH} = 8.4$ Hz, H₃); 8.07 (d, 1H, $^3J_{HH} = 7.8$ Hz, H₆); 7.94 (d, 1H, $^3J_{HH} = 7.8$ Hz, H₄); 7.82 (t, 1H, $^3J_{HH} = 7.8$ Hz, H₅); 7.71 (dd, 1H, $^3J_{HH} = 5.1$ Hz, $^3J_{HH} = 8.4$ Hz, H₃); 7.09 (d, slightly br, 1H, $^3J_{HH} = 7.7$ Hz, H₉); 6.76 (s, br, 1H, H₇); 6.56 (t, slightly br, 1H, $^3J_{HH} = 7.7$ Hz, H₈); 6.11 (s, slightly br, 1H, NH); 5.26 (d, slightly br, 1H, $^2J_{HH} = 13.1$ Hz, CH₂); 4.55 (d, slightly br, 1H, $^2J_{HH} = 13.1$ Hz, CH₂); 1.34 (s, 9H, ^tBu).

^{13}C { 1H } NMR (CD_2Cl_2 , 298 K; refer to Scheme 1 for the numeration of aromatic C atoms): 153.0 C₁; 141.6 C₃; 128.9–127.8 C₆, C₄, C₅, C₉, C₇; 122.9 C₃, 120.6 C₉, 56.1 CH₂, 34.6 quaternary ^tBu; 29.6 ^tBu.

2.3. Synthesis of $[ZrCl_2(qadph)]$ (**3**) ($C_{20}H_{20}Cl_2N_2OZr$, $M_W = 467.52$)

A solution of the ligand qamph^H (0.460 g, 1.5 mmol) in THF (25 mL) was cooled to -80 °C and 20 mL of a 0.16 M solution of butyllithium in THF/hexanes, corresponding to 3.2 mmol, was added dropwise while keeping constant the temperature. The resulting red solution was warmed until -40 °C and then slowly added to a cooled (-40 °C) solution of $ZrCl_4(THF)_2$ (0.566 g, 1.5 mmol) in THF (20 mL). The resulting reaction mixture was allowed to reach room temperature and left overnight under stirring. After elimination by centrifugation of the LiCl formed, the solution was concentrated to ca. 2 mL under reduced pressure and the crude product was separated by addition of *n*-hexane. After filtration, the product was dissolved in dichloromethane (20 mL) and the solution was centrifuged to remove the by-products. The resulting clear CH_2Cl_2 solution was then concentrated to ca. 5 mL under reduced pressure. A pale pink product was separated by addition of diethylether (10 mL) after one night at -25 °C. The microcrystalline product was filtered, washed with diethylether and dried under vacuum. Yield = 0.449 g (64%).

2.3.1. Characterization of $[ZrCl_2(qadph)]$ (**3**)

Elemental analysis: found (%): C 51.4, H 4.55, N 6.00, Cl 15.2. Calcd. for $C_{20}H_{20}Cl_2N_2OZr$, $M_W = 467.52$ (%): C 51.38, H 4.53, N 5.99, Cl 15.17.

1H NMR (THF- d_8 , 298 K; refer to Scheme 1 for the numeration of aromatic H atoms): 8.42 (d, 1H, $^3J_{HH} = 8.2$ Hz, H₃); 8.02 (d, 1H, $^3J_{HH} = 7.3$ Hz, H₆); 7.80 (d, 1H, $^3J_{HH} = 7.3$ Hz, H₄); 7.67 (t, 1H, $^3J_{HH} = 7.3$ Hz, H₅); 7.60 (dd, 1H, $^3J_{HH} = 8.2$ Hz, $^3J_{HH} = 4.9$ Hz, H₂); 6.83 (d, 1H, $^3J_{HH} = 7.7$ Hz, H₉); 6.56 (d, 1H, $^3J_{HH} = 7.7$ Hz, H₇); 6.26 (d, 1H, $^3J_{HH} = 7.7$ Hz, H₈); 5.08 (d, br, 1H, $^2J_{HH} = 11.6$ Hz, CH₂); 4.46 (d, br, 1H, $^2J_{HH} = 11.6$ Hz, CH₂); 1.27 (s, 9H, ^tBu). H₁ was detected after cooling the sample at 230 K: 8.90 (d, 1H, $^3J_{HH} = 4.9$ Hz, H₁).

^{13}C { 1H } NMR (HSQC projection, THF- d_8 , 298 K; refer to Scheme 1 for the numeration of aromatic C atoms): 141.4 C₃; 129.4 C₇; 129.2 C₆; 129.0 C₅; 128.7 C₄; 127.7 C₉; 123.2 C₂; 119.5 C₈; 56.4 CH₂; 30.6 ^tBu.

Any attempts to obtain crystal of **1–3** suitable for X-ray structural determinations failed also by using a programmable Thermo Scientific C25P cryostat device having a Phoenix II controlling unit.

2.4. Polymerization procedure

The polymerizations at 1 atm of monomer pressure were performed in a magnetically stirred glass reactor (100 cm³). High pressure polymerization runs were carried out in a 500 mL Büchi glass autoclave equipped with a mechanical stirrer and a

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