## **Supporting Information for**

# Alternative Aluminum-Based Cocatalysts for the Iron-Catalyzed Oligomerization of Ethylene

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## **General considerations**

All reactions and manipulations were handled in oven-dried glassware under argon atmosphere using Schlenk techniques. Toluene was purified using a MBraun Solvent Purification System (SPS-M-Braun) and its water content was checked using Karl-Fischer titration prior to use. Deuterated benzene was purchased from Sigma-Aldrich or Eurisotop, freeze-pumped and stored over 4 Å molecular sieves under argon. Trimethylaluminum was purchased from Chemtura. The iron(II)-bis(imino)pyridine and iron(III) complexes **A** and **B**,respectively, were prepared according to literature: *J. Organomet. Chem.* **2007**, *692*, 4580-4592 and *Organometallics* **2011**, *30*, 2640-2642. Alcohol-, phenol- and diol-derivatives were dried prior to use. The solid organic compounds were dried by co-evaporation with toluene (3 times) and placed under vacuum at 40°C for 2 h. Liquid alcohols were degassed and dried over molecular sieves.

NMR spectra were recorded at room temperature on Bruker AV 300 spectrometer (<sup>1</sup>H: 300 MHz). Chemical shifts are reported in  $\delta$  (parts per million) relative to tetramethylsilane (<sup>1</sup>H/<sup>13</sup>C) and referenced to the residual <sup>1</sup>H/<sup>13</sup>C of the deuterated benzene (<sup>1</sup>H ( $\delta$ ): 7.15; 13C ( $\delta$ ): 128.62). Gas chromatographic analyses were performed on a Agilent 6850 series II equipped with a flame ionization detector and using an Agilent Pona column (50 m, 0.2 mm diameter, 0.5 µm film thickness)

## Procedure for cocatalysts formed in situ

To a solution of organic compound **OC** (alcohol, phenol or diol) at -78°C in dry toluene was added dropwise the AlMe<sub>3</sub> (see footnotes of the different tables for ratios). The solution was stirred for 30 min. at -

78 °C. The colorless solution was brought to room temperature and stirred for additional 30 min. Without further treatment, the cocatalyst mixture thus prepared was used in iron-catalyzed oligomerization of ethylene.



<sup>1</sup>H NMR of the crude solution of AlMe<sub>3</sub> and 1,2-catechol

#### Synthesis of complex 16

To a suspension of 1,2-catechol (1.10 g, 10 mmol) in 30 mL of dried toluene (4.1 ppm of water) at -78 °C was added dropwise a solution of AlMe<sub>3</sub> (1.47 mL, 15 mmol) within 30 min in 20 mL of dried toluene. The colorless solution was stirred at -78 °C for 30 min. and warmed to room temperature. After 2 h stirring at room temperature, some white blurred appeared and the solvent was distilled off under vacuum. The complex was sublimed off (T = 150 °C, p = 10<sup>-3</sup> Torr) as a white solid from the post reaction mixture (0.620 g, 32% yield).

<sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$ : 6.73 – 6.40 (m, 8H), -0.12 (s, 6H), -0.34 (s, 3H), -0.79 (s, 6H). <sup>13</sup>C NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  = 144.6, 123.6, 116.5, -9.7, -13.0.





#### Synthesis of complex 17

To a suspension of 2,2'-dihydroxybiphenyl (3.74 g, 20.1 mmol) in 50 mL of dried toluene (3.9 ppm of water) at -78 °C was added dropwise within 30 min a solution of AlMe<sub>3</sub> (2.17 mL, 30.2 mmol) in 60 mL of dried toluene. The colorless solution was stirred at -78°C for 30 min and warmed to room temperature. After 2 h stirring at room temperature, some white blurred appeared and the solvent was distilled off under vacuum. The complex was sublimed (T = 190 °C,  $p = 10^{-5}$  Torr) as a white solid from the post reaction mixture (2.10 g, 40% yield).

<sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$ : 7.40 (dd, J = 8.2, 0.9 Hz, 2H), 7.10 (dd, J = 7.6, 1.5 Hz, 2H), 6.99 (dd, J = 7.6, 1.9 Hz, 2H), 6.93 – 6.71 (m, 10H), -0.34 (s, 6H), -0.59 (s, 3H), -0.60 (s, 6H). <sup>13</sup>C NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  = 151.4, 149.3, 135.2, 132.0, 131.1, 129.9, 129.7, 124.8, 123.9, 121.7, 119.5, -7.3, -9.9.









## <sup>13</sup>H NMR of complex **17**

#### **Ethylene oligomerization**

Studies were performed either in a 6-parallel semi-batch autoclaves (100 mL, equipped with mechanical stirring) or semi-batch mono autoclave (250 mL, equipped with magnetic stirring). All tests were duplicated. The reactor was under an atmosphere of ethylene before the toluene, the iron precursor and the cocatalyst (or cocatalyst mixture) were introduced. The total volume of solutions introduced was 25 mL. The reactor was sealed and fed with ethylene at 30 bar. The reactor was heated at the desired temperature and the reaction mixture was stirred. During catalysis, the pressure was maintained through a continuous feed of ethylene and the ethylene consumption was monitored. At the end of the test after 1 h or after ~25 g of ethylene was consumed unless noted, stirring was stopped and the reactor was cooled down to 25 °C and depressurized. The liquid effluents were collected and weighed. The catalyst and the cocatalyst were quenched by addition of 2 mL of a 10%  $H_2SO_4$  solution in water. Aliquots of liquid effluents were then analyzed by GC.

Catalytic tests profiles are given in SI.  $C_2H_4$  uptake, reactor temperature and  $C_2H_4$  pressure are represented.

It should be noted that the catalytic tests are stopped (no ethylene feed) after 1h or 25 g  $C_2H_4$  consumed, except for MAO (Table 1 Entry 16) where in our experimental conditions 62 g  $C_2H_4$  were consumed in ~5 minutes and the reaction temperature was not controlled.

 $TMA = AlMe_3$  (trimethylaluminum)

























Table 2

















Table 3





