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Group 4 metal bis(chelate) complexes of 2-anilidomethylpyridine ligands: Synthesis and catalytic activity for olefin polymerization

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ABSTRACT

A series of monoanionic, bidentate 2-anilidomethylpyridine ligands were synthesized and used to prepare bis(chelate) Zr(IV) and Hf(IV) bis(dimethylamido) complexes. All complexes were characterized by NMR spectroscopy and elemental analysis. The solution structures of the complexes were more or less fluxional, depending on the substituent on the ligands. The complexes were tested as catalysts for the polymerization of ethylene and propene, in combination with different activators. Use of Al^iBu_2H – methylaluminoxane as the co-catalyst resulted in the generation of catalysts producing high molecular weight polyethylenes with good activities, but yielding only stereoirregular and poorly regioregular polypropylenes.

1. Introduction

The design of new olefin polymerization catalysts remains a topic of interest in both academic and industrial research. A large variety of metal-ligand combinations has been explored, resulting in the development of several classes of highly active homogeneous catalysts able to produce polyolefins with different and controlled features (including stereoregularity, molecular weight, MWD, comonomer incorporation, etc.) [1]. In particular, Group 4 metal complexes bearing polydentate nitrogen-based ligands, e.g. amidinate [2], α-diimine [3], iminopyridine [4], iminopyrrolide [5], amidopyridine [6–8], amidopyrrolidepyridine [9], have recently emerged as promising catalysts. Simple aminopyridinato ligands were widely employed, providing a variety of mono-, bis-, tris- and tetrakis-aminopyridinato complexes [10–12]. In this framework, we recently reported some bis(chelate) Zr(IV) complexes bearing pentafluoro-*N*-((pyridin-2-yl)methyl)aniline ligands featuring an increased size of the chelating ring with respect to aminopyridinato complexes [13]. In this paper we report the synthesis and the characterization of some new suitably substituted N-((pyridin-2-yl)methyl)aniline ligands and their bis(chelate) zirconium and hafnium complexes, as well as the investigation of their performances as catalysts for the polymerization of ethylene and propene.

2. Experimental

2.1. General procedures

Manipulation of sensitive materials was carried out under a nitrogen atmosphere using Schlenk or glove box techniques. Hexane, benzene and toluene were dried by distillation over sodium/benzophenone; methylene chloride was dried by distillation over calcium hydride. $CDCl_3$, CD_2Cl_2 and C_6D_6 were dried over calcium hydride, distilled prior to use and stored on molecular sieves. Methylaluminoxane (MAO) was purchased from Sigma–Aldrich as a 10 wt.% toluene solution; the residual $AlMe_3$ contained in it was removed by distilling the volatile under reduced pressure, washing the resulting solid with dry hexane and drying the obtained white powder in vacuo. Ethylene and propene were purchased from SON and used without further purification; 1-hexene was distilled over calcium hydride prior to use. NMR spectra were recorded on a Bruker Avance 400 MHz, 300 MHz and 250 MHz spectrometers. Chemical shift (δ in ppm) are referenced vs. tetramethylsilane (TMS). ^{13}C NMR polymer spectra were recorded on an Bruker AM-250 spectrometer (62.5 MHz) in 1,1,2,2-tetrachloroethane-*d2* ($C_2D_2Cl_4$) at 100 °C and reported vs. hexamethyldisiloxane (HDMS). Elemental analysis were measured on a Thermo Finnigan Flash EA 1112 series C,H,N,S Analyzer. Molecular weights (M_n and M_w) and polydispersities (M_w/M_n) of polyethylene and polypropylene samples were determined by high-temperature gel permeation chromatography (HT-GPC) using PL-GPC210 with PL-Gel Mixed A Columns, a RALLS detector (Precision Detector, PD2040 at 800 nm), a

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H502 viscometer (Viscotek,), a refractive detector and a DM400 data manager. The measurements were recorded at 150° using 1,2,4-trichlorobenzene as solvent and narrow molecular weight distribution polystyrene standards as reference. Some GPC measurements were performed on Waters GPC-V200 RI detector at 135 °C using 1,2-dichlorobenzene as solvent and Styragel columns (range 10^7–10^3). Every value was the average of two independent measurements. Polymer melting points (*T*m) were measured by differential scanning calorimetry (DSC) using a DSC 2920 TA instrument in nitrogen flow with a heating and cooling rate of 10 °C min^{-1}. Melting temperatures were reported for the second heating cycle.

2.2. Synthesis of the ligands and of the complexes

N-((pyridin-2-yl)methyl)aniline (**1**). To a solution of 2-pyridinecarboxaldehyde (1.50 g, 14 mmol) and aniline (1.49 g, 16 mmol) in toluene (100 ml), containing 3 Å molecular sieves, was added p-toluenesulfonic acid (200 mg) at room temperature. The resulting solution was refluxed for 18 h. After filtration, the solvent was distilled off by rotary evaporation. The crude product was purified from dichloromethane/hexane obtaining a dark yellow solid (2.19 g, 85%). Reduction of the imine function was achieved by using $NaBH_3CN$ in methanol, following a previously reported procedure [13], yielding the ligand as a light yellow powder (2.10 g, 95%).

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K):δ 4.46 (br s, 2H, –CH_2), 4.78 (br s, 1H, NH), 6.66 (d, *J* = 8.4 Hz, 2H, ArH), 6.70 (t, *J* = 7.4 Hz, 1H, ArH), 7.16–7.20 (m, 3H, ArH), 7.33 (d, *J* = 7.8 Hz, 1H, ArH), 7.63 (t, *J* = 7.8 Hz, 1H, ArH), 8.58 (d, *J* = 5.5 Hz, 1H, *o*-PyH). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 49.54 (CH_2), 113.28, 117.83, 121.80, 122.30, 129.46, 136.82, 149.45 (Ar–C).

Anal. found (calcd.) for $C_{12}H_{12}N_2$ (%): C, 77.99 (78.23); H, 6.48 (6.57); N, 15.01 (15.21).

N-((6-methylpyridin-2-yl)methyl)aniline (**2**). The imine ligand 2 was obtained using a procedure similar to that described for the synthesis of 1, allowing to react 6-methyl-2-pyridinecarboxaldehyde (2.30 g, 18 mmol) and aniline (1.76 g, 19 mmol) (3.14 g, 88%). Subsequent reduction reaction with $NaBH_3CN$ gave the amino ligand as a light brown powder (3.10 g, 98%).

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 2.58 (s, 3H, –CH_3), 4.36 (br s, 1H, NH), 4.43 (s, 2H, –CH_2), 6.65 (d, *J* = 8.4 Hz, 2H, ArH), 6.72 (t, *J* = 7.3 Hz, 1H, ArH), 7.05 (d, *J* = 7.6 Hz, 1H, ArH), 7.14–7.19 (m, 3H, ArH), 7.54 (t, *J* = 7.6 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 24.46 (CH_3), 49.38 (CH_2), 113.20, 117.73, 118.75, 121.93, 129.39, 137.34, 148.01, 158.01 (Ar–C).

Anal. found (calcd.) for $C_{13}H_{14}N_2$ (%): C, 78.69 (78.75); H, 7.08 (7.12); N, 13.96 (14.13).

N-((6-bromopyridin-2-yl)methyl)aniline (**3**). The imine ligand was obtained using a procedure similar to that described for the synthesis of 1, allowing to react 6-bromo-2-pyridinecarboxaldehyde (1.2 g, 6.8 mmol) and aniline (0.67 g, 7.2 mmol). The crude product was purified by column chromatography on neutral alumina, using hexane/diethyl ether (1.35 g, 76%). The subsequent reduction reaction with $NaBH_3CN$ gave the amino ligand (1.07 g, 79%).

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 4.45 (br d, 2H, –CH_2), 6.62 (d, *J* = 7.7 Hz, 2H, ArH), 6.73 (t, *J* = 7.1 Hz, 1H, ArH), 7.17 (dd, 2H, ArH), 7.30 (d, *J* = 7.7 Hz, 1H, ArH), 7.38 (t, *J* = 7.7 Hz, 1H, ArH), 7.48 (t, *J* = 7.6 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 50.44 (CH_2), 113.5, 120.64, 123.6, 127.22, 139.30, 142.20, 147.5, 159.13 (Ar–C).

Anal. found (calcd.) for $C_{12}H_{11}BrN_2$ (%): C, 54.59 (54.77); H, 3.81 (4.21); N, 10.68 (10.65).

N-(1-(pyridin-2-yl)ethyl)aniline (**4**). To a stirred solution of the imine ligand (2.15 g, 11.8 mmol, obtained as above) in dry toluene (50 ml) at 0° C, was added dropwise a solution of trimethylaluminium (23.6 mmol) in toluene (20 ml). The mixture was stirred for 30 min at 0 °C, then warmed to room temperature and stirred overnight. The reaction was quenched by adding a sodium hydroxide water solution. The organic phase was separated, while the aqueous phase was extracted with chloroform (2× 50 ml). The organic phases were combined, dried over $MgSO_4$ and the solvent was removed by rotary evaporation. The crude product was dried in vacuum resulting in a pale yellow powder (2.24 g, 96%).

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 1.53 (d, *J* = 6.8 Hz, 3H, –CH_3), 4.63 (q, 2H, –CH), 4.56 (br s, 1H, N*H*), 6.55 (d, *J* = 7.9 Hz, 2H, ArH), 6.58 (t, *J* = 7.6 Hz, 1H, ArH), 7.17 (m, 3H, ArH), 7.42 (d, *J* = 7.9 Hz,1H, ArH), 7.64 (m, 1H, ArH), 8.58 (d, *J* = 4.8 Hz, 1H, *o*-PyH). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 23.43 (CH_3), 54.92 (CH), 113.59, 117.60, 120.53, 122.20, 129.36, 137.11, 147.26, 149.45, 164.07 (Ar–C).

Anal. found (calcd.) for $C_{13}H_{14}N_2$ (%): C, 78.72 (78.75); H, 7.05 (7.12); N, 14.16 (14.13).

Complex 1a. 0.500 g of ligand 1 (2.7 mmol) were dissolved in 20 ml of benzene. To this solution was added dropwise a toluene solution (5 ml) of tetrakis(dimethylamido)zirconium (0.362 g, 1.35 mmol). The resulting dark solution was stirred for 1 h at room temperature. The solvent was then distilled off in vacuo and the resulting powder washed twice with hexane (2× 5 ml). The complex was recrystallized from toluene (0.652 g, 88%).

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 2.80 (s, 6H, –$N(CH_3)_2$), 4.60 (AB pattern, *J* = 19.1 Hz, 2H, –CH_2), 6.66 (t, *J* = 7.1 Hz, 1H, ArH), 7.00–7.24 (m, 6H, ArH), 7.61 (t, *J* = 7.8 Hz, 1H, ArH), 8.16 (d, *J* = 4.8 Hz, 1H, *o*-PyH). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 44.47 ($N(CH_3)_2$), 59.47 (CH_2), 115.78, 116.99, 121.51, 121.89, 128.82, 129.25, 137.73, 148.10, 156.78, 164.39 (Ar–C).

Anal. found (calcd.) for $C_{28}H_{34}N_6Zr$ (%): C, 61.34 (61.61); H, 6.18 (6.28); N, 15.19 (15.40).

Complex 1b. 1b was obtained using a procedure similar to that described for the synthesis of 1a, allowing to react 0.368 g of ligand 1 (2.0 mmol) and tetrakis(dimethylamido)hafnium (0.358 g, 1.0 mmol) in 10 ml of benzene (0.601 g, 95%).

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 2.74 (br s, 6H, –$N(CH_3)_2$), 4.56 (AB pattern, *J* = 18.0 Hz, 2H, –CH_2), 6.59 (t, *J* = 7.3 Hz, 1H, ArH), 6.96–7.03 (m, 4H, ArH), 7.15–7.19 (t, *J* = 7.6 Hz, 2H, ArH), 7.54 (t, *J* = 8.0 Hz, 1H, ArH), 8.15 (d, *J* = 5.1 Hz, 1H, *o*-PyH). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 44.37 ($N(CH_3)_2$), 59.87 (CH_2), 115.93, 117.56, 121.59, 122.06, 128. 74, 137.94, 148.34, 157.17 (Ar–C).

Anal. found (calcd.) for $C_{28}H_{34}N_6Hf$ (%): C, 53.06 (53.12); H, 5.18 (5.41); N, 13.27 (13.19).

Complex 2a. 2a was obtained using a procedure similar to that described for the synthesis of 1a, allowing to react 0.500 g of ligand 2 (2.5 mmol) and tetrakis(dimethylamido)zirconium (0.332 g, 1.25 mmol) in 15 ml of benzene (0.681 g, 95%).

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 2.33 (s, 3H, CH_3), 3.11 (br s, 6H, –$N(CH_3)_2$), 3.74 (d, *J* = 18.9 Hz, 1H, –CH_2), 4.25 (d, *J* = 18.9 Hz, 1H, –CH_2), 6.64 (t, 1H, ArH), 6.71 (d, *J* = 7.7 Hz, 1H, ArH), 7.01 (m, 3H, ArH), 7.22 (d, *J* = 7.2 Hz, 2H, ArH), 7.43 (t, *J* = 7.2 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 22.54 (CH_3), 45.35 ($N(CH_3)_2$), 58.33 (CH_2), 115.76, 116.78, 117.95, 122.30, 128.75, 137.32, 157.52, 159.74, 163.75 (Ar–C).

Anal. found (calcd.) for $C_{30}H_{38}N_6Zr$ (%): C, 62.57 (62.79); H, 6.55 (6.67); N, 14.49 (14.64).

Complex 2b. 2b was obtained using a procedure similar to that described for the synthesis of 1a, allowing to react 0.260 g of ligand 2 (1.31 mmol) and tetrakis(dimethylamido)hafnium (0.232 g, 0.65 mmol) in 15 ml of benzene (0.410 g, 95%).

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 2.37 (s, 3H, CH_3), 3.14 (br s, 6H, –$N(CH_3)_2$), 3.77 (d, *J* = 18.8 Hz, 1H, –CH_2), 4.42 (d, *J* = 18.8 Hz, 1H, –CH_2), 6.64 (t, *J* = 7.2 Hz, 1H, ArH), 6.72 (d, *J* = 7.7 Hz, 1H, ArH), 7.01–7.06 (m, 3H, ArH), 7.25 (m, 2H, ArH), 7.44 (t, *J* = 7.7 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 22.51 (CH_3), 45.10

($N(CH_3)_2$), 58.66 (CH_2), 113.25, 115.79, 117.24, 117.92, 122.49, 128.65, 137.38, 157.99, 160.14 164.03 (Ar–C).

Anal. found (calcd.) for $C_{30}H_{38}N_6Hf$ (%): C, 54.46 (54.50); H, 5.38 (5.79); N, 12.69 (12.71).

Complex 3a. 3a was obtained using a procedure similar to that described for the synthesis of 1a, allowing to react 0.500 g of ligand 3 (1.9 mmol) and tetrakis(dimethylamido)zirconium (0.253 g, 0.95 mmol) in 18 ml of benzene. The complex was recrystallized from CH_2Cl_2 (0.528 g, 79%).

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 2.97 (br s, 6H, –$N(CH_3)_2$), 4.59 (br s, 2H, CH_2), 6.62 (t, J = 7.0 Hz, 1H, ArH), 6.93 (d, J = 7.8 Hz, 2H, ArH), 7.11 (d, J = 7.4 Hz, 1H, ArH), 7.13 (m, 2H, ArH), 7.35 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 43.93 ($N(CH_3)_2$), 58.40 (CH_2), 113.24, 116.93, 117.97, 120.14, 127.00, 128.32, 129.51, 138.82, 141.85, 148.29, 156.23, 166.19 (Ar–C).

Anal. found (calcd.) for $C_{28}H_{32}Br_2N_6Zr$ (%): C, 47.72 (47.80); H, 4.31 (4.58); N, 12.00 (11.94). C, 47.80; H, 4.58; N, 11.94%.

Complex 3b. 3b was obtained using a procedure similar to that described for the synthesis of 1a, allowing to react 0.427 g of ligand 3 (1.62 mmol) and tetrakis(dimethylamido)hafnium (0.287 g, 0.81 mmol) in 18 ml of benzene. The complex was recrystallized from CH_2Cl_2 (0.468 g, 73%).

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 3.10 (br s, 6H, –$N(CH_3)_2$), 4.69 (s, 2H, –CH_2), 6.64 (t, J = 7.2 Hz, 1H, ArH), 6.96 (d, J = 7.7 Hz, 2H, ArH), 7.05 (m, 1H, ArH), 7.16 (m, 2H, ArH) 7.36 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$, 400 MHz, 298 K): δ 43.66 ($N(CH_3)_2$), 58.76 (CH_2), 117.21, 118.71, 120.09, 127.20, 128.23, 138.82, 156.43, 166.36 (Ar–C).

Anal. found (calcd.) for $C_{28}H_{32}Br_2N_6Hf$ (%): C, 42.46 (42.52); H, 3.98 (4.08); N, 10.69 (10.63).

Complex 4a. 0.700 g of ligand 4 (3.52 mmol) were dissolved in 20 ml of benzene. To this solution was added dropwise a benzene solution (5 ml) of tetrakis(dimethylamido)zirconium (0.470 g, 1.76 mmol). The resulting solution was stirred for 5 h at room temperature. The solvent was then distilled off in vacuo and the resulting powder was washed twice with hexane (2× 5 ml). The complex was recrystallized from dichloromethane/hexane (0.500 g, 50%).

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 1.45 (d, J = 6.3 Hz, 3H, CH_3), 2.51 (br s, 6H, –$N(CH_3)_2$), 5.21 (m, 1H, –CH), 6.57 (t, J = 7.0 Hz, 1H, ArH), 6.78 (t, J = 6.5 Hz, 1H, ArH), 6.94 (d, J = 8.0 Hz, 2H, ArH), 7.09 (dd, J = 7.0 Hz, 2H, ArH), 7.18 (d, J = 7.5 Hz, 1H, ArH), 7.49 (t, J = 7.5 Hz, 1H, ArH), 8.05 (d, J = 4.2 Hz, 1H, *o*-Py). ^{13}C NMR ($CDCl_3$, 400 MHz, 298 K): δ 22.75 (CH_3), 44.53 ($N(CH_3)_2$), 64.05 (CH), 115.98, 119.31, 121.73, 128.10, 137.81, 149.05, 156.37, 168.64 (Ar–C).

Anal. found (calcd.) for $C_{30}H_{38}N_6Zr$ (%): C, 62.69 (62.79); H, 6.58 (6.67); N, 14.69 (14.64).

2.3. Line shape and Eyring analysis

Variable-temperature ^{1}H NMR experiments were performed on a Bruker AVANCE 400 in $CD_3C_6D_5$ using NMR tubes equipped with J Young valves. NMR spectral simulations were performed using the gNMR Simulation Package by Budzelaar [14]. The activation parameters for the processes were obtained using the linear form of the Eyring equation:

$$\ln \frac{k}{T} = \frac{-\Delta H^{\neq}}{R} \cdot \frac{1}{T} + \frac{k_B}{h} + \frac{\Delta S^{\neq}}{R}$$

where k is the exchange rate constant, k_B is the Boltzmann constant and h is the Plank constant. Estimated standard deviation (σ) in the slope and y intercept of the Eyring plot determined the error in $\Delta H^{\neq}$ and $\Delta S^{\neq}$, respectively. The standard deviation in $\Delta G^{\neq}$ was determined from the formula $\sigma^2(\Delta G^{\neq}) = \sigma^2(\Delta H^{\neq}) + T^2\sigma^2(\Delta S^{\neq}) - 2T\sigma(\Delta H^{\neq})\sigma(\Delta S^{\neq})$.

2.4. 2D DOSY -^{1}H NMR experiments details

2D DOSY NMR experiments for diffusion measurements were performed for complex 1a and complex 3a (C_6D_6, 6.0 mM) on a Bruker Avance 400 spectrometer, equipped with a 5 mm Multinuclear inverse Z-grad z8202/104 probe, at 298 K without spinning of the sample. The measurements of diffusion has been carried out by using 2D sequence for diffusion measurement using stimulated echo (STE) with bipolar gradients (BPP) pulses and longitudinal eddy current delay (LED) [15]. The shape of the gradients was rectangular, their duration (δ) was 1.1 ms and their strength (G) has been varied during the experiments. All spectra have been obtained using 32 K points and a spectral width of 5000 Hz. Tetrakis-(trimethylsilyl)silane (TMSS; r_H (hydrodynamic radius) $\approx r_{vdW}$ (van der Waals radius) = 4.28 Å) was added as internal standard (6.0 mM) to account for possible changes in solution viscosity, temperature, and gradient strength. The most intense signals (methyl protons of the dimethylamide ligands) were investigated for both complexes. The dependence of the resonance intensity (I) on the gradient strength (G) is described by the following equation:

$$I = I_0 \quad \exp\left\{-D\gamma^2 G\delta^2\left(\Delta - \frac{\delta}{3}\right)\right\}$$

where I is the observed intensity (attenuated signal intensity), I_0 is the reference intensity (unattenuated signal intensity), D is the diffusion coefficient, γ is the nucleus gyromagnetic ratio, G is the gradient strength, δ is the gradient duration, and Δ is the diffusion delay. The parameters δ and Δ were kept constant during the experiments, whereas G varied from 2 to 95% in 16 steps. The values of Δ were 1300 and 1200 μs for 1a and 3a, respectively.

A nonlinear regression on I and G^2 data was performed to obtain the coefficients D for both the samples and the corresponding internal standard signals (D^{sample} and D^{TMSS}, respectively). The following expression (on the basis of the Stokes–Einstein equation) was applied and numerically resolved to get the hydrodynamic radius of each sample

$$\frac{D^{sample}}{D^{TMSS}} = \frac{c^{TMSS} r_H{}^{SS}}{c^{sample} r_H{}^{sample}}$$

The coefficients c^{sample} and c^{TMSS} can be estimated from the semiempirical equation [16]

$$c^x = \frac{6}{(1 + 0.695 r^{solv}/r_H{}^x)^{2.234}}$$

where x is the sample or TMSS, and $r^{solv} \approx$ van der Waals radius of the solvent (2.7 Å for C_6D_6). Hydrodynamic volumes were calculated from the respective radii: $V_H = 4/3\pi\,(r_H)^3$.

The van der Waals volumes (V_{vdW}) [17] for 1a and 3a were computed for DFT optimized structures using the software package DS Viewer Pro 5.0 (Table 1).

2.5. Polymerizations

Ethylene and propene polymerizations were performed into a 500 ml Büchi glass autoclave. The reactor vessel was charged sequentially with MAO and a solution of the pre-catalyst in toluene (2 ml), pre-aged for 10 min with a toluene solution of Al*i*Bu_2H. The mixture was thermostated at the required temperature and the monomer gas feed was started and maintained at constant pressure during the run. After the required polymerization time, the mixture was poured into acidified ethanol. The polymers were recovered by filtration, and dried at 40 °C under vacuum. The polymers were recovered by filtration, and dried at 40 °C under vacuum. The main

Table 1
Calculated van der Waals volumes (V_{vdW}) for 1a and 3a.

Complex	Δ (P30)	D^{1a} ($\times 10^{-10}$ m^2/s)	D^{TMSS} ($\times 10^{-9}$ m^2/s)	r_H (Å)	V_H (Å^3)
1a	1300	7.03	1.12	5.86	840.38
3a	1200	7.07	1.17	5.85	836.08

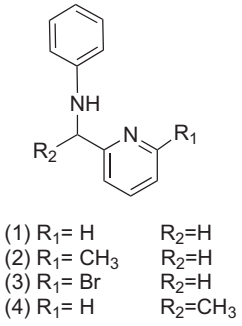
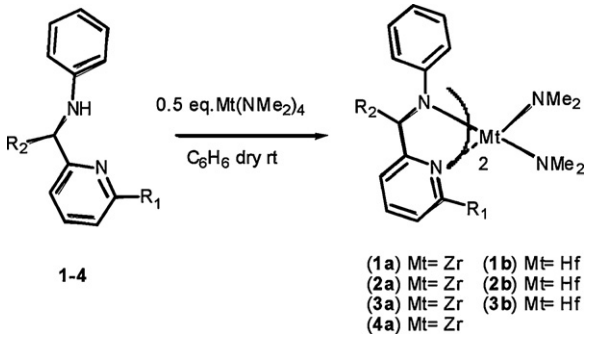


Chart 1. Schematic representation of ligands 1–4.



Scheme 1. General synthetic scheme for complexes 1a–4a and 1b–3b.

conditions and results of ethylene polymerizations are reported in Table 4, while those of propene polymerizations are reported in the supplementary materials.

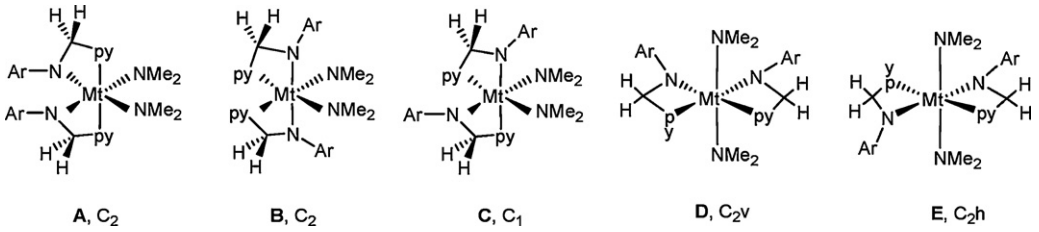
3. Results and discussion

The ligands 1–4 were prepared by condensation reactions between *ortho*-substituted anilines and the proper pyridinecarboxyaldehyde, followed by either reduction ($NaBH_3CN$) or reductive methylation ($AlMe_3$), and then hydrolysis (Chart 1).

The corresponding bis(dimethylamido) zirconium (IV) and hafnium(IV) complexes were prepared by reaction of 2 equiv. of the ligand and tetrakis(dimethylamido)zirconium or tetrakis(dimethylamido)hafnium in benzene, producing complexes 1a–4a and 1b–3b in good yields (60–90%) as yellow-brown powders (Scheme 1). The ligands and the complexes were characterized by elemental analysis and ^{1}H and ^{13}C NMR spectroscopy. For octahedral bis(chelate) complexes 1a–3a and 1b–3b five isomers are possible, three of which (A-C) are chiral while the other two (D, E) are not (Scheme 2). ^{1}H NMR analysis provided significant information on the solution structures of the complexes.

The ^{1}H NMR spectrum of 1a showed, at room temperature, a pattern of signals attributable to a C_2-symmetric species (isomer A or B of Scheme 2), as indicated by the presence of one singlet at 3.14 ppm for the two dimethylamido groups and one set of signals for the remaining protons of the two ligands, with the Py-CH_2-NAr methylene resonance appearing as a pair of AB doublets. Variable temperature NMR analysis between 298 and 353 K showed coalescence of the AB pattern of the methylene group in a singlet, while all other resonances sharpened, indicating the occurrence of a fluxional equilibrium involving enantiomer interconversion at high temperature (see Fig. 1). Kinetic parameters were calculated for complex 1a using line shape analysis of the ^{1}H NMR data measured over the temperature range 298–353 K. The free energy of activation associated to the fluxional process was calculated to be $\Delta G^{\neq} = 16.39 \pm 0.04$ kcal mol^{-1} at 298 K. Activation parameters resulted to be $\Delta H^{\neq} = 14.6 \pm 0.3$ kcal mol^{-1} and $\Delta S^{\neq} = -6.1 \pm 0.5$ cal mol^{-1} K^{-1}. Exchange phenomena in octahedral complexes may occur either *via* a dissociative mechanism, involving metal-donor atom bond rupture, or *via* a non-dissociative mechanism, involving a trigonal twist with retention of the six-coordinated geometry [18]. For instance, a dynamic interchange mechanism, involving N-pyridine bond cleavage and formation of a configurationally labile five-coordinate intermediate, was previously proposed for bis(8-quinolato) group 4 metal alkoxide [19] and alkyl [20] complexes, and, more recently, for bis(amidopyridine)zirconium complexes [12b]. In the latter case, *N*-pyridine dissociation is promoted by the presence of *trans* dimethylamide, a strong *trans* directing ligand [12b]. On the other hand, for several other bis(chelate) octahedral complexes a non-dissociative mechanism was proposed on the basis of the observed negative values of the entropy of activation [21–23]. The latter mechanism could be operative also for complex 1a, based on the negative $\Delta S^{\neq}$ value. The different behavior with respect to the above mentioned closely related bis(amidopyridine)zirconium complexes [12b] could be justified hypothesizing the preferential formation of isomer A, having mutually *trans* pyridine ligands (which would also agree with the higher stereo rigidity at room temperature).

The solution structure of hafnium complex 1b is similar to that of 1a, as indicated by VT ^{1}H NMR analysis: in particular, the Py-CH_2-NAr methylene resonance appears as a pair of AB doublets at room temperature and becomes a sharp singlet upon increasing the temperature up to 353 K, with $\Delta G^{\neq} = 14.6 \pm 0.2$ kcal mol^{-1} at 298 K. Calculated activation parameters are $\Delta H^{\neq} = 12.4 \pm 0.3$ kcal mol^{-1} and $\Delta S^{\neq} = -7.5 \pm 0.5$ cal mol^{-1} K^{-1}.



Scheme 2. Representation of the five possible isomers for octahedral complexes 1a–3a and 1b–3b.

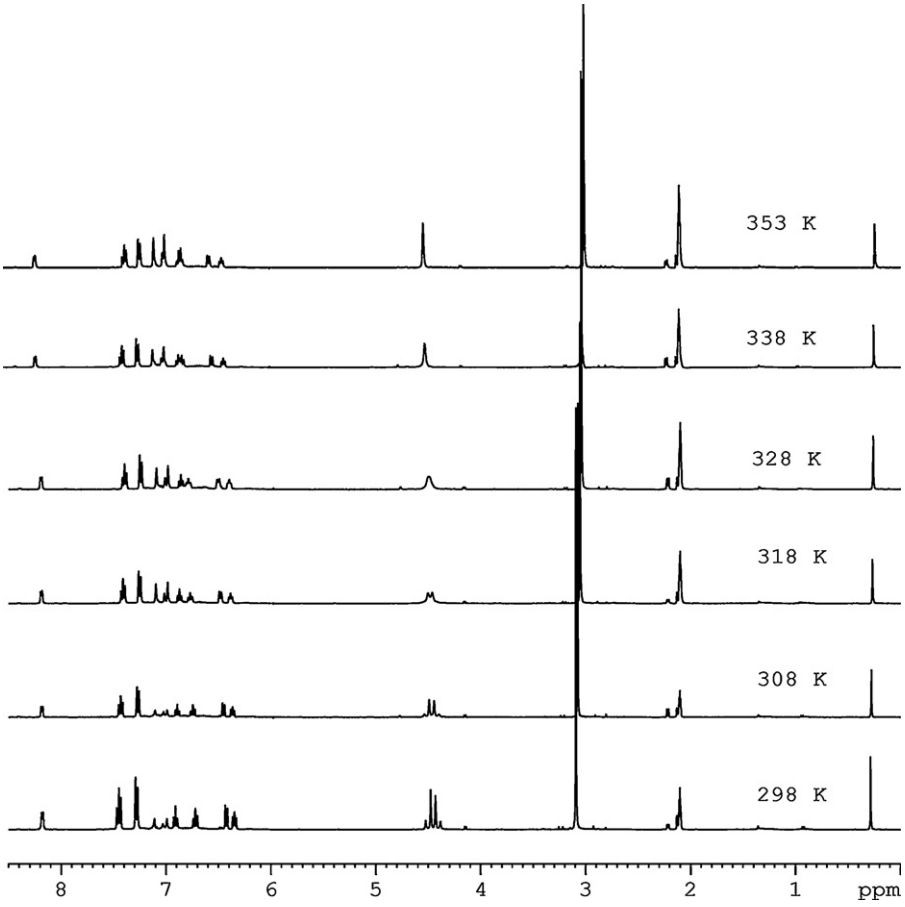


Fig. 1. ^{1}H NMR spectra of the complex 1a at variable temperature ($CD_3C_6D_5$).

The room temperature ^{1}H NMR spectra of compounds 2a and 2b also showed patterns of signals indicative of C_2 symmetric structures (A or B isomers), with the Py-CH_2-NAr methylene resonance appearing as AB systems. In these cases, however, the ^{1}H NMR spectra remain substantially unchanged also increasing the temperature up to 353 K, suggesting a higher stereorigidity of 2a and 2b vs. 1a and 1b, reasonably as a consequence of the introduction of a methyl substituent in the *ortho*-position of the pyridine ring. In agreement with this hypothesis, the ^{1}H NMR spectra of both 2a and 2b resulted unchanged at low temperature (193 K).

The room temperature ^{1}H NMR spectra of compounds 3a and 3b showed, in both cases, a single set of sharp resonances. In particular, The Py-CH_2-NAr methylene signals appeared as sharp singlets at 4.6 and 4.7 ppm, respectively. Variable-temperature NMR analysis between 193 and 353 K did not show any significant change in the spectra, suggesting that 3a and 3b are in the fast exchange regime in this range of temperatures, or, less probably, that symmetric isomers are preferentially formed. The same behavior was previously observed for the analogous bis (perfluorophenyl)methylamido-6-bromopyridine)zirconium(IV) bis(dimethylamide) complex [13], and could be related to the lower basicity of bromo-pyridine.

Following the suggestion by a reviewer that the fluxional processes observed in solution may involve the formation of dimers (or higher aggregates), we analyzed complexes 3a (which is fluxional) and, for comparison, complex 1a (which is stereorigid at room temperature) by 2D DOSY ^{1}H NMR measurements. This NMR technique provides information of the translational diffusion coefficient of the molecular species in solution and it has been successfully used for characterizing various organometallic systems and supramolecular structures in solution, including ones involved in monomer/dimer equilibria [24–26]. The 2D DOSY ^{1}H NMR method assesses translational motion of the analyte in solution through determination of the diffusion coefficient, a quantity inversely related to its effective hydrodynamic volume. The diffusion coefficients (D) can be related to the hydrodynamic radius (r) of the species in solution by the Stokes–Einstein equation (Eq. (1)) where T is the temperature, η is the viscosity of the solvent, r is the hydrodynamic radius of the molecule or assembly, and K is the Boltzmann constant.

$$D = \frac{KT}{6\pi\eta r} \quad (1)$$

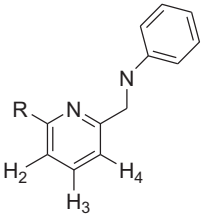
The diffusion coefficients of both species (3a and 1a) have been determined in analogous 2D DOSY ^{1}H experiments in C_6D_6 with identical solvent viscosity and at the same temperature. Since the other parameters are identical, the size of the corresponding species can be compared based on their diffusion coefficients. The experimentally determined values of D and r_H and the calculated ones for both complexes are listed in Table 2.

The close agreement between the D and r_H data evaluated for solutions of the two complexes suggests that 3a is very similar in size to the monomeric species 1a. For comparison, the hydrodynamic radii determined from experimental 2D DOSY ^{1}H results for

Table 2
2D DOSY ^{1}H experimental results compared to estimated data from DFT optimized structures.

Complex	D ($\times 10^{-10}$ m^2 s^{-1})	r_H (Å)	V_H (Å^3)	r' (Å)
1a	7.03	5.86	842.48	6.25
3a	7.07	5.85	838.18	6.21

Table 3
Chemical shift (ppm) for the aromatic proton H_4 in the free ligand and complexes ($CDCl_3$, 298 K).



Ligand	$\delta(H_4)$	Complex	$\delta(H_4)$	$\Delta\delta(H_4)$[a]
1	7.33	1a	7.02	0.31
		1b	6.97	0.36
2	7.05	2a	6.70	0.35
		2b	6.62	0.43
3	7.30	3a	7.11	0.19
		3b	7.16	0.14
4	7.42	4a	7.18	0.24

[a] $\Delta\delta(H_4) = \delta(H_4)_{\text{free ligand}} - \delta(H_4)_{\text{complex}}$.

1a and 3a were compared with the molecular radii (r', Table 2) estimated from DFT optimized structures by measuring the lengths between centers of distant hydrogen atoms on the molecular periphery. The good agreement observed supported the hypothesis of the monomeric nature of 3a in solution at room temperature. This was also confirmed by the comparison of the hydrodynamic and calculated volumes of complexes 1a and 3a (assuming that they have a spherical shape) with the volume of an analogous complex [13] calculated from X-ray crystal structure by dividing the crystallographic unit cell volume by the number of molecular entities contained in the unit cell (775.93 Å^3). In conclusion, these experiments suggest that the dynamic processes observed in solution for complex 3a are not attributable to monomer/dimer equilibration and more reasonably can be related to intramolecular rearrangements.

An indication of the weaker coordination of the pyridine moiety to the metal center in complexes 3a and 3b vs. e.g. 2a and 2b came from analysis of the chemical shift difference, $\Delta\delta$, of the aromatic protons of the pyridine moiety in the free ligands and in the complexes [27]. The calculated values for the aromatic proton H_4 are reported in Table 3. For instance, the chemical shift difference in the free ligand 2 and in the corresponding zirconium complex 2a, for which we know that the pyridine nitrogen is strongly coordinated, is 0.35 ppm, while in the case of 3 and 3a resulted to be only 0.19 ppm. For the Hf complexes, $\Delta\delta$ is 0.43 for 2 vs. 2b, while is only 0.14 for 3 vs. 3b. These findings agree with the hypothesis that complexes 3a and 3b are in fast fluxional equilibrium in solution due to a weaker coordination of bromopyridine. In general, the trend of the $\Delta\delta$ values is in nice agreement with the VT NMR analysis, i.e. with the stereorigidity increasing in the order 3a,b < 1a,b < 2a,b.

The ^{1}H NMR spectrum of complex 4a, bearing a chiral center on the ligand framework, showed one singlet at 2.50 ppm for the two dimethylamide ligands and one set of signals for the protons of the two chelating ligands. This picture suggests that interconversion between different isomers of 4a is fast on the NMR timescale at room temperature. The $\Delta\delta$ value (0.24 ppm) in this case is slightly higher than that observed for (fluxional) 3a, but lower than that of (stereorigid) 1a. Variable-temperature ^{1}H NMR studies between 298 and 193 K showed little change in the main pattern of signals, consisting in a broadening of the resonances and the appearance of some additional minor resonances, possibly arising from other diastereomers.

3.1. Polymerizations

All the complexes were tested as pre-catalysts for the polymerization of ethylene under 6 atm of monomer pressure using different activators. The obtained polymers were characterized by NMR spectroscopy, DSC and GPC analyses. The main polymerization conditions and results are collected in Table 4.

Polymerization of ethylene resulted in all cases in the production of linear polyethylenes (m.p. = 133–137 °C), with moderate to good activities. Several co-catalysts were tested in combination with complex 1a (runs 1–3, 6, Table 4): use of methylalumoxane (MAO) alone resulted in very poor activity, probably owing to difficult alkylation of 1a by MAO, as previously observed for other dimethylamido complexes [28]. On the contrary, a mixture of Al^iBu_2H and MAO was a very efficient activator. The less reactive dimethylamido zirconium complexes require the presence of Al^iBu_2H to generate the Zr–H or Zr–alkyl bonds where the polyinsertion may start. The reaction between Al^iBu_2H and dimethylamido zirconium catalysts has been previously studied by Kim for rac-[ethylen-1,2-bis(1-indenyl)zirconium(IV)bis(dimethylamido)] complex which, in combination with Al^iBu_2H, produced zirconium hydride complex [28c]. Al^iBu_2H alone and the mixtures of Al^iBu_2H and $[CPh_3][B(C_6F_5)_4]$ did not result in good catalytic activity. Thus, the

Table 4
Ethylene polymerization conditions and results.

Run[a]	Pre-catalyst	Co-catalyst	T (°C)	Activity[b]	T_m (°C)	M_w ($\times 10^3$)	M_w/M_n
1	1a	MAO	25	0.4	133	N.d.	N.d.
2	1a	Al^iBu_2H	25	1.2	134	826	3.9
3[c]	1a	Al^iBu_2H/MAO	25	78.5	137	1324	3.4
4[c]	1a	Al^iBu_2H/MAO	50	94.3	136	2113	5.5
5[d]	1a	Al^iBu_2H/MAO	75	255	135	831	6.6
6[e]	1a	$Al^iBu_2H/[CPh_3][B(C_6F_5)_4]$	50	3.0	136	1057	2.5
7	2a	Al^iBu_2H/MAO	25	16.9	134	1019	2.6
8	3a	Al^iBu_2H/MAO	25	15.3	135	2492	2.1
9	4a	Al^iBu_2H/MAO	25	34.8	135	2356	2.4
10	1b	Al^iBu_2H/MAO	25	4.8	134	1466	3,6
11	2b	Al^iBu_2H/MAO	50	2.4	134	3052	2.4
12	3b	Al^iBu_2H/MAO	50	1.2	134	580	9.1
13[f]	3b	Al^iBu_2H/MAO	75	64.6	134	N.d.	N.d.

[a] Conditions: pre-catalyst = 20 μmol; Al^iBu_2H/Mt = 30; $Al_{(MAO)}$/Mt = 1000; ethylene pressure = 6 atm; toluene = 90 ml; time = 60 min. MAO dried obtained by distilling off the solvent from the commercial solution.
[b] Activity = kg of polymer × (mol of Mt × h × atm)$^{-1}$.
[c] Time = 30 min.
[d] Time = 10 min.
[e] Time = 90 min, $[CPh_3][B(C_6F_5)_4]$ = 1.1 equiv.
[f] Pre-catalyst = 10 μmol; time = 10 min.; n.d. = not determined.

Al^iBu_2H/MAO co-catalyst system was used to activate all the complexes.

The activity of the system 1a/Al^iBu_2H/MAO was tested at different temperatures: the activity increases while the temperature increases from 25 to 75 °C (runs 3–5, Table 4).

The activities of the complexes are significantly affected by the substituents (Scheme 1, R_1 and R_2) of the ligand: zirconium complexes 2a and 3a, bearing *ortho* substituents on the pyridine moiety, afforded less active catalyst than 1a (cf. runs 3, 7, 8, Table 4). Compound 4a, which differs from 1a only for the presence of a methyl group on the carbon in α position respect to the amido nitrogen of the ligand, also showed a lower activity (cf. runs 3 and 9, Table 4).

Anyway, all complexes resulted more active (40–50% increased activity) than the previously reported octahedral zirconium complexes bearing perfluorophenylaminomethylpyridine ligands [13]. This finding has precedent in the behavior of metallocene catalysts for which a reduced activity was generally observed as a consequence of introducing electron-withdrawing substituents in cyclopentadienyl (Cp) ligands [29]. On the contrary, for bis(phenoxy-imine) group 4 metal complexes the opposite effect was often observed [30].

The bis(amidomethylpyridine)hafnium(IV) complexes 1b–3b afforded much less active catalysts than the corresponding zirconium complexes 1a–3a; however, complex 3b becomes significantly more active at 75 °C (run 13, Table 4).

Analysis of the polymer samples by GPC revealed in any case high molecular weights with molecular weight distributions ranging between those expected for a single site catalyst (cf. runs 7–9, Table 4) and much broader ones (cf. runs 5, 10, 12, Table 4), depending on the pre-catalyst and the polymerization temperature. This behavior could be related to the fluxional character of the complexes, leading to different catalytic species in solution, depending on the reaction conditions [13,23,29c], and/or to chain transfer to Al proceeding with different rates under different conditions [31].

Polymerizations of propene were also carried out at a monomer pressure of 6 atm, by using Al^iBu_2H/MAO as the activator. All the complexes resulted poorly active, affording substantially stereoirregular, high molecular weight polymers. E.g., catalyst 1a produced at 25 °C a stereoirregular, slightly syndiotactic-enriched ([*rr*] = 36%) polypropylene, having 16% regioinversions [32]. Complexes 2a and 3a afforded even less active catalysts than 1a, producing more regioregular (3% regioinverted units) atactic polypropylene, and slightly isotactic-enriched, very regioregular polypropylene ([*mm*] = 40%), respectively. The hafnium complexes 1b–3b also showed very low activities, producing, in all cases, regioregular atactic polymers (see supplementary material). The poor activities with respect to ethylene polymerizations, as well as the different molecular weight distributions, could be also related to the poor regiospecificity of propene insertion, resulting in a significant fraction of "dormant" or less reactive propagating species.

4. Conclusions

In this work, several 2-anilidomethylpyridine ligands and the corresponding bis(chelate) zirconium and hafnium complexes $L_2Mt(NMe_2)_2$ have been synthesized and characterized. Variable temperature NMR analysis showed that the complexes have a more or less fluxional behavior in solution, depending on the substituent in the *ortho* position of the pyridine moiety: thus, complexes 1a and 1b, bearing the simple unsubstituted 2-anilidomethylpyridine ligand, are stereorigid at room temperature on the NMR time scale and become fluxional at higher temperatures, while complexes 2a and 2b, bearing a methyl substituent, are stereorigid even at high temperature, and finally complexes 3a and 3b, bearing a Br substituent, are in fast fluxional equilibrium even at −80 °C, possibly due to a weaker coordination of bromopyridine. All complexes after activation with Al^iBu_2H/MAO efficiently promoted the polymerization of ethylene, producing polymers with generally broad molecular weight distributions. The molecular weight distributions of the polymers are narrower for the more stereorigid complexes. In general, hafnium complexes resulted less active than their zirconium analogues. The activities of the bis(chelate) Zr complexes reported here are significantly higher than those of the previously reported complexes bearing perfluorophenylamidopyridine ligands [13], indicating a deleterious effect of electron-withdrawing substituent on the activity of this class of catalysts, as previously observed for metallocene catalysts. The same catalytic systems were tested also in the polymerization of propene, resulting in rather poor performance in terms of activities, stereo- and regiospecificities. Extension of these studies to other complexes bearing ligands of this class for the polymerization of olefins as well as of other unsaturated hydrocarbon monomers are in progress and will be reported subsequently.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2011.01.004

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