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Isospecific polymerization of propene by new indolyl-pyridylamido Zr(IV) catalysts

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ABSTRACT

New zirconium complexes bearing indolyl-pyridylamido ligands [$^{-}$NNN^{-}] have been synthesized and used as catalysts in ethylene and propene polymerization in the presence of Al^{i}Bu$_2$H/MAO as cocatalytic system. Complexes **1** and **2**, bearing ligands with a different steric hindrance on the carbon bridging the pyridine and the aniline moieties, exhibited remarkable catalytic activity for ethylene and propene polymerization, affording ultrahigh molecular weight polymers with monomodal molecular weight distributions. Moreover, the presence of the 2-isopropyl phenyl substituent on the bridging carbon (complex **2**) resulted in higher stereoselectivity and regioselectivity providing a polypropylene sample with an [mmmm] content up to 96% and 1.3% of regioinversion. On the other hand, the change of the substituents of the aniline moiety (complex **3**) gave a zirconium complex which resulted completely inactive both in the ethylene and propene polymerization.

1. Introduction

Recent research in the field of olefin polymerization has been focused on a variety of polydentate ligand frameworks based on nitrogen and/or oxygen and/or sulfur donors, resulting in the discovery of catalysts displaying excellent performance and peculiar features, such as living polymerization at high temperature and chain shuttling between two different active species, allowing the synthesis of novel macromolecular architectures [1]. One of the most successful class of stereoselective catalysts recently introduced is based on arylpyridylamido Hf(IV) complexes, discovered and optimized by researchers at Dow and Symyx using high throughput screening technologies and currently used in commercial production of some polypropylene-based resins [2]. The excellent performance of these catalysts for the production of highly isotactic, high molecular weight polypropylene at high temperature in solution processes depends on in situ arylcyclometallation reactions, changing a [NN—] monoanionic ligand into a [—CNN—] dianionic tridentate one and, possibly, by further ligand modifications, such as monomer insertion into a Hf—C_{aryl} bond [2,3]. In this respect, we have previously reported penta-coordinate group 4 metal complexes bearing dianionic pyrrolylpyridylamido [$^{-}$NNN^{-}] tridentate ligands [4] (Chart 1, complexes I) which resulted in stereospecific catalysts, producing high molecular weight polypropylenes (M_w up to 10^6 g/mol) with high isotacticity ([mmmm] up to 95%), and high melting temperatures (T_m > 150 °C). The same class of ligands were used for the synthesis of group 3 and aluminum complexes active in the ring-opening polymerization of cyclic esters. [5] We report here the synthesis of some related Zr(IV) complexes bearing tridentate [$^{-}$NNN^{-}] ligands, in which the pyrrolide group was replaced by the bulkier and more electron donating indolyde group (Chart 1, complexes II), and their use as precatalysts for the polymerization of ethylene and propene.

2. Experimental

2.1. General procedures

All manipulations of air- and/or water-sensitive compounds were carried out under nitrogen atmosphere using standard Schlenk or glovebox techniques. All solvents, purchased from Carlo Erba, were refluxed over sodium/benzophenone or calcium hydride (CaH_2) and then distilled under nitrogen atmosphere before use. 1-Bromo-2-isopropylbenzene was purchased from Alfa Aesar and used as received. All other chemicals were purchased from Sigma–Aldrich and used as received. Solid MAO (10 wt% solution in toluene) was obtained by distilling off the volatile materials under reduced pressure and excess of trimethylaluminum was removed by washing the resulting solid with dry hexane, and drying under vacuum the obtained white powder. Ethylene

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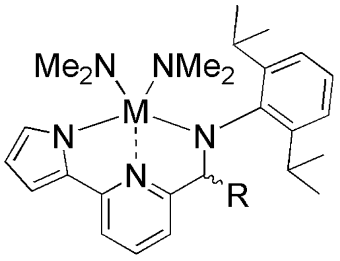

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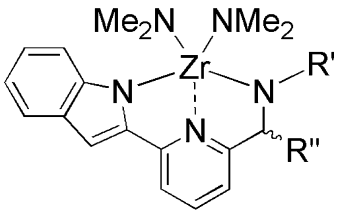


II

Complex **I-a**: M = Zr; R = H
Complex **I-b**: M = Zr; R = 2-iPrC$_6$H$_4$

Chart 1. Pyrrolylpyridylamido group 4 complexes (I) previously reported and indolylpyridylamido zirconium complexes (II) synthesized in this work.

and propene were purchased from SON and used without further purification. N-(t-butoxycarbonyl)-indole-2-boronic acid [6] and 4,6-dimethyl-2-(2-phenylethyl)aniline [7] were prepared by literatures procedures.

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance spectrometer operating at 400 MHz and 100.6 MHz, respectively. ^{13}C NMR spectra of polymers were recorded on a Bruker AM-250 spectrometer operating at 62.5 MHz in 1,1,2,2-tetrachloroethane-d_2 ($C_2D_2Cl_4$) at 100 °C and referenced vs hexamethyldisiloxane (HMDS).

Molecular weights (M_n and M_w) and polydispersity indexes (PDI) of polymers were determined by high-temperature GPC using a Waters GPC-V200 RI detector. The measurements were recorded at 135 °C using 1,2-dichlorobenzene as a solvent and Styragel columns (range 10^3–10^6 Å). Every value was the average of two independent measurements.

Polymers melting points (T_m) were measured by differential scanning calorimetry using a TA Instruments DSC 2920 in nitrogen flow with a heating and cooling rate of 10 °C/min. Melting temperatures were reported for the second heating cycle.

2.2. Synthesis of the proligands

2.2.1. Compound *A*

Palladium(II)acetate (50 mg, 0.2 mmol), 2-dicyclohexylphosphino-2,6-dimethoxybiphenyl (0.186 g, 0.4 mmol) N-(t-butoxycarbonyl)-indole-2-boronic acid (1.24 g, 4.75 mmol), 6-bromo-2-pyridine-carboxaldehyde (0.71 g, 3.82 mmol), and K_3PO_4 (2.233 g, 10.5 mmol) were mixed in 10 mL of distilled n-butanol in a 50 mL Schlenk flask under nitrogen atmosphere. The resulting mixture was heated to 80 °C and stirred for 2 h. The reaction mixture was allowed to cool to room temperature, then, it was filtered. The solvent was distilled off by rotary evaporation. The crude product was purified via column chromatography on silica gel using 9:1 hexane/ethyl acetate as the eluent, obtaining the product as white solid (1.06 g, 86%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): 1.35 (s, 9H, C*H*$_3$), 6.87 (s, 1H, indole—*H*), 7.29 (d, *J* = 7.3 Hz, 1H, Py—*H*), 7.40 (t, 1H, Py—*H*), 7.62 (d, *J* = 7.3 Hz, 1H, Py—*H*), 7.75 (m, 1H, indole—*H*), 7.95 (m, 2H, indole—*H*), 8.19 (d, *J* = 8.4 Hz, 1H, indole—*H*), 10.11 (s, 1H, *H*C═O). ^{13}C NMR (100.62 MHz, $CDCl_3$, 25 °C): 27.90 (*C*H$_3$), 84.01 (*C*(CH$_3$)$_3$), 112.31, 115.34, 120.08, 121.42, 123.38, 125.66, 127.64, 137.34, 138.00, 150.07, 152.28, 154.10, 193.68 (*C*O).

2.2.2. Compound *B*

To a solution of tert-butyl 2-(6-formylpyridin-2-yl)-1H-indole-1-carboxylate (0.86 g, 2.67 mmol) in toluene (20 mL) was added silica gel (1.60 g, 10 equiv.). The mixture was refluxed and stirred for 1 h and then cooled to room temperature. 2,6-Diisopropylaniline (0.50 g, 2.82 mmol) and molecular sieves were added and the resulting mixture was refluxed for 1 h. The solvent was distilled off by rotary evaporation. The crude product was purified via column chromatography on silica gel using 9:1 hexane/ethyl acetate as eluent. The removal of the solvent by rotary evaporation afforded a light yellow solid (0.79 g, yield: 78%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): 1.20 (d, *J* = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 3.00 (sept, 2H, C*H*(CH$_3$)$_2$), 7.09–7.24 (m, 6H, Ar—*H*), 7.45 (dd, *J* = 8.1 Hz, 1H, Ar—*H*), 7.67 (d, *J* = 8.1 Hz, 1H, Ar—*H*), 7.90 (m, 2H, Ar—*H*), 8.14(dd, *J* = 7.2 Hz, 1H, Ar—*H*), 8.36 (s, 1H, *H*C═N), 9.61 (s, 1H, indole—N*H*). ^{13}C NMR (100.62 MHz, $CDCl_3$, 25 °C): 23.67, 28.18, 101.29, 111.65, 119.70, 120.45, 121.47, 121.56, 123.27, 123.62, 124.68, 129.29, 136.30, 136.71, 137.42, 137.52, 148.72, 150.52, 153.91, and 163.16.

2.2.3. Synthesis of H_2L^1

To a solution of compound **B** (250 mg, 0.66 mmol) in 20 mL of methanol, 3 drops of CHOOH (88%) were added. Then, $NaBH_3CN$ (78 mg, 1.24 mmol) was added into the solution. The yellow solution turned to colorless. The solution was refluxed for one hour and then cooled to room temperature. After removal of the solvent by rotary evaporation, the solid was dissolved in diethyl ether and water. The organic phase was separated and reserved. The aqueous phase was extracted with diethyl ether (3 × 30 mL). The combined organic phases were washed with water (2 × 30 mL) and brine (1 × 30 mL). The organic phase was dried over Na_2SO_4. The solvent was distilled off by rotary evaporation. The crude product was purified by flash column chromatography on silica gel using hexane/diethyl ether (9/1) as eluent. The colorless oil was concentrated under vacuum, affording a colorless solid (215 mg, 85%). ^{1}H NMR (300 MHz; $CDCl_3$, 25 °C): 1.29 (12H, d, *J* = 6.9 Hz, CH(C*H*$_3$)$_2$), 3.45 (2H, C*H*(CH$_3$)$_2$), 4.25 (2H, s, —C*H*$_2$N—), 7.04–7.24 (7H, m, Ar—*H*), 7.43 (1H, *d* = 8.4 MHz, Ar—*H*), 7.66–7.72 (3H, m, Ar—*H*), 9.43 (1H, s, indole—*H*). ^{13}C NMR (100.62 MHz; $CDCl_3$, 25 °C): 24.42, 28.11, 56.68, 100.86, 111.47, 118.47, 120.41, 121.44, 123.45, 123.85, 124.07, 129.37, 136.60, 136.81, 137.40, 142.57, 143.50, 149.93, and 158.54.

2.2.4. Synthesis of H_2L^2

n-Butyl lithium (1.45 mL, 3.63 mmol, 2.5 M in hexane) was added dropwise to a solution of 1-bromo-2-isopropylbenzene (678 mg, 3.41 mmol) in dry diethyl ether (10 mL) at 0 °C. The colorless solution was warmed to room temperature and stirred for 3 h. Then, the solution was added dropwise to a dry diethyl ether (5 mL) solution of compound **B** (434 mg, 1.14 mmol) at −78 °C. The yellow solution was warmed to room temperature and stirred for 30 min.

The color turned to red. The reaction was followed by TLC and then quenched with NH_4Cl (aq) at 0 °C. The organic phase was separated and reserved. The aqueous phase was extracted with diethyl ether (3 × 30 mL). The combined organic phases were washed with water (2 × 30 mL) and brine (1 × 30 mL). The organic phase was dried over Na_2SO_4. The solvent was distilled off by rotary evaporation. The crude product was purified by flash column chromatography on silica gel using hexane/diethyl ether (20/1) as eluent. The product was isolated as a yellow solid (120 mg, yield: 88%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): 0.96 (9H, CH(CH_3)$_2$), 0.98 (3H, d, J = 6.8 Hz, CH(CH_3)$_2$), 1.05 (6H, d, J = 6.8 Hz, CH(CH_3)$_2$), 2.89 (2H, sept, CH(CH_3)$_2$), 3.02 (1H, sept, CH(CH_3)$_2$), 4.19 (1H, br, NH), 5.52 (1H, s, NCH), 6.96 (2H, m, Ar—H), 7.07 (3H, s, Ar—H), 7.11 (1H, d, J = 1.2 Hz, Ar—H), 7.21 (1H, m, Ar—H), 7.28–7.39 (3H, m, Ar—H), 7.37 (1H, d, J = 7.6 Hz, Py—H), 7.57–7.64 (3H, m, Ar—H), 7.68–7.71 (1H, m, Ar—H), 8.97 (1H, s, indole—NH). ^{13}C NMR (100.62 MHz, $CDCl_3$, 25 °C): δ = 23.97, 24.01, 24.05, 24.30, 28.00, 28.82, 66.18, 100.43, 111.54, 117.97, 119.74, 120.26, 121.33, 123.27, 123.63, 123.71, 125.81, 126.17, 127.47, 127.72, 129.31, 136.45, 136.87, 137.30, 139.43, 137.30, 139.43, 142.56, 142.96, 146.56, 149.53, and 162.48.

2.2.5. Synthesis of H_2L^3

Molecular sieves were added to a solution of 6-bromo-2-pyridine-carboxaldehyde (0.205 g, 1.1 mmol), 2, 4-dimethyl-6-(1-phenylethyl)benzenamine (0.225 g, 1 mmol) and p-toluenesulfonic acid. The resulting mixture was refluxed for 3 h. After cooled to room temperature, the solvent was distilled off by rotary evaporation. The crude product was purified via column chromatography on silica gel using 9:1 hexane/diethyl ether as the eluent. The removal of the solvent by rotary evaporation afforded light yellow solid (yield: 87%). ^{1}H NMR (400 MHz; $CDCl_3$, 25 °C): 1.58 (3H, d, J = 7.2 Hz, ArCHCH_3), 2.09 (3H, s, CH_3), 2.33 (3H, s, CH_3), 4.22 (1H, t, J = 7.2 Hz, Ar—CH—CH_3), 6.96 (2H, d, J = 13.2 Hz, Ar—H) 7.09–7.19 (4H, m, Ar—H), 7.58 (1H, d, J = 7.8 Hz, Ar—H), 7.68 (1H, t, J = 7.8 Hz, CH=N), 7.99 (1H, s, Ar—H), 8.14 (1H, d, J = 6.9 Hz, Ar—H). ^{13}C NMR (100.62 MHz; $CDCl_3$, 25 °C): 18.67, 21.36, 21.81, 39.78, 120.07, 125.81, 125.88, 126.02, 127.90, 128.40, 129.75, 129.90, 133.98, 136.04, 139.09, 141.95, 146.65, 147.13, 155.81, and 162.66.

The Suzuky–Miyaura cross coupling reaction was carried out by the same procedure described for the synthesis of compound **A** (yield: 78%). ^{1}H NMR (400 MHz; $CDCl_3$): 1.59 (3H, d, J = 7.81 Hz, ArCHCH_3), 2.15 (3H, s, CH_3), 2.21 (3H, s, CH_3), 4.51 (1H, m, ArCHCH$_3$), 6.77 (2H, d, J = 10.7 Hz, Ar—H), 6.87(2H, s, Ar—H), 6.97–7.36 (10H, m, Ar—H), 7.73 (1H, d, J = 9.7 Hz, Py—H), 8.03(1H, t, Py—H), 8.17 (1H, s, CH=N), 9.30 (1H, s, indole—H). H_2L^3 was then synthesized by reduction of the imino moiety as described for ligand H_2L^1 (yield: 40%). ^{1}H NMR (400 MHz; C_6D_6, 25 °C): 1.49 (3H, d, J = 7.2 Hz, ArCHCH_3), 2.19 (3H, s, CH_3), 2.29 (3H, s, CH_3), 3.89 (1H, br, NH—), 4.07 (2H, s, Py—CH_2N—), 4.43 (1H, q, J = 7.2 Hz, ArCHCH$_3$), 6.69 (1H, d, J = 8 Hz, Ar—H), 6.90 (2H, s, Ar—H), 6.98 (1H, t, J = 7.2 Hz, Ar—H), 7.00–7.36 (10H, m, Ar—H), 7.73 (1H, d, J = 7.8 Hz, Py—H), 9.21 (1H, s, indole—NH); ^{13}C NMR (100.62 MHz; C_6D_6, 25 °C): 18.94, 21.17, 23.01, 40.04, 54.96, 101.33, 111.86, 118.16, 119.93, 120.71, 121.69, 123.67, 126.36, 127.82, 128.06, 128.30, 128.89, 129.86, 130.56, 131.47, 132.13, 132.17, 136.94, 137.10, 138.53, 143.68, 147.04, 150.39, and 159.47.

2.3. Synthesis of the complexes

2.3.1. $L^1Zr(NMe_2)_2$ complex 1

A solution of $Zr(NMe_2)_4$ (122 mg, 0.456 mmol) in benzene (5 mL) was added dropwise into a stirred solution of H_2L^1 (175 mg, 0.456 mmol) in benzene (5 mL). The solution was stirred for 30 min at ambient temperature. All volatiles were removed under vacuum to yield a yellow solid which was washed with pentane. The light yellow product was obtained in 70% yield (180 mg). ^{1}H NMR (400 MHz; CD_2Cl_2, 25 °C): 1.17 (12H, CH(CH_3)$_2$), 2.79 (12H, s, NMe_2), 3.45 (2H, sept, CH(CH_3)$_2$), 4.89 (2H, s, CH_2N), 6.92–7.16 (7H, Ar—H), 7.45 (1H, d, J = 8 Hz, Ar—H), 7.57 (1H, d, J = 8 Hz, Ar—H), 7.72 (1H, d, J = 8 Hz, Ar—H), 7.85 (1H, t, J = 8 Hz, Ar—H). ^{13}C NMR (100.62 MHz; CD_2Cl_2, 25 °C): 24.14 (CH(CH_3)$_2$), 26.79 (CH(CH_3)$_2$), 28.12 (CH(CH_3)$_2$), 40.68 (N(CH_3)$_2$), 66.05 (NCH_2), 101.74, 116.51, 117.11, 119.44, 121.10, 122.99, 123.65 (2C), 124.57, 128.71, 131.90, 140.42, 146.48, 146.98, 147.06, 149.28, 155.10, and 164.64. Elemental analysis: Calcd for $C_{30}H_{39}N_5Zr$ (%): C, 64.24; H, 7.01; N, 12.49. Found (%): C, 63.92; H, 6.95; N, 12.62.

2.3.2. $L^2Zr(NMe_2)_2$ complex 2

A solution of $Zr(NMe_2)_4$ (160 mg, 0.600 mmol) in benzene (5 mL) was added dropwise into a stirred solution of H_2L^2 (310 mg, 0.600 mmol) in benzene (5 mL). The solution was stirred for 30 min at room temperature. All volatiles were removed under vacuum to yield a yellow solid that was washed with pentane. The light yellow product was obtained in 93% yield (380 mg, 0.56 mmol). ^{1}H NMR (400 MHz; CD_2Cl_2, 25 °C): 0.09 (3H, d, J = 9.6 Hz, CH(CH_3)$_2$), 0.57 (3H, d, J = 8.8 Hz, CH(CH_3)$_2$), 1.04–1.11 (9H, CH(CH_3)$_2$), 1.31 (3H, d, J = 9.2 Hz, CH(CH_3)$_2$), 2.57 (1H, sept, CH(CH_3)$_2$), 2.65 (6H, s, Zr—N(CH_3)$_2$), 2.95 (1H, sept, CH(CH_3)$_2$), 3.00 (1H, s, Zr—N(CH_3)$_2$), 3.33 (1H, sept, CH(CH_3)$_2$), 6.06 (1H, s, NCHAr), 6.70 (1H, m, Ar—H), 6.95–7.19 (9H, m, H—Ar), 7.49 (1H, d, J = 11.2 Hz, H—Ar), 7.58 (1H, d, J = 10.8 Hz, H—Ar), 7.72–7.77 (2H, H—Ar). ^{13}C NMR (100.62 MHz; CD_2Cl_2, 25 °C): 22.31 (CH(CH_3)$_2$), 23.96 (CH(CH_3)$_2$), 25.22 (CH(CH_3)$_2$), 25.79–25.90 (3C, CH(CH_3)$_2$), 28.03 (CH(CH_3)$_2$), 28.58 (CH(CH_3)$_2$), 28.79 (CH(CH_3)$_2$), 40.92 (N(CH_3)$_2$), 42.41 (N(CH_3)$_2$), 75.25 (NCH), 101.88, 116.74, 117.03, 119.17, 119.63, 121.16, 123.10, 123.96, 124.54, 124.63, 125.59, 126.53, 127.71, 128.74, 130.48, 132.05, 140.71, 141.81, 146.23, 146.91, 147.11, 147.26, 147.48, 147.95, 154.84, and 169.66. Elemental analysis: Calcd for $C_{39}H_{49}N_5Zr$ (%): C, 68.98; H, 7.27; N, 10.31. Found (%): C, 69.21; H, 7.53; N, 10.12.

2.3.3. $L^3Zr(NMe_2)_2$ complex 3

Complex **3** was synthesized following a similar procedure to that used for complex **2** (yield: 78%). ^{1}H NMR (400 MHz; C_6D_6, 25 °C): 1.60 (3H, d, J = 7.2 Hz, CH_3CHAr), 2.14 (3H, s, CH_3—Ar), 2.27 (3H, s, CH_3—Ar), 2.70 (6H, s, NMe_2), 2.83 (6H, s, NMe_2), 4.11 (1H, d, J = 20.5 Hz, —NCHH—Py), 4.33 (1H, d, J = 20.5 Hz, —NCHH—Py), 4.99 (1H, m, CH$_3$CHAr), 6.03 (1H, J = 7.7 Hz, Ar—H), 6.83 (1H, t, Ar—H), 6.96–7.26 (10H, m, Ar—H), 7.42 (1H, t, J = 7.4 Hz, Py—H), 7.83 (2H, d, J = 8.6 Hz, Ar—H), 7.88 (2H, d, J = 7.8 Hz, Ar—H). ^{13}C NMR (100.62 MHz; C_6D_6, 25 °C) 18.77, 21.38, 22.71, 24.05, 39.20, 40.56, 40.87, 63.57, 102.86, 115.75, 116.39, 116.75, 120.19, 121.66, 123.77, 125.65, 126.32, 129.75, 132.50, 133.05, 136.24, 139.41, 143.33, 146.57, 147.62, 147.68, 149.44, 155.22, and 165.27.

2.4. General procedure for ethylene and propene polymerization

The polymerization experiments were carried out in a magnetically stirred flask (250 mL) or in a Büchi glass autoclave (500 mL). Under nitrogen atmosphere, the required equivalents of Al^iBu_2H were added to a solution of the precatalyst in toluene (2 mL) and then stirred for 10 min at room temperature. The reactor vessels were charged sequentially with toluene, dried MAO and a solution of the precatalyst in toluene. The stirred mixture was thermostated at the required temperature and then the monomer gas feed was started. After the prescribed time, the polymerization mixture was poured into acidified ethanol. The polymers were filtered, washed with ethanol, and dried in vacuum oven at 40 °C overnight.

3. Results and discussion

3.1. Synthesis and characterization of proligands and complexes

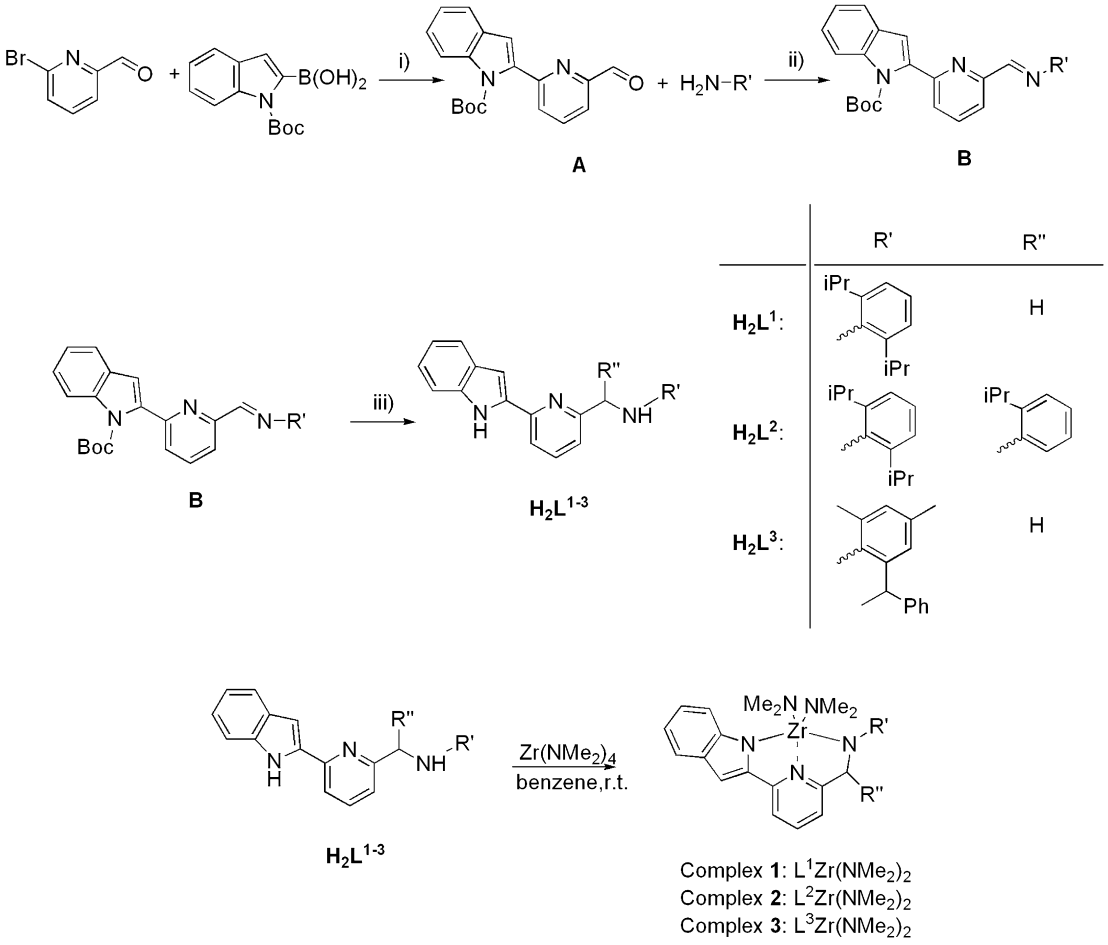
Indolyl-pyridylamine proligands $\mathbf{H_2L^1}$ and $\mathbf{H_2L^2}$ were synthesized via the Suzuky-Miyaura cross-coupling reaction [4a,8] of 6-bromo-2-pyridine-carboxaldehyde with N-Boc-indole-2-boronic acid (Boc = tert-butyloxycarbonyl), affording tert-butyl 2-(6-formylpyridine-2-yl)-1H-indole-1-carboxylate (**A**) as yellow solid in 86% yield (see Scheme 1). A condensation reaction between **A** and 2,6-diisopropylaniline gave the indolylpyridylimine compound **B** as light yellow solid (yield: 78%); subsequent reduction with $NaBH_3CN$ or, alternatively, alkylation with 2-$iPrC_6H_4Li$, gave indolyl-pyridylamine proligands (yields: 85% for $\mathbf{H_2L^1}$, 88% for $\mathbf{H_2L^2}$, respectively). $\mathbf{H_2L^3}$ was synthesized via the condensation reaction of 4,6-dimethyl-2-(2-phenylethyl)aniline with 6-bromo-2-pyridine-carboxaldehyde and subsequent Suzuky-Miyaura cross-coupling reaction with N-Boc-indole-2-boronic acid [4a], affording **B** as a yellow solid (71% yield). After reduction with $NaBH_3CN$ and Boc removal by silica gel 60, $\mathbf{H_2L^3}$ was obtained in 40% yield. All the compounds were fully characterized by NMR spectroscopy.

Complexes **1**–**3** were synthesized in benzene by treatment of the corresponding proligands with one equivalent of tetrakis(dimethylamido)-zirconium(IV) at room temperature, and isolated as light-yellow solids in high yield (70% for **1**, 91% for **2**, 78% for **3**, respectively).

^{1}H NMR analysis of complex **1** indicated a "time-averaged" C_s-symmetry in solution, as suggested, e.g., by the presence of one singlet for the CH_2N_{amido} methylene protons at 4.89 ppm and of one sharp singlet for the Zr—NMe_2 amido protons. In contrast, the ^{1}H NMR spectra of complexes **2** and **3** suggested a C_1-symmetry in solution. For complex **2**, three septets were observed for the methine protons of isopropyl groups and two sharp singlets for the Zr—NMe_2 protons (2.65 and 3.00 ppm). In the spectrum of complex **3** the two protons of the methylene bridge appear as an AB pattern, and two sharp singlets for Zr—NMe_2 (2.85 and 2.70 ppm) were observed. The ^{1}H NMR spectrum of complex **3** showed the presence of two species at a ratio of ca. 9:1. A plausible explanation is the coexistence of two rotational diasteroisomers due to the hindered rotation around the C—N bond of the 4,6-dimethyl-2-(2-phenylethyl)anilido moiety [9].

3.2. Ethylene and propene polymerization

Indolylpyridylamido complexes **1**–**3** were tested as precatalysts for ethylene polymerization in combination with $AliBu_2H$ as alkylating agent (in view of the well-known difficult alkylation of dimethylamido group 4 complexes by MAO alone) [10] and MAO as ionizing activator. As explored in previous papers [4] this is the most efficient cocatalytic system for this class of complexes. The main polymerization data are summarized in Table 1, where the results previously reported [4] for the analogous pyrrolylpyridylamido zirconium complexes (see Chart 1) are also displayed for



Scheme 1. Synthesis of proligands $\mathbf{H_2L^{1-3}}$ and complexes **1–3**. General conditions: (i) K_3PO_4, $Pd(OAc)_2$/sphos (1:2), n-Butanol, 80 °C; (ii) refluxing toluene; (iii) $NaBH_3CN$/HCOOH for H_2L^1 and H_2L^3; 2-$iPrC_6H_4Li$ for H_2L^2. In the case of ligand H_2L^3 step (ii) preceded step (i).

Table 1
Ethylene polymerization results.[a]

Run	Precatalyst	Yield (g)	Activity[b]	T_m (°C)	M_w (kg/mol)	M_w/M_n
1	**1**	0.42	1.4	135	710	2.8
2	**2**	0.84	2.9	136	1870	3.9
3	**3**	Trace	–	–	–	–
4	**I-a**[c]	0.54	1.8	137	1850	2.1
5	**I-b**	0.90	3.1	137	1410	2.1

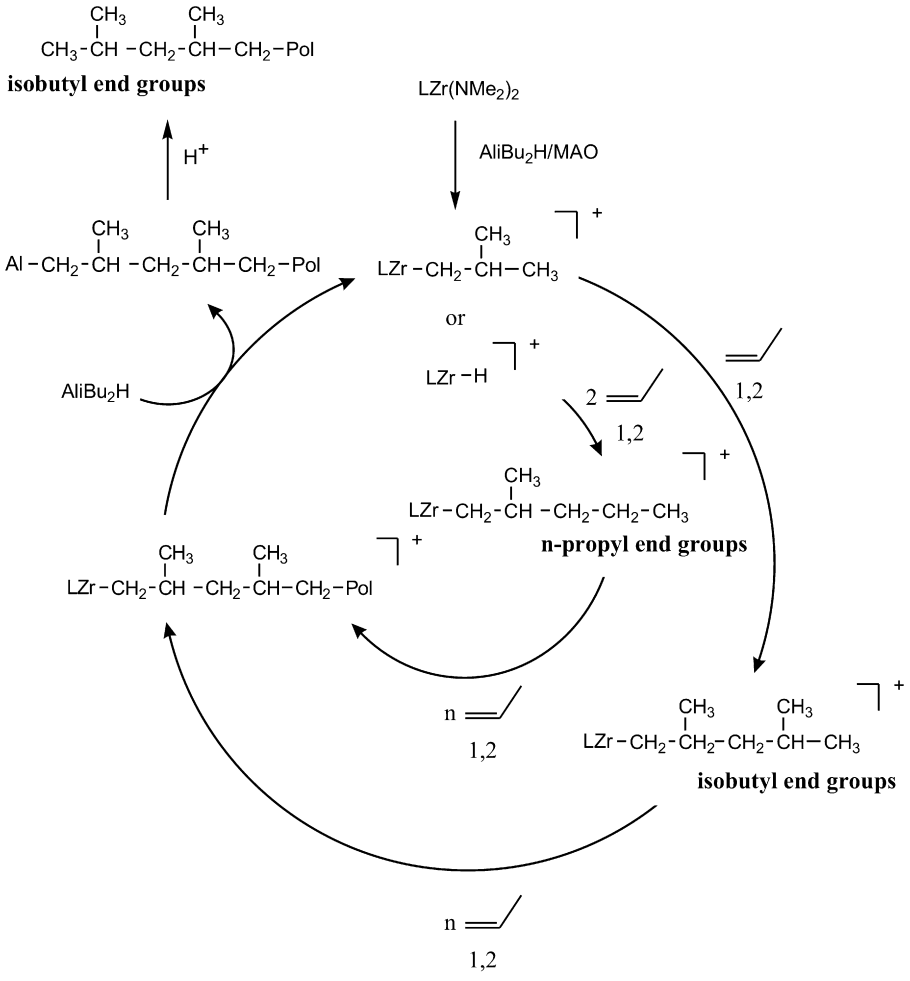
[a] General conditions: catalyst: 2.5 μmol; toluene: 100 mL; cocatalyst: $Al^iBu_2H/Zr = 30$, $Al_{(dried\ MAO)}/Zr = 1000$; ethylene pressure: 1 atm; polymerization time: 7 min.
[b] Activity: $kg_{PE}\ (mmol_{(Zr)}\ h\ atm)^{-1}$.
[c] Ref. [4a].

comparison. Complexes **1** and **2** were active ethylene polymerization catalysts (runs 1 and 2), producing highly linear polyethylenes (T_m: 135–136 °C). As previously observed [4], the introduction of a bulky substituent on the carbon bridging the pyridyl and the anilido moieties resulted in a more active catalyst (a 2-fold increase is observed). In comparison with the corresponding pyrrolylpyridylamido zirconium catalysts (runs 4 and 5), the activities of **1** and **2** are comparable. GPC analysis of the polyethylene samples produced by **1** and **2** revealed ultra high molecular weights (710 kg/mol for **1**; 1900 kg/mol for **2**) and slightly broad molecular weight distributions, in line with the results achieved by the pyrrolylpyridylamido catalysts. On the contrary, complex **3**, bearing

Table 2
Propene polymerization results.[a]

Run	Precatalyst	T (°C)	Activity[b]	[mmmm] %	Regioinversion %	T_m (°C)	M_w (kg/mol)	M_w/M_n
6	**1**	25	198	86	5.4	130	19	1.2
7	**1**	75	40	82	6.3	115	15	1.1
8	**2**	25	121	96	1.3	152	861	1.6
9	**2**	75	83	95	3.9	143	103	1.7
10	**3**	25	Trace	–	–	–	–	–
11	**I-a**[c]	25	4	73	3.0	–	39	1.4
12	**I-b**[d]	25	98	95	1.4	150	950	3.5
13	**I-b**[d]	75	14	93	2.4	140	16	2.2

[a] General condition: precatalyst: 10 μmol; toluene: 100 mL; cocatalyst: $Al^iBu_2H/[Zr] = 30$, $Al_{(MAO)}/[Zr] = 1000$; polymerization time: 60 min; propene pressure: 6 atm.
[b] Activity: $kg_{PP}\ (mol_{[Zr]}\ h\ atm)^{-1}$.
[c] Ref. [4a].
[d] Ref. [4b].



Scheme 2. Catalytic cycle for the polymerization of propene promoted by complexes **1**–**2**.

a substituted 4,6-dimethyl-2-(2-phenylethyl)anilido moiety, was inactive for ethylene polymerization (run 3). A similar finding was reported by Coates et al. [3], for an arylpyridylamido hafnium catalyst bearing a ligand with two 4-*tert*-butylphenyl group in the *ortho* positions of the anilido moiety, and tentatively explained suggesting a possible η^6-binding of the 4-tert-butylphenyl group to the cationic hafnium center precluding monomer binding.

Complexes **1**–**3** were then tested for propene polymerization after activation with Al^iBu_2H/MAO under 6 atm monomer pressure. The main polymerization data are summarized in Table 2, where the results previously reported [4] for the analogous pyrrolylpyridylamido complexes (runs 11–13) are also displayed for comparison. The unsubstituted catalyst **1** promoted polymerization of propene, producing isotactic polypropylene ([mmmm] = 86%) with rather low MW and quite narrow molecular weight distribution (PDI = 1.2). Interestingly, the performance in terms of both activity and stereoselectivity are significantly better than the corresponding unsubstituted pyrrolylpyridylamido Zr(IV) catalyst **Ia** (run 6 vs run 11). Also in the case of C_s-symmetric complex **1**, the polymer microstructure is that expected for an "enantiomorphic sites" mechanism of steric control, as previously observed for **Ia** and for a C_s-symmetric arylpyridylamido Hf complex [3]. In the latter case, a modification of the catalyst structure by propene insertion into a Hf-aryl bond resulting in a C_1-symmetric active species was suggested. The same mechanism would be unlikely for complexes **1** and **I-a**, for which different hypotheses have been suggested [4a]. The isopropylphenyl-substituted C_1-symmetric indolylpyridylamido zirconium catalyst **2** also showed better performance than the corresponding pyrrolylpyridylamido zirconium catalyst **I-b** (run 8 vs run 12). In both cases, the introduction of a bulky substituent on the carbon bridging the pyridine and the aniline moieties resulted in higher stereoselectivity and regioselectivity.

Polymerization at higher temperature (run 7) resulted in a 4 to 5-fold decrease of activity of unsubstituted catalyst **1**. However, only a slight decrease of activity was observed for polymerization at 75 °C using substituted catalyst **2** (run 9), while a greater loss of activity was observed for the corresponding pyrrolyl catalyst **I-b** (run 13). The features of the polypropylene sample derived from catalyst **2** at high temperature (run 9), in terms of molecular weight (>100 kg/mol), melting point (143 °C) and narrow molecular weight distribution (PDI = 1.7), are comparable to those of the polymers obtained by the highly optimized metallocene catalysts (M_w = 95 kg/mol, T_m = 142 °C, PDI = 2, polymerization performance at 90 °C) [1a].

For all the polypropylene samples, some regiodefects, deriving from head-to-head or tail-to-tail misinsertions, were detected by NMR analysis [11,12]. As previously observed for arylpyridylamido [2c] and other "post-metallocene" [4,11b] catalysts, regioinverted units with vicinal methyls in *threo* configuration in the Fischer projection were exclusively present, indicating that primary (1,2) and secondary (2,1) monomer insertion occur with the same enantioface selectivity.

In the ^{13}C NMR spectrum of the low molecular weight polypropylene sample produced by catalyst **1**, additional low intensity resonances were detected (Fig. S4 in the supporting information). According to the literatures [13], low intensity resonances at 45.4, 23.7, 21.8, 20.5 ppm are attributable to isobutyl end groups, while resonances at 37.6, 28.4, 17.9, 12.4 ppm are attributable to n-propyl end groups, reasonably arising from two consecutive primary (1,2) propene insertions into Zr—hydrogen bonds, generated from the reaction of amido Zr(IV) complexes with Al^iBu_2H. An alternative path producing n-propyl end groups would involve termination by hydrolysis of a growing chain after a 2,1 insertion of propene into a Zr-primary growing chain. For the related C_s-symmetric pyrrolylpyridylamido Zr(IV) complex **Ia**, a deuterium labeling experiment ruled out the latter path [4a]. The ratio between n-propyl and isobutyl end-groups is about 1:2. The proposed catalytic cycle for the polymerization of propene promoted by complexes **1** and **2** is shown in Scheme 2.

As observed for ethylene polymerization, complex **3** was substantially inactive also for the polymerization of propene.

4. Conclusions

We have reported the synthesis and characterization of three new zirconium complexes bearing dianionic indolyl-pyridylamido [$^-$NNN$^-$] tridentate ligands. All complexes have been tested as catalysts for ethylene and propene polymerization after activation with $AliBu_2H$/MAO.

Complexes **1** and **2** were able to catalyze the ethylene polymerization under mild conditions (25 °C and 1 atm of monomer pressure), yielding ultrahigh-molecular-weight PE's (M_w up to 1900 kg/mol).

They also promote polymerization of propene, producing isotactic polypropylene ([mmmm] up to 96%) with narrow molecular weight distribution (PDI = 1.2).

^{13}C NMR analysis of the obtained polypropylenes revealed a microstructure in agreement with the "enantiomorphic sites" mechanism of the stereoselective propagation. The analysis of the chain end groups suggests that 1,2 insertion is the main regiochemistry of propagation. The analysis of the regioinverted units in the polymer chains indicate that primary and secondary monomer insertions occur with the same enantioface selectivity.

Both catalysts show, in the propene polymerization, higher activity and stereoselectivity than the corresponding pyrrolylpyridylamido Zr(IV) catalysts suggesting that the bulkier and more electron donating indolide group has a beneficial effect on the performance of this class of complexes.

On the other hand, complex **3** bearing the substituted 4,6-dimethyl-2-(2-phenylethyl) anilido moiety was inactive for both ethylene and propene polymerization. A plausible explanation is the η^6-binding of the phenyl group to the cationic zirconium center which may preclude monomer binding [3] although steric effects cannot be excluded.

These results confirm that the effects of variation of structural parameters on reactivity and stereoselectivity are difficult to predict also for the members of a single class of catalysts.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2012.12.008.

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