SUPPORTING INFORMATION

Simultaneous Polymerization and Schulz-Flory Oligomerization of Ethylene Made Possible by Activation with MAO of a Single C_1-Symmetric [2,6-Bis(arylimino)pyridyl]iron Dichloride Precursor

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Experimental Section

All air- and/or water-sensitive reactions were performed under a nitrogen atmosphere in flame-dried flasks using standard Schlenk techniques. Solid complexes were collected on sintered-glass frits and washed with appropriate solvents before being dried in a stream of nitrogen. The compounds 1-{6-[(2,6-diisopropylphenyl)ethanimidoyl]-2-pyridinyl}-1-ethanone and 2-[1-(2,6-diisopropylphenylimino)ethyl]-6-[1-((1R)-1-phenylethylimino)ethyl]pyridine (**L5**) were prepared according to literature procedures.[1] Anhydrous toluene, THF and Et_2O were obtained by distillation under nitrogen from sodium-benzophenone ketyl, while MeOH was distilled over Mg. A 10 wt % solution of methylaluminoxane (MAO) in toluene (d = 0.88 g mL^{-1}) was purchased from Crompton GmbH. All the other reagents and solvents were used as purchased from commercial suppliers. Catalytic reactions were performed with a 500 mL stainless steel reactor, constructed at the ICCOM-CNR (Firenze, Italy), equipped with a magnetic drive stirrer, a Parr 4842 temperature and pressure controller. The reactor was connected to an ethylene reservoir to maintain a constant pressure throughout the catalytic runs. Deuterated solvents for routine NMR measurements were dried over molecular sieves. ^1H, $^{13}C\{^1H\}$ NMR spectra were obtained on a Varian VXR 300 instrument working at 300.13 and 75.03 MHz, respectively. Chemical shifts are reported in ppm (δ) relative to TMS, referenced to the

chemical shifts of residual solvent resonances. The multiplicity of the $^{13}C\{^1H\}$ NMR spectra were determined by the DEPT 135 technique and quoted as: CH_3, CH_2, CH and C for primary, secondary, tertiary and quaternary carbon atoms, respectively. ^1H and $^{13}C\{1H\}$ NMR spectra of polyethylene samples were taken in tetrachloroethane-d_2 and 1:1 (v:v) tetrachloroethane-d_2:1,2-dichlorobenzene, respectively, at 115 °C. ^1H NMR of paramagnetic compounds were recorded on a Bruker Avance DRX-400 spectrometer operating at 400.13 MHz. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FT-IR spectrophotometer using samples mulled in Nujol between KBr plates. Elemental analyses were performed using a Carlo Erba Model 1106 elemental analyzer with an accepted tolerance of ± 0.4 units on carbon (C), hydrogen (H) and nitrogen (N). Melting points were recorded on a Stuart Scientific SMP3 apparatus. UV-VIS spectra were recorded on a Perkin-Elmer Lamda 9 spectrophotometer. Molar susceptibility analyses were performed on a Sherwood Scientific MSB AUTO balance. GC analyses were performed on a Shimadzu GC-17A equipped with a flame ionization detector and a 30 m (0.25 mm i.d., 0.25 μm film thickness) SPB-1 Supelco fused silica capillary column. GC/MS analyses were performed on a Shimadzu QP 5000 apparatus equipped with a column identical with that used for GC analysis. Gel permeation chromatography (GPC) was performed on a Water alliance GPCV-2000 Series System instrument equipped with three columns Waters Styragel Mixed 6E and one column Waters Styragel HT3 in 1,2,4-trichlorobenzene at 145 °C (1 mL/min) using polystyrene calibration. Melting temperatures of samples were determined by differential scanning calorimetry (DSC) with a Perkin-Elmer DSC7 calibrated by using In and Zn as reference standards for temperature at a heating rate of 20 °C/min.

2-[1-(2,6-Diisopropylphenylimino)ethyl]-6-[1-(phenylimino)ethyl]pyridine (L1). A mixture of 1-{6-[(2,6-diisopropylphenyl)ethanimidoyl]-2-pyridinyl}-1-ethanone (300 mg, 0.93 mmol) and freshly distilled aniline (0.70 mL, 7.68 mmol) was deaerated and heated at 100 °C without stirring for 15 h in the presence of activated 4 Å molecular sieves collected in a suspended bag. The resulting mixture was diluted with 4 mL of MeOH and cooled to 0 °C. After 5 h, yellow microcrystals of the product were isolated by filtration and washed with cold MeOH (10 mL). A double recrystallization from MeOH (two times) removed all unreacted α-keto-pyridin-imine (188 mg, 0.47 mmol, yield 51%). Mp 112-114 °C. IR (Nujol mull, KBr): $\nu_{C=N}$ 1641 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 1.03 (m, 12H, CH*Me*$_2$), 2.14 (s, 3H, N=CMe), 2.23 (s, 3H, N=CMe), 2.63 (spt, J = 6.8 Hz, 2H, C*H*Me$_2$), 6.72 (m, 2H, Ar), 6.91-7.09 (m, 4H, Ar), 7.24 (m, 2H, Ar), 7.80 (t, J = 7.6 Hz, 1H, 4-Py), 8.22 (d, J = 7.6 Hz, 1H,

3/5-Py), 8.32 (d, *J* = 7.6 Hz, 1H, 3/5-Py). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ 167.8 (N=*C*Me), 166.60 (N=*C*Me), 156.3, 156.1, 155.7, 152.0, 147.1, 137.4, 136.3, 129.5, 124.1, 124.0, 123.5, 122.7, 122.6, 119.7 (Py and Ar), 28.8 (*C*HMe$_2$), 23.5 (CHMe*Me*), 23.1 (CH*Me*Me), 17.5 (N=C*Me*), 16.5 (N=C*Me*). Anal. Calcd for $C_{27}H_{31}N_3$: C, 81.57; H, 7.86; N, 10.57. Found: C, 81.43; H, 7.77; N, 10.39.

2-[1-(2,6-Diisopropylphenylimino)ethyl]-6-[1-(tolylimino)ethyl]pyridine (L2). A mixture of 1-{6-[(2,6-diisopropylphenyl)ethanimidoyl]-2-pyridinyl}-1-ethanone (300 mg, 0.93 mmol) and freshly distilled *o*-toluidine (0.60 mL, 5.59 mmol) was deaerated and heated at 100 °C without stirring for 15 h in the presence of activated 4 Å molecular sieves collected in a suspended bag. The resulting mixture was diluted with 4 mL of MeOH and cooled to 0 °C. After 5 h, yellow microcrystals of the product were isolated by filtration and washed with cold MeOH (10 mL). All unreacted α-keto-pyridin-imine was removed by recrystallization from hot MeOH (308 mg, 0.75 mmol, yield 80%). Mp 118-119 °C. IR (Nujol mull, KBr): $\nu_{C=N}$ 1642 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 1.02 (m, 12H, CH*Me*$_2$), 1.98 (s, 3H, N=CMe), 2.14 (s, 3H, Me(Ar)), 2.22 (s, 3H, N=CMe), 2.65 (spt, *J* = 6.9 Hz, 2H, C*H*Me$_2$), 6.56 (d, *J* = 7.5 Hz, 1H, Ar), 6.85-7.18 (m, 6H, Ar), 7.82 (t, *J* = 7.6 Hz, 1H, 4-Py), 8.32 (t, *J* = 7.6 Hz, 2H, 3/5-Py). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ 167.9 (N=*C*Me), 167.7 (N=*C*Me), 156.4, 156.0, 151.0, 147.4, 137.7, 136.7, 131.2, 128.0, 127.2, 124.4, 124.3, 123.9, 123.0, 122.9, 118.9 (Py and Ar), 29.1 (*C*HMe$_2$), 23.9 (CHMe*Me*), 23.4 (CH*Me*Me), 18.4 (Me(Ar)), 17.8 (N=C*Me*), 16.9 (N=C*Me*). Anal. Calcd for $C_{28}H_{33}N_3$: C, 81.71; H, 8.08; N, 10.21. Found: C, 81.66; H, 7.99; N, 10.10.

2-[1-(2,6-Diisopropylphenylimino)ethyl]-6-[1-(2,6-dimethylphenylimino)ethyl]pyridine[2] (L3). To a deaerated solution of 1-{6-[(2,6-diisopropylphenyl)ethanimidoyl]-2-pyridinyl}-1-ethanone (400 mg, 1.24 mmol) in isopropyl alcohol (25 mL) were added in sequenece an excess of freshly distilled 2,6-dimethyl-aniline (0.76 mL, 6.20 mmol) and five drops of formic acid. The reaction mixture was heated to 75 °C and maintained at that temperature under stirring for 4 days in the presence of activated 4Å molecular sieves collected in a suspended bag. The resulting solution was allowed to cool at -15 °C and after 1 day yellow microcrystals of the pure product were isolated by filtration (268 mg, 0.63 mmol, yield 51%). Mp 176-178 °C. $\nu_{C=N}$ 1642 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 1.16 (m, 12H, CH*Me*$_2$), 2.05 (s, 6H, Me(Ar)), 2.24 (s, 3H, N=CMe), 2.27 (s, 3H, N=CMe), 2.78 (spt, *J* = 6.9 Hz, 2H, C*H*Me$_2$), 6.95 (t, *J* = 7.6 Hz, 1H, Ar), 7.08-7.20 (m, 5H, Ar), 7.97 (t, *J* = 7.8 Hz, 1H, 4-Py), 8.47 (d, *J* = 7.6 Hz, 1H, 3/5-Py), 8.50 (d, *J* = 7.6 Hz, 1H, 3/5-Py). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ 168.0 (N=*C*Me), 167.9 (N=*C*Me), 156.1, 156.0, 149.8, 147.4, 137.7, 136.7,

128.7, 126.2, 124.4, 123.9, 123.8, 123.0 (Py and Ar), 29.2 (*C*HMe$_2$), 23.9 (CHMe*Me*), 23.4 (CH*Me*Me), 18.5 (Me(Ar)), 17.8 (N=C*Me*), 17.1 (N=C*Me*). Anal. Calcd for $C_{29}H_{35}N_3$: C, 81.84; H, 8.29; N, 9.87. Found C, 81.72; H, 8.20; N, 10.01.

2-[1-(2,6-Diisopropylphenylimino)ethyl]-6-[1-(benzylimino)ethyl]pyridine (L4). A suspension of 1-{6-[(2,6-diisopropylphenyl)ethanimidoyl]-2-pyridinyl}-1-ethanone (220 mg, 0.68 mmol) and benzylamine (0.15 mL, 1.36 mmol) in EtOH (3 mL) was deaerated and heated at reflux temperature for 24 h. The resulting mixture was allowed to cool at room temperature under stirring until a yellow pale microcrystalline product precipitated. The product was filtered and washed with cold MeOH. (218 mg, 0.53 mmol, yield 78%). Mp 135-137 °C. $\nu_{C=N}$ 1638 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.35 (d, *J* = 6.9 Hz, 12H, CH*Me*$_2$), 2.46 (s, 3H, N=CMe), 2.74 (s, 3H, N=CMe), 2.96 (spt, *J* = 6.9 Hz, 2H, C*H*Me$_2$), 5.01 (s, 2H, CH_2Ph), 7.27-7.37 (m, 3H, Ar), 7.43-7.47 (m, 1H, Ar), 7.54-7.60 (m, 2H, Ar), 7.63-7.68 (m, 2H, Ar), 8.02 (t, *J* = 7.8 Hz, 1H, 4-Py), 8.51 (d, *J* = 7.8 Hz, 1H, 3/5-Py), 8.56 (d, *J* = 7.8 Hz, 1H, 3/5-Py). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 167.4 (1C, aryl-N=*C*Me), 167.0 (1C, alkyl-N=*C*Me), 156.3 (CαPy), 154.8 (CαPy), 146.5, 140.3, 137.3, 136.7, 135.8, 128.4, 127.2, 126.7, 123.5, 123.0, 122.0, 121.6 (Py and Ar), 56.1 (NCH_2Ph), 28.3 (*C*HMe$_2$), 23.2 (CHMe*Me*), 22.9 (CH*Me*Me), 17.2 (aryl-N=C*Me*), 14.1 (alkyl-N=C*Me*). Anal. Calcd for $C_{28}H_{33}N_3$: C, 81.71; H, 8.08; N, 10.21. Found: C, 81.79; H, 8.21; N, 10.37.

General Procedure for the Synthesis of the [2,6-Bis(imino)pyridy]iron Dichloride Complexes 1-5. The appropriate ligand (0.20 mmol) was added in one portion to a suspension of $FeCl_2$ (0.18 mmol) in dry, deaerated THF (7 mL) at room temperature under nitrogen. Overnight stirring led to the formation of a crystalline precipitate which was filtered off and washed with Et_2O.

1. Blue microcrystals, yield 90%. IR (Nujol mull, KBr): $\nu_{C=N}$ 1586 cm^{-1}. μeff = 5.42 BM (25 °C). Anal. Calcd for $C_{27}H_{31}Cl_2FeN_3$: C, 61.85; H, 5.96; N, 8.01. Found: C, 61.70; H, 5.81; N, 7.94.

2. Blue microcrystals, yield 96%. IR (Nujol mull, KBr): $\nu_{C=N}$ 1590 cm^{-1}. μeff = 5.34 BM (25 °C). Electronic spectra: diffuse reflectance spectra (40000-5550 cm^{-1}): 18900 sh, 14600, 8300; solution spectra (CH_2Cl_2, 28500-6250 cm^{-1}): 20300 (ε 260), 7900 (ε 6). Anal. Calcd for $C_{28}H_{33}Cl_2FeN_3$: C, 62.47; H, 6.18; N, 7.81. Found: C, 62.39; H, 6.03; N, 7.71.

^{1}H NMR assignments for **2** (CD_2Cl_2, 22 °C, 400.13 MHz)

Nucleus	δ (ppm)[a]
3/5-Py	s, 80.56 (1H); s, 78.44 (1H)
4-Py	s, 56.20 (1H)
N=C-CH_3	s, 9.86 (3H); s, -41.33 (3H)
o-aryl	s, 16.52 (1H)
m-aryl	brs, 18.62 (1H); brs, 12.21 (1H); brs, 10.73 (2H)
p-aryl	brs, -24.48 (1H); s, 12.44 (1H)
CH_3-*i*Pr	s, 2.02 (3H); s, -2.75 (3H); s, -3.25 (3H); s, -13.20 (3H)
CH-*i*Pr	s, -9.22 (1H), s, -2.7 (1H) [b]
CH_3-tolyl	s, -14.65 (3H)

[a] *s*, singlet; *br*, broad. [b]Masked by other resonances.

3. Blue microcrystals, yield 91%. IR (Nujol): $\nu_{C=N}$ 1588 cm^{-1}. μeff = 5.58 BM (25 °C). Anal. Calcd for $C_{29}H_{35}Cl_2FeN_3$: C, 63.06; H, 6.39; N, 7.61. Found: C, 63.23; H, 6.50; N, 7.77.

4. Blue microcrystals, yield 93%. IR (Nujol): $\nu_{C=N}$ 1586 cm^{-1}. μeff = 5.41 BM (25 °C). Anal. Calcd for $C_{28}H_{33}Cl_2FeN_3$: C, 62.47; H, 6.18; N, 7.81. Found: C, 62.56; H, 6.23; N, 7.80.

5. Blue microcrystals, yield 89%. IR (Nujol): $\nu_{C=N}$ 1584 cm^{-1}. μeff = 5.56 BM (25 °C). Electronic spectra: diffuse reflectance spectra (40000-5550 cm^{-1}): 18000 sh, 14600, 8100; solution spectra (CH_2Cl_2, 28500-6250 cm^{-1}): 20300 (ε 250), 7700 (ε 8). Anal. Calcd for $C_{29}H_{35}Cl_2FeN_3$: C, 63.06; H, 6.39; N, 7.61. Found: C, 62.68; H, 6.28; N, 7.59.

Catalytic Reactions. A 500 mL stainless steel reactor was heated at 60 °C under vacuum overnight and then cooled to room temperature under a nitrogen atmosphere. **Procedure A**. The solid precatalyst (12 μmol) was charged into the reactor which was sealed and placed under vacuum. An oxygen-free toluene solution of MAO (3.6 mmol), prepared by adding 2.4 mL of a solution of MAO in toluene into 97.6 mL of toluene, was then introduced into the reactor by suction. The reaction mixture was stirred at room temperature for about 1 min. The reactor was then pressurized with ethylene to 5 bar and stirred at 1500 rpm.

Procedure B. 2.4 mL of a solution of MAO in toluene (3.6 mmol) was diluted with 92.6 mL of oxygen-free toluene and the resultant solution was introduced by suction into the reactor previously evacuated by a vacuum pump. The system was pressurized with ethylene to the desired pressure and stirred for 5 min. The ethylene pressure was then released slowly, 5 mL of a precatalyst solution, prepared by dissolving the solid precatalyst (12 μmol) in 50 mL of oxygen-free toluene, was syringed into the reactor. The system was re-pressurized to the desired pressure and stirred at 1500 rpm.

Procedure C. The solid precatalyst (12 μmol) was introduced into the reactor which was sealed and placed under vacuum. An oxygen-free toluene solution of MAO (3.6 mmol), prepared by diluting 2.4 mL of a solution of MAO in toluene with 97.6 mL of toluene, was treated with 371 mg of 2,6-di-tert-butyl phenol[3] (1800 μmol) under stirring for 1 h. The resulting solution was introduced into the reactor by suction and the reaction mixture was stirred at room temperature for about 1 min. The reactor was then pressurized with ethylene to 5 bar and stirred at 1500 rpm.

Irrespective of the procedure, ethylene was continuously fed to maintain the reactor pressure at the desired value. The temperature inside the reactor increased due to the exothermicity of the reactions and reached a maximum value within 5-7 min. After 15 min, the reactions were stopped by cooling the reactor with an ice-water bath, depressurizing and introducing 2 mL of acidic MeOH (5% HCl). Pentadecane (200 μl) was injected into the reactor as the GC internal standard. The reactor contents were stirred at 1500 rpm for 10 min. The solid products were filtered off, washed with cold toluene, MeOH and dried in a vacuum oven at 50 °C. The filtrates were analyzed by GC and GC-MS. The moles of the oligomer fractions were determined by GC using calibration curves with standard toluene solutions containing concentrations of 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, and 1-octadecene as close as possible to those in the sample under analysis. Schulz-Flory α constants were determined by the average value of the molar ratio of the couples C18/C16, C16/C14, C14/C12, and C12/C10. The moles of the even oligomers in the C4-C8 range were calculated by the Schulz-Flory α constant and the moles of C10 by the formula moles(Ci) = moles(C10)/$\alpha^{10-i/2}$, whereas the moles of the even oligomers in the C20-C100 range were calculated by the Schulz-Flory α constant and the moles of C18 by the formula moles(Ci) = moles(C18)x$\alpha^{i-18/2}$. The total moles of converted ethylene was obtained by the formula: moles(C_2H_4) = Σmoles(Ci) x i/2 with i = 4-100; therefore, the TOFs were obtained.

Depending on the precatalyst employed in the catalysis experiment, the isolated solid was either the insoluble fraction of α-olefins in Schulz-Flory distribution (precatalysts **1** and **4**), or polyethylene (precatalyst **3**), or their mixtures (precatalysts **2** and **5**). The separation of the PE from the α-olefins in the latter mixtures was carried out by extraction with acetone in an Soxlet apparatus for 6 h. Concentrating the acetone phase to dryness gave a residue the weight of which allowed to determine the amount of α-olefins in the mixture. Roughly, this amount was calculated by assuming that oligomers higher than C40 were completely insoluble in toluene. GPC analyses for the PE fractions gave PDI values comparable to those

of the crude solid products, which is consistent with the small amount of oligomers higher than >C40. As an example, under the reaction conditions of run 2 in Table 1, the isolated product contained ca. 0.2 g of >C40 oligomers together with ca. 15.6 g of PE.

In some experiments, the temperature of the catalytic mixture was controlled by dipping the reactor into either an ice-water bath (ca. 0 °C) or an ice/NaCl bath (ca. -20 °C). However, the exothermicity of the oligo/polymerization process did not allow to carry out the reactions at constant temperature.

References

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