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Zirconium and hafnium complexes with new tetra-azane ligands: Synthesis, characterization and catalytic properties for ethylene polymerization

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ABSTRACT

Two new anilido-imine tetra-azane ligands, 1,2-[(2′-(ArNH)C_6H_4HC=N)]$_2C_6H_4$ (Ar = 2,6-$Me_2C_6H_3$ (**L**^{1}H_2) and 2,6-^{i}$Pr_2C_6H_3$ (**L**^{2}H_2)), were synthesized by the condensation reaction of *o*-phenylenediamine with the corresponding 2-(arylamino)benzaldehyde, and their zirconium and hafnium complexes, **L**^{1}MCl_2 (M = Zr (**1b**), Hf (**1c**)) and **L**^{2}MCl_2 (M = Zr (**2b**), Hf (**2c**)), were synthesized in high yields (61–66%) by the reactions of **L**^{1}Li_2 and **L**^{2}Li_2 with MCl_4 in toluene. Direct HCl-elimination reactions of **L**^{1}H_2 with MCl_4 (M = Ti, Zr, Hf) in toluene at 140 °C under vacuum afforded the products **L**^{1}$HMCl_3$ [M = Ti (**1a**′), Zr (**1b**′), Hf (**1c**′)] with a partially deprotonated tridentate ligand in good to high yields (48–70%). All the new complexes were characterized by ^{1}H and ^{13}C NMR spectroscopy and the molecular structures of **1b** and **2c** were determined by single crystal X-ray diffraction analysis. The metal centers in both complexes are six-coordinated with a distorted octahedral geometry. Upon activation with MAO or AlR_3/$Ph_3CB(C_6F_5)_4$, complexes **1b**–**1c** and **2b**–**2c** all exhibit moderate catalytic activity for ethylene polymerization and produce linear polyethylene with ultra-high molar masses (100–184 × 10^4 g/mol).

1. Introduction

Non-metallocene complexes of early transition metals as catalysts have attracted considerable attention in recent years as high performance catalysts for olefin polymerization reactions in both academic and industrial communities due to their easy preparation and structural modification [1–3]. A large number of complexes bearing didentate and tridentate chelating ligands with N, O, P and S donors have been developed and their catalytic properties been studied [4–7]. Early transition metal complexes carrying different tetradentate ligands have also been extensively investigated [8]. Especially, some group 4 metal complexes with tetradentate ligands have been found to show good catalytic properties for various olefin polymerization reactions [9]. For examples, group 4 metal complexes supported by a salen-type ligand were reported to be efficient catalysts for the polymerization reactions of ethylene, propylene and α-olefin [10]. Titanium and zirconium complexes bearing a C_2-symmetric salan ligand were found to catalyze the polymerization of 1-hexene, 4-methyl-1-pentene and 1,5-hexadiene [11]. Group 4 metal complexes with a salalen ligand were also studied as catalysts for ethylene, propylene and 1-hexene polymerization reactions [12]. Titanium and zirconium complexes with a chiral bipyrrolidine/bisphenolato-based salan ligand have been reported to show relatively high isospecific selectivity in 1-hexene polymerization [13]. Group 4 metal complexes carrying a [OSSO] ligand have also been systematically investigated for ethylene and 1-hexene polymerization [14]. In recent years, we have synthesized some main group and transition metal complexes supported by an anilido-imine type of ligand [15]. So far, bi-, tri- and tetra-dentate ligands containing the anilido-imine unit(s) have been developed. We have previously synthesized some chiral rare-earth metal complexes with tetra-azane chelating ligands, (1R,2R)-*N*,*N*′-bis(ortho-arylaminobenzylidene)-1,2-diaminocyclohexane, and investigated their catalytic properties for the intramolecular asymmetric hydroamination reaction of terminal aminoalkenes [16]. To extend the chemistry of this type of ligand, we have now synthesized two new achiral tetra-azane ligands, 1,2-[(2′-(ArNH)C_6H_4HC=N)]$_2C_6H_4$ [Ar = 2,6-$Me_2C_6H_3$ (**L**^{1}H_2), 2,6-^{i}$Pr_2C_6H_3$ (**L**^{2}H_2)], and their zirconium and hafnium complexes, **L**^{1}MCl_2 [M = Zr (**1b**), Hf (**1c**)] and **L**^{2}MCl_2 [M = Zr (**2b**), Hf (**2c**)], and have studied the catalytic performances of the new complexes for ethylene polymerization. It was found that these new Zr and Hf complexes, upon activation with MAO or AlR_3/$Ph_3CB(C_6F_5)_4$, show moderate catalytic activity for ethylene polymerization and produce linear polyethylene with ultra-high

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molar masses (viscosity-averaged molecular weight M_η up to 184×10^4 g/mol). In addition, in an attempt to develop a new synthetic method for the new complexes, complexes $\mathbf{L^1}HMCl_3$ [M = Ti (**1a**′), Zr (**1b**′), Hf (**1c**′)], with a partially deprotonated tridentate ligand, were obtained in good to high yields (48–70%) from the one-pot HCl elimination reactions of MCl_4 with $\mathbf{L^1}H_2$. In the present paper, we report these results in detail.

2. Experimental

2.1. General considerations

All manipulations involving air- and/or moisture-sensitive compounds were carried out under a nitrogen atmosphere using either standard Schlenk or glove box techniques. Toluene and *n*-hexane were dried over sodium/benzophenone and distilled under nitrogen prior to use. CH_2Cl_2 was dried and distilled over calcium hydride before use. Polymerization grade ethylene was further purified by passage through columns of 4 Å molecular sieves and MnO. $TiCl_4$, $ZrCl_4$, $HfCl_4$, *n*-BuLi, *o*-phenylenediamine, $Pd(OAc)_2$, NaO^tBu, DPEphos, 2,6-dimethylaniline and 2,6-diisopropylaniline were purchased from Aldrich or Acros. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance III-400 NMR spectrometer at room temperature in $CDCl_3$. ^{13}C NMR spectra of the polyethylenes were recorded at 135 °C with *o*-$C_6D_4Cl_2$ as the solvent. The elemental analysis was performed on a Vario EL cube analyzer. The intrinsic viscosity (η) values of the polyethylenes were measured in decahydronaphthalene at 135 °C using an Ubbelohde viscometer. Viscosity average molecular weight [17] (M_η) values of the polyethylenes were calculated according to the following equation: $[\eta] = (6.77 \times 10^{-4})\ M_\eta^{0.67}$. The melting points of the polyethylenes were measured by differential scanning calorimetry (DSC) on a NETZSCH DSC 204 at a heating/cooling rate of 10 °C/min from 35 to 160 °C and the data from the second heating scan were used. 2-(2′,6′-Dimethylphenylamino)-benzaldehyde, 2-(2′,6′-diisopropylphenylamino)benzaldehyde [18] and $Ph_3CB(C_6F_5)_4$ [19] were prepared according to the literature procedures.

2.2. Synthesis of the compounds

2.2.1. Synthesis of 1,2-[(2′-(2″,6″-$Me_2C_6H_3NH$)C_6H_4 C═N)]$_2C_6H_4$ ($\mathbf{L^1}H_2$)

To a solution of 2-(2′,6′-dimethylphenylamino)benzaldehyde (2.25 g, 10.0 mmol) and *o*-phenylenediamine (0.54 g, 5.0 mmol) in toluene was added *p*-TsOH (0.10 g) at room temperature. The mixture was refluxed with a Dean–stark trap for 10 h, cooled to room temperature and the solvent was then removed by rotary evaporation to give a deep yellow solid. The crude product was purified by column chromatography on silica gel eluting with ethyl acetate/petroleum ether (v/v = 1:15, 1% Et_3N) to give the pure product (2.11 g, 4.04 mmol, 81%). *Anal.* Calc. for $C_{36}H_{34}N_4$ (522.28): C, 82.72; H, 6.56; N, 10.72. Found: C, 82.70; H, 6.52; N, 10.89%. ^1H NMR (400 MHz, $CDCl_3$, 298 K, δ, ppm): 10.34 (s, 2H, N*H*), 8.62 (s, 2H, C*H*═NAr), 7.04–7.28 (m, 14H, Ar*H*), 6.58 (t, J = 12 Hz, 2H, Ar*H*), 6.19 (d, J = 8.4 Hz, 2H, Ar*H*), 1.95 (s, 12 H, ArCH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K, δ, ppm): 165.31, 148.21, 144.01, 137.47, 136.53, 134.69, 132.10, 128.17, 126.08, 125.78, 121.63, 117.18, 115.47, 111.72, 18.12.

2.2.2. Synthesis of 1,2-[(2′-(2″,6″-^{i}Pr$_2C_6H_3NH$)C_6H_4HC═N)]$_2C_6H_4$ ($\mathbf{L^2}H_2$)

$\mathbf{L^2}H_2$ was synthesized in the same way as described above for the synthesis of $\mathbf{L^1}H_2$ with 2-(2′,6′-diisopropylphenylamino)benzaldehyde (2.81 g, 10.0 mmol) and *o*-phenylenediamine (0.54 g, 5.0 mmol) as the starting materials. After the crude product was purified by column chromatography on silica gel eluting with ethyl acetate/petroleum ether (v/v = 1:15, 1% Et_3N), 2.36 g of pure product (3.72 mmol, 74%) was obtained. *Anal.* Calc. for $C_{44}H_{50}N_4$ (634.40): C, 83.24; H, 7.94; N, 8.82. Found: C, 83.20; H, 7.86; N, 8.78%. ^1H NMR (400 MHz, $CDCl_3$, 298 K, δ, ppm): 10.32 (s, 2H, N*H*), 8.65 (s, 2H, C*H*═NAr), 7.04–7.28 (m, 14H, Ar*H*), 6.58 (t, J = 16 Hz, 2H, ArH), 6.14 (d, J = 8.4 Hz, 2H, Ar*H*), 2.98 (m, 4H, C*H*Me_2), 1.01 (d, J = 6.8 Hz, 12H, CH(CH_3)$_2$), 0.87 (d, J = 6.8 Hz, 12H, CH(CH_3)$_2$). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K, δ, ppm): 165.64, 149.78, 147.45, 143.99, 134.82, 134.62, 132.06, 127.29, 125.72, 123.63, 122.42, 116.91, 115.31, 112.11, 28.40, 24.42, 22.81.

2.2.3. Synthesis of complex **1a**′

To a stirred solution of $\mathbf{L^1}H_2$ (0.52 g, 1.0 mmol) in 30 mL of toluene was added $TiCl_4$ (0.11 mL, 1.0 mmol) in toluene (10 mL) at 0 °C, during which period a red suspension was formed immediately. The mixture was allowed to warm to room temperature, the solvent was removed under reduced pressure and the residue was heated to 140 °C under vacuum for 3 h. The crude product was extracted with CH_2Cl_2 (2×10 mL) and recrystallized from CH_2Cl_2/*n*-hexane to give the pure product **1a**′ (0.47 g, 0.69 mmol, 70%) as deep red crystals. *Anal.* Calc. for $C_{36}H_{33}Cl_3N_4Ti$ (674.13): C, 63.97; H, 4.92; N, 8.29. Found: C, 64.12; H, 5.05; N, 8.35%. ^1H NMR (400 MHz, $CDCl_3$, 298 K, δ, ppm): 9.86 (s, 1H, C*H*═NAr), 8.83 (s, 1H, C*H*═NAr), 5.93–7.82 (m, 18H, Ar*H*), 5.93 (s, 1H, N*H*), 2.25 (s, 6H, ArCH_3), 1.87 (s, 6H, ArCH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K, δ, ppm): 170.27, 161.88, 150.96, 146.08, 143.48, 141.98, 141.78, 137.66, 137.25, 136.86, 136.49, 133.19, 129.84, 129.50, 129.25, 129.18, 128.52, 126.66, 125.71, 123.75, 121.60, 118.95, 118.35, 117.92, 114.52, 113.13, 99.99, 20.00, 18.22.

2.2.4. Synthesis of complex **1b**′

To a stirred solution of $\mathbf{L^1}H_2$ (0.52 g, 1.0 mmol) in 30 mL of toluene was added $ZrCl_4$ (0.23 g, 1.0 mmol) in toluene (10 mL) at 0 °C. The mixture was stirred at 50 °C for 2 h, during which period a red suspension was formed. The solvent was removed under reduced pressure and the residue was heated to 140 °C under vacuum for 3 h. The crude product was extracted with CH_2Cl_2 (2×10 mL) and recrystallized from CH_2Cl_2/*n*-hexane to give the pure product **1b**′ (0.38 g, 0.53 mmol, 54%) as reddish brown crystals. *Anal.* Calc. for $C_{36}H_{33}Cl_3N_4Zr$ (716.08): C, 60.12; H, 4.62; N, 7.79. Found: C, 60.23; H, 4.61; N, 7.85%. ^1H NMR (400 MHz, $CDCl_3$, 298 K, δ, ppm): 9.72 (s, 1H, C*H*═NAr), 8.79 (s, 1H, C*H*═NAr), 6.09–7.92 (m, 18H, Ar*H*), 5.79 (s, 1H, N*H*), 2.34 (s, 6H, ArCH_3), 1.93 (s, 6H, ArCH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K, δ, ppm): 170.05, 163.72, 149.79, 145.84, 144.44, 142.71, 137.64, 137.29, 136.98, 136.83, 133.97, 130.79, 130.23, 130.21, 129.97, 129.31, 129.05, 128.60, 126.88, 122.95, 121.61, 120.03, 119.11, 118.41, 117.95, 116.08, 113.55, 19.67, 18.22.

2.2.5. Synthesis of complex **1c**′

Complex **1c**′ was synthesized in the same way as described above for the synthesis of complex **1b**′ with the free ligand $\mathbf{L^1}H_2$ (0.52 g, 1.0 mmol) and $HfCl_4$ (0.32 g, 1.0 mmol) as starting materials. Recrystallization of the crude product from CH_2Cl_2/*n*-hexane gave the pure product **1c**′ (0.38 g, 0.47 mmol, 48%) as reddish brown crystals. *Anal.* Calc. for $C_{36}H_{33}Cl_3N_4Hf$ (806.12): C, 53.61; H, 4.12; N, 6.95. Found: C, 53.29; H, 4.21; N, 6.86%. ^1H NMR (400 MHz, $CDCl_3$, 298 K, δ, ppm): 9.66 (s, 1H, C*H*═NAr), 8.12 (s, 1H, C*H*═NAr), 6.15–7.67 (m, 18H, Ar*H*), 5.73 (s, 1H, N*H*), 2.31 (s, 6H, ArCH_3), 1.95 (s, 6H, ArCH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K, δ, ppm): 170.26, 166.59, 148.95, 146.89, 145.52, 142.34, 137.75, 137.54, 136.79, 136.68, 133.28, 131.64, 130.72, 130.44, 129.66, 129.26, 128.90, 128.64, 126.96, 122.93, 121.76, 119.47, 119.18, 118.69, 118.02, 117.17, 113.70, 19.54, 18.21.