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## **Efficient Ethylene Polymerisation Catalysis by a Cationic Benzyl Hafnium Complex Containing Pyrrolide-Imine Ligands**

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**[1] General Considerations**

**[2] Preparation of Ligand Precursors and Complexes**

**[3] Polymerization Procedure**

## [1] General Considerations

Toluene and *n*-pentane used for complex synthesis were distilled from sodium/benzophenone ketyl. Toluene and *n*-heptane used as polymerization solvent were dried over Al<sub>2</sub>O<sub>3</sub> and degassed by bubbling of nitrogen. Starting materials for ligand precursor synthesis (HL<sup>1-3</sup>), 2-carboxypyrolaldehyde, 4-isopropylaniline, isopropylamine, and *t*-butylamine, were purchased from Acros Organics or Aldrich Inc and used without further purification. Hf(CH<sub>2</sub>Ph)<sub>4</sub> and Zr(CH<sub>2</sub>Ph)<sub>4</sub> were prepared according to literature procedures [U. Zucchini, E. Alizzati and U. Giannini, *J. Organomet. Chem.*, 1971, **26**, 357]. B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> was synthesized according to the literature [A. G. Massey, A. J. Park, *J. Organomet. Chem.*, 1964, **2**, 245]. Ethylene was obtained from Sumitomo Seika Co. [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (Asahi Glass Co., Ltd.) and *i*-Bu<sub>3</sub>Al (Tosoh Akzo Corporation) were used as received. Methylalumoxane (MAO) was purchased from Albemarle as a 1.2 M of a toluene solution, and remaining trimethylaluminum was evaporated *in vacuo* prior to use. NMR spectra were recorded on Bruker DRX-400 spectrometers at 25 °C (unless otherwise described). Chemical shifts for <sup>1</sup>H-NMR were reported in δ units (number of protons, peak multiplicity, coupling constant if appropriate). NMR solvents (benzene-d<sub>6</sub>, bromobenzene-d<sub>5</sub> and toluene-d<sub>8</sub>) were distilled from Na and stored under argon. NOESY experiment was performed at room temperature. The X-ray diffraction measurements were carried out on an Enraf Nonius CAD4 diffractometer using MoKα (λ = 0.71073 Å) radiation. The structure was solved by a heavy atom and Difference Fourier methods (SHELXS-86) and was refined against all F<sub>2</sub> reflections using the program SHELXL-96. Elemental analysis of the ligand precursors HL<sup>1-3</sup> for CHN was carried out by Heraeus Vario EL. The elemental analysis of the hafnium and zirconium complexes was performed: consistently low carbon values were obtained. *M<sub>w</sub>* values and molecular weight distribution (*M<sub>w</sub>*/*M<sub>n</sub>*) values of the polymer thus obtained were determined using a Waters 150-C gel permeation chromatograph at 145 °C using polyethylene calibration and equipped with three TSKgel columns (two sets of TSKgelGMH<sub>HR</sub>-H(S)HT and TSKgelGMH<sub>6</sub>-HTL). *o*-Dichlorobenzene was employed as a solvent at a flow rate of 1.0 ml/min. Transition melting temperatures (*T<sub>m</sub>*) of the polymers were determined by DSC with a Perkin Elmer DSC-7 differential-scanning calorimeter in the following manner. First, the sample was heated to 200 °C at 20 °C/min, maintained at 200 °C for 10 min, and then cooled to 30 °C at 10 °C/min for crystallization followed by reheating at 10 °C/min. The thermogram of the sample was recorded in the second heating run in order to remove the thermal history. The instrument was calibrated by the melting points of indium and lead.

## [2] Preparation of Ligand Precursors and Complexes

Ligand syntheses were carried out under nitrogen in oven-dried glassware. All manipulations of complex syntheses were performed with exclusion of oxygen and moisture under argon using standard Schlenk techniques in oven-dried glassware.

**HL<sup>1</sup>**: Pyrrole-2-carboxyaldehyde (4.83 g, 50.80 mmol) was dissolved in ethanol (100mL). To this solution, 4-isopropylaniline (7.44 g, 55.00 mmol) and a catalytic amount of *p*-toluenesulfonic acid as a catalyst were added. The reaction mixture was stirred for 12h at 50 °C. After the evaporation of the ethanol, the resulting mixture was purified by column chromatography on silica gel using *n*-hexane / ethyl acetate (19 / 1) as eluent, and recrystallization was attempted from ethanol to give a N-(2-pyrrolidene)-4-isopropylaniline (**HL<sup>1</sup>**) as white crystals in 57.1% yield (7.32 g, 28.99 mmol).

<sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>) δ: 1.26 (d, *J* = 6.8 Hz, 6H, CH<sub>3</sub>), 2.83 (q, *J* = 6.8 Hz, 1H, CH), 6.24 (dd, *J* = 6.8 Hz, 2.4 and 1.2 Hz, 1H, pyrrole-4-H), 6.43 (dd, *J* = 3.6 and 1.8 Hz, 1H, pyrrole-3-H), 6.58 (br s, 1H, pyrrole-5-H), 7.17-7.26 (m, 2H, Ar-H), 8.15 (s, 1H, CH=N), 10.09 (brs, 1H, NH). <sup>13</sup>C-NMR (C<sub>6</sub>D<sub>6</sub>) δ: 23.81, 33.60, 109.99, 116.45, 121.00, 123.08, 127.01, 130.92, 145.79, 149.28, 149.93. Anal Calcd for C<sub>14</sub>H<sub>16</sub>N<sub>2</sub>: C, 79.21, H, 7.60, N, 13.20. Found: C; 79.19, H; 7.67, N; 13.26.

**1** (mixture): To a stirred solution of Hf(CH<sub>2</sub>Ph)<sub>4</sub> (127 mg, 0.234 mmol) in toluene (8 mL) at -78 °C with shielded light, a solution of **1** (99 mg, 0.468 mmol) in toluene (4 mL) was added dropwise over a 5 min period under an argon atmosphere and stirred for 3h. The reaction mixture was allowed to warm to -30 °C and stored overnight. The resulting mixture was evaporated at 0 °C to obtain 150 mg of orange solid as a crude mixture.

<sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>) δ: 1.05-1.28 (m, CH<sub>3</sub>), 2.61-2.80 (m, CH), 2.73 (s, CH<sub>2</sub>), 6.35-7.49 (m, Ar-H + pyrrole-H), 7.72-7.73 (m, CH=N). <sup>13</sup>C-NMR (C<sub>6</sub>D<sub>6</sub>) δ: 23.51, 23.60, 23.73, 33.44, 33.63, 82.70, 113.69, 114.64, 121.68, 121.85, 121.94, 122.33, 122.39, 125.81, 126.12, 126.24, 126.36, 128.11, 128.23, 128.87, 138.84, 139.87, 141.30, 146.05, 146.43, 158.43, 158.92.

**HL<sup>2</sup>**: Pyrrole-2-carboxyaldehyde (1.06 g, 11.03 mmol) was dissolved in ethanol (5 mL). To this solution, isopropylamine (1.18 g, 20.00 mmol), was added. The reaction mixture was stirred for 17h at room temperature. After the evaporation of the ethanol, the resulting mixture was distilled under reduced pressure to give a N-(2-pyrrolidene)-isopropylamine (**HL<sup>2</sup>**) as a colorless liquid in 72.2% yield (1.08 g, 7.96 mmol). bp 67 °C/2.3 mbar.

<sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>) δ: 1.21 (d, *J* = 6.8 Hz, 6H, CH<sub>3</sub>), 3.29 (q, *J* = 6.8 Hz, 1H, CH), 6.29 (dd, *J* = 3.2 and 0.8 Hz, 1H, pyrrole-4-H), 6.50 (d, *J* = 3.2 Hz, 1H, pyrrole-3-H), 6.55 (br s, 1H, pyrrole-5-H), 7.90 (s, 1H, CH=N), 10.42 (br s, 1H, NH). <sup>13</sup>C-NMR (C<sub>6</sub>D<sub>6</sub>) δ: 24.13, 60.62, 109.29, 113.73, 121.39, 149.22. Anal Calcd for C<sub>8</sub>H<sub>12</sub>N<sub>2</sub>: C, 70.55, H, 8.88, N, 20.57. Found: C; 70.43, H; 8.74, N; 20.67.

**2:** To a stirred solution of  $\text{Hf}(\text{CH}_2\text{Ph})_4$  (203 mg, 0.374 mmol) in toluene (10 mL) at  $-78^\circ\text{C}$  with shielded light, a solution of  $\text{HL}^2$  (102 mg, 0.748 mmol) in toluene (5 mL) was added dropwise over a 5 min period under an argon atmosphere and stirred for 3h. The reaction mixture was allowed to warm to  $-30^\circ\text{C}$  and stored overnight. The resulting mixture was evaporated at  $0^\circ\text{C}$ . The solid was washed by toluene (0.5 mL) / *n*-pentane (5 mL) at  $-30^\circ\text{C}$  to give an orange solid (38 mg, 0.061 mmol) in 16.3% yield.  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$ : 0.63 (d,  $J = 6.8$  Hz, 12H,  $\text{CH}_3$ ), 2.83 (s, 4H, CH), 3.17 (q,  $J = 6.8$  Hz, 2H,  $\text{CH}_2$ ), 6.46 (m, 2H, pyrrole-4-H), 6.69 (m, 2H, pyrrole-3-H), 6.80-7.24 (m, 20H, Ar-H), 7.51 (s, 2H, pyrrole-5-H), 7.57 (s, 2H,  $\text{CH}=\text{N}$ ).  $^{13}\text{C-NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$ : 22.47, 54.50, 82.15, 113.48, 119.48, 121.43, 125.23, 128.87, 138.99, 140.01, 146.28, 158.30.

$\text{HL}^3$ : Pyrrole-2-carboxyaldehyde (3.12 g, 32.75 mmol) was dissolved in ethanol (50mL). To this solution, *t*-butylamine (3.66 g, 50.00 mmol), was added. The reaction mixture was stirred for 24h at room temperature. After the evaporation of the ethanol, the resulting mixture was distilled under reduced pressure to give a N-(2-pyrrolidene)-*t*-butylamine ( $\text{HL}^3$ ) as a yellow crystals in 70.7% yield (3.97 g, 23.17 mmol). b.p.  $66-68^\circ\text{C}/1.8$  mbar.

$^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$ : 1.26 (s, 9H, *t*-Bu), 6.31 (dd, 3.2 and 0.4 Hz, 1H, pyrrole-4-H), 6.49 (br s, 1H, pyrrole-3-H), 6.52 (d,  $J = 3.6$  Hz, 1H, pyrrole-5-H), 8.05 (s, 1H,  $\text{CH}=\text{N}$ ), 9.71 (br s, 1H, NH).  $^{13}\text{C-NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$ : 29.49, 56.06, 109.30, 113.16, 120.80, 131.20, 145.77. Anal Calcd for  $\text{C}_9\text{H}_{14}\text{N}_2$ : C, 71.96, H, 9.39, N, 18.65. Found: C, 71.83; H 9.19; N 18.62.

**3:** To a stirred solution of  $\text{Hf}(\text{CH}_2\text{Ph})_4$  (0.545 g, 1.00 mmol) in toluene (15 mL) at  $-78^\circ\text{C}$  with shielded light, a solution of **3** (0.300 g, 2.00 mmol) in toluene (5 mL) was added dropwise over a 5 min period under an argon atmosphere and stirred for 3h. The reaction mixture was allowed to warm to  $-30^\circ\text{C}$  and stored overnight. The resulting mixture was evaporated at  $0^\circ\text{C}$ . The solid was recrystarized from toluene (0.5 mL) / *n*-pentane (5 mL) at  $-78^\circ\text{C}$  to give orange crystals (0.458 g, 0.843 mmol) in 84.3% yield.

$^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$ : 0.83 (s, 18H, *t*-Bu), 2.59, 2.80 (AB q,  $J = 12.0$  Hz, 4H,  $\text{CH}_2$ ), 6.49 (dd,  $J = 3.3$  and 1.2 Hz, 2H, pyrrole-4-H), 6.72 (dd,  $J = 3.3$  and 1.0 Hz, 2H, pyrrole-3-H), 6.85 (t, 2H,  $J = 7.6$  Hz, Ar-H(*p*)), 6.94 (d, 4H,  $J = 7.2$  Hz, Ar-H(*o*)), 7.22 (t, 4H,  $J = 7.6$  Hz, Ar-H(*m*)), 7.71 (br s, 2H, pyrrole-3-H), 7.84 (s, 2H,  $\text{CH}=\text{N}$ ).  $^{13}\text{C-NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$ : 29.90, 58.38, 84.23, 113.91, 120.92, 121.46, 126.48, 127.84, 138.66, 139.98, 149.98, 158.44

**4:** One equivalent of  $\text{B}(\text{C}_6\text{F}_5)_3$  was added to **3** in bromobenzene- $\text{d}_5$  at  $-30^\circ\text{C}$  under argon atmosphere.

$^1\text{H-NMR}$  ( $\text{C}_6\text{D}_5\text{Br}$ ,  $-25^\circ\text{C}$ )  $\delta$ : 0.90 (s, 18H, *t*-Bu), 2.54 (s, 2H,  $\text{CH}_2\text{Hf}$ ), 3.66 (s, 2H  $\text{CH}_2\text{B}$ ), 6.45-6.48 (d,  $J = 7.2$  Hz, 2H, pyrrole-4-H), 6.58 (br s, 2H, pyrrole-3-H), 6.97-7.46 (m, 10H), 7.50 (br s, 2H, pyrrole-5-H), 8.27 (s, 2H,  $\text{CH}=\text{N}$ ).  $^{13}\text{C-NMR}$  ( $\text{C}_6\text{D}_5\text{Br}$ ,  $-25^\circ\text{C}$ )  $\delta$ : 29.86, 61.11, 83.12, 117.48, 134.86, 141.87, 149.70, 159.42, (145-150).  $^{19}\text{F-NMR}$  ( $\text{C}_6\text{D}_5\text{Br}$ ,  $-25^\circ\text{C}$ )  $\delta$ :  $-130.25$  (*o*-F),  $-162.93$  (*p*-F),  $-165.71$  (*m*-F).

**5:** To a stirred solution of  $\text{Zr}(\text{CH}_2\text{Ph})_4$  (214 mg, 0.47 mmol) in toluene (10 mL) at  $-78^\circ\text{C}$  with shielding light, a solution of **5** (141 mg, 0.94 mmol) in toluene (5 mL) was added dropwise over a 5 min period under an argon atmosphere and stirred for 1h. The reaction mixture was allowed to warm to room temperature and stored for overnight. The resulting mixture was evaporated and recrystallized from toluene (0.5 mL) / *n*-pentane (5 mL) at  $-78^\circ\text{C}$  to give yellow solids (35 mg, 0.06mmol) in 12.7 % yield.

$^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$ : 0.85 (s, 18H, *t*-Bu), 2.92, 3.10 (AB q,  $J = 11.6$  Hz, 4H,  $\text{CH}_2$ ), 6.51 (dd,  $J = 2.0, 3.2$  Hz, 2H, pyrrole-4-H), 6.77 (d,  $J = 3.2$  Hz, 2H, pyrrole-3-H), 6.86-7.20 (m, 10H, Ar-H), 7.73 (br s, 2H, pyrrole-5-H), 7.76 (s, 2H,  $\text{CH}=\text{N}$ ).  
 $^{13}\text{C-NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$ : 29.97, 57.82, 81.98 (t,  $J_{\text{C-H}} = 121$  Hz,  $\text{CH}_2$ ), 113.42, 121.32, 125.23, 126.88, 128.87, 138.73, 139.64, 147.83, 157.89.

### [3] Polymerization Procedure

Ethylene polymerization was carried out under atmospheric pressure in a 500-mL glass reactor equipped with a propeller-like stirrer. Solvent (250 mL: toluene or *n*-heptane) was introduced into the nitrogen-purged reactor and stirred (600 rpm). The solvent was thermostated to a prescribed polymerization temperature, and then the monomer gas feed (100 L/h) was started. After 15 min, polymerization was initiated by adding a toluene solution of the cocatalyst followed by toluene solution of catalyst into the reactor with vigorous stirring (600 rpm). After 5 min, *i*-butyl alcohol (10 mL) was added to terminate the polymerization and the ethylene gas feed was stopped. To the resulting mixture, methanol (1000 mL) and conc. HCl (2 mL) were added. The polymer was collected by filtration, washed with methanol (200 mL) and dried *in vacuo* at  $80^\circ\text{C}$  for 10 h.