

Dendritic effects on ethylene polymerization promoted by peripheral nickel catalysts.

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ELECTRONIC SUPPLEMENTARY INFORMATION

Reagents and General Considerations

All operations were performed under an argon atmosphere using Schlenk or dry-box techniques. Compounds **1** and **2** were synthesized by adapting a reported procedure,¹ whereas $[\text{NiBr}_2(\text{DME})]^{2-}$ and carbosilane dendrimers $G_n(\text{Cl})_m$ ($n = 1, m = 4$; $n = 2, m = 8$; $n = 3, m = 16$) according to literature procedures.³ Pyridylimine dendritic ligands **3-5** were prepared similarly to **2**, in reactions of **1** with the corresponding chlorosilane dendrimer $G_n(\text{Cl})_m$. Nickel compounds **6-9** were obtained as illustrated below for **9**. Chemical shifts (δ) are reported in ppm referenced to SiMe_4 for ^1H , ^{13}C and ^{29}Si , and assignments for the iminopyridyl ligands are according to the numbering scheme depicted in Figure S1. Elemental analyses and mass spectra were performed by the Microanalytical Laboratories of the University of Alcalá (MLUAH), and MALDI-TOF MS were performed by the Analytical Services of the Universidad Autónoma de Madrid using samples in a 1,8,9-trihydroxyanthracene (dithranol) matrix. Polymethylaluminoxane improved process (PMAO-IP) in toluene (13 wt% Al) was purchased from Akzo Nobel. Oligomer products were analyzed on a gas chromatograph using a CP-Sil 5CB capillary column (10 m, 0.25 mm i.d., 0.12 μm df) under the following conditions: injector and detector temperature, 250 °C; oven temperature program, 100 °C/5 min, 5 °C/min ramp, 250 °C/15 min. Polyethylene molecular weight determinations were made by MLUAH in a Waters GPCV 2000 equipment operating at 135 °C with 1,2,4-trichlorobenzene (TCB) solvent and polystyrene calibration standards.

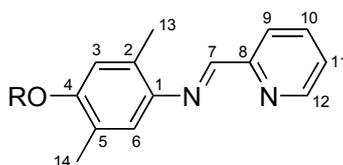


Figure S1. Numbering scheme for pyridylimine fragment

Characterization Data

[HO-4-(2,5-Me₂Ph)-N=CH-2-Py] (1): Yellow solid (91%). Anal. Calc. for C₁₄H₁₄N₂O (226.28): C, 74.31; H, 6.24; N, 12.38%. Found: C, 74.43; H, 6.44; N, 12.11%. ¹H NMR (CDCl₃): δ 2.23 (s, 3H, Me¹⁴), 2.34 (s, 3H, Me¹³), 5.21 (broad s, 1H, OH), 6.66 (s, 1H, H³), 6.89 (s, 1H, H⁶), 7.33 (dd, 1H, *J*_{H,H} = 7.5, 4.9 Hz, H¹¹), 7.79 (*pt*, 1H, H¹⁰), 8.22 (d, 1H, *J*_{H,H} = 7.9 Hz, H⁹), 8.51 (s, 1H, H⁷), 8.67 (d, 1H, *J*_{H,H} = 4.9 Hz, H¹²). ¹³C{¹H} NMR (CDCl₃): δ 15.6 and 17.5 (Me^{13,14}), 116.8 (C³), 119.8 (C⁶), 121.4 (C⁹), 122.1 (C⁵), 124.7 (C¹¹), 132.3 (C²), 136.7 (C¹⁰), 142.1 (C¹), 149.1 (C¹²), 153.2 (C⁴), 155.0 (C⁸), 156.7 (C⁷). IR (KBr): ν 1624 cm⁻¹ (m., C=N), 1589 and 1559 cm⁻¹ (s. and vs., py-ring). MS (70 eV, EI): *m/z*: 226 [M]⁺.

G0-(ONNMe₂) (2): Yellow oil (75 %). Anal. Calc. for C₁₇H₂₂N₂OSi (298.46): C, 68.41; H, 7.43; N, 9.39%. Found: C, 67.97; H, 7.44; N, 9.28%. ¹H NMR (CDCl₃): δ 0.26 (s, 9H, SiMe₃), 2.15 (s, 3H, Me¹⁴), 2.34 (s, 3H, Me¹³), 6.64 (s, 1H, H³), 6.91 (s, 1H, H⁶), 7.31 (dd, 1H, *J*_{H,H} = 7.5, 4.9 Hz, H¹¹), 7.77 (*pt*, 1H, H¹⁰), 8.21 (d, 1H, *J*_{H,H} = 7.9 Hz, H⁹), 8.51 (s, 1H, H⁷), 8.66 (d, 1H, *J*_{H,H} = 4.9 Hz, H¹²). ¹³C{¹H} NMR (CDCl₃): δ 0.5 (SiMe₃), 16.3 and 17.6 (Me^{13,14}), 119.6 (C³), 120.7 (C⁶), 121.2 (C⁹), 124.5 (C¹¹), 126.9 (C⁵), 131.6 (C²), 136.4 (C¹⁰), 142.9 (C¹), 149.4 (C¹²), 152.5 (C⁴), 155.2 (C⁸), 157.5 (C⁷). ²⁹Si{¹H} NMR (CDCl₃): δ 19.2 (SiMe₃). IR (Nujol/CsI): ν 1626 cm⁻¹ (s., C=N), 1604 (w., C=C), 1586 and 1567 cm⁻¹ (s., py-ring). MS (70 eV, EI): *m/z*: 298 [M]⁺.

G1-(ONNMe₂)₄ (3): Yellow viscous oil (92 %). Anal. Calc. for C₇₆H₁₀₀N₈O₄Si₅ (1330.11): C, 68.63; H, 7.58; N, 8.42%. Found: C, 68.22; H, 8.02; N, 8.43%. ¹H NMR (CDCl₃): δ 0.23 (s, 6H, SiMe₂), 0.60 (m, 2H, SiCH₂), 0.81 (m, 2H, CH₂SiMe₂), 1.42 (m, 2H, CH₂CH₂CH₂), 2.14 (s, 3H, Me¹⁴), 2.33 (s, 3H, Me¹³), 6.62 (s, 1H, H³), 6.89 (s, 1H, H⁶), 7.30 (m, 1H, H¹¹), 7.75 (*pt*, 1H, H¹⁰), 8.20 (d, 1H, *J*_{H,H} = 7.9 Hz, H⁹), 8.49 (s, 1H, H⁷), 8.65 (d, 1H, *J*_{H,H} = 4.6 Hz, H¹²). ¹³C{¹H} NMR (CDCl₃): δ -1.2 (SiMe₂), 16.4 and 17.7 (Me^{13,14}), 17.1 (CH₂), 17.9 (CH₂), 21.9 (CH₂), 119.6 (C³), 120.6 (C⁶), 121.2 (C⁹), 124.5 (C¹¹), 126.8 (C⁵), 131.7 (C²), 136.4 (C¹⁰), 142.8 (C¹), 149.4 (C¹²), 152.6 (C⁴), 155.2 (C⁸), 157.4 (C⁷). ²⁹Si{¹H} NMR (CDCl₃): δ 18.3 (SiMe₂), 0.8 (central Si). IR (Nujol/CsI): ν 1626 cm⁻¹ (s., C=N), 1597 (w., C=C), 1582 and 1567 cm⁻¹ (vs. and s., py-ring). MS (MALDI-TOF in dithranol): *m/z*: 1330.8 [M + H]⁺.

G2-(ONNMe₂)₈ (4): Brownish sticky oil (84 %). Anal. Calc. for C₁₆₈H₂₃₆N₁₆O₈Si₁₃ (2972.94): C, 67.87; H, 8.00; N, 7.54%. Found: C, 67.89; H, 8.46; N, 7.19%. ¹H NMR (CDCl₃): δ -0.08 (s, 3H, SiMe), 0.22 (s, 12H, SiMe₂), 0.56 (m, 8H, SiCH₂), 0.81 (m, 4H, CH₂SiMe₂), 1.29 (m, 2H, CH₂CH₂CH₂), 1.43 (m, 4H, CH₂CH₂CH₂), 2.13 (s, 6H, Me¹⁴), 2.32 (s, 6H, Me¹³), 6.61 (s, 1H, H³), 6.88 (s, 1H, H⁶), 7.29 (*pt*, 1H, H¹¹), 7.73 (*pt*, 1H, H¹⁰), 8.19 (d, 1H, *J*_{H,H} = 7.7 Hz, H⁹), 8.48 (s, 1H, H⁷), 8.64 (d, 1H, *J*_{H,H} = 4.0 Hz, H¹²). ¹³C{¹H} NMR (CDCl₃): δ -5.1 (SiMe), -1.0 (SiMe₂), 16.3 and

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17.6 (Me^{13,14}), 17.8, 18.5, 18.6, 19.1 and 21.7 (CH₂), 119.6 (C³), 120.7 (C⁶), 121.3 (C⁹), 124.5 (C¹¹), 126.8 (C⁵), 131.7 (C²), 136.4 (C¹⁰), 142.9 (C¹), 149.4 (C¹²), 152.7 (C⁴), 155.4 (C⁸), 157.4 (C⁷). ²⁹Si{¹H} NMR (CDCl₃): δ 18.4 (SiMe₂), 1.18 (SiMe), 0.5 (central Si). IR (Nujol/CsI): ν 1628 cm⁻¹ (s., C=N), 1603 (w., C=C), 1585 and 1568 cm⁻¹ (s., py-ring). MS (MALDI-TOF in dithranol): *m/z*: 2973.5 [M + H]⁺.

G3-(ONNMe₂)₁₆ (5): Brownish oil (91 %). Anal. Calc. for C₃₅₂H₅₀₈N₃₂O₁₆Si₂₉ (6258.59): C, 67.55; H, 8.18; N, 7.16%. Found: C, 66.84; H, 8.23; N, 6.88%. ¹H NMR (CDCl₃): δ -0.09 (s, 9H, SiMe), 0.21 (s, 24H, SiMe₂), 0.53 (m, 20H, SiCH₂), 0.80 (m, 8H, CH₂SiMe₂), 1.30 (m, 6H, CH₂CH₂CH₂), 1.43 (m, 8H, CH₂CH₂CH₂), 2.13 (s, 12H, Me¹⁴), 2.31 (s, 12H, Me¹³), 6.60 (s, 1H, H³), 6.87 (s, 1H, H⁶), 7.28 (*pt*, 1H, H¹¹), 7.73 (*pt*, 1H, H¹⁰), 8.19 (d, 1H, *J*_{H,H} = 7.0 Hz, H⁹), 8.48 (s, 1H, H⁷), 8.64 (d, 1H, *J*_{H,H} = 4.5 Hz, H¹²). ¹³C{¹H} NMR (CDCl₃): δ -5.0 (SiMe, only one peak can be distinguished), -0.8 (SiMe₂), 16.5 and 17.7 (Me^{13,14}), 17.9, 18.6, 19.1 and 21.8 (CH₂), 119.6 (C³), 120.6 (C⁶), 121.2 (C⁹), 124.5 (C¹¹), 126.8 (C⁵), 131.6 (C²), 136.4 (C¹⁰), 142.7(C¹), 149.3 (C¹²), 152.6 (C⁴), 155.1 (C⁸), 157.3 (C⁷). ²⁹Si{¹H} NMR (CDCl₃): δ 18.1 (SiMe₂), 0.8 (outermost SiMe), 0.6 (SiMe), 0.1 (central Si). IR (Nujol/CsI): ν 1627 cm⁻¹ (s., C=N), 1598 (w., C=C), 1584 and 1567 (s., py-ring).

G0-[(ONNMe₂)NiBr₂] (6): Red paramagnetic solid (80%). Anal. Calc. for C₁₇H₂₂N₂OSiBr₂Ni (516.96): C, 39.50; H, 4.29; N, 5.42%. Found: C, 39.46; H, 4.09; N, 5.03%. IR (KBr): ν 1630 cm⁻¹ (w.), 1595 cm⁻¹ (vs., C=N). MS (70 eV, EI): *m/z*: 298 [2]⁺; (ESI+ in CH₃CN): *m/z*: 478 [M - Br + CH₃CN]⁺.

H-[(ONNMe₂)NiBr₂] (6^{OH}): Orange paramagnetic solid obtained as described below for **9** starting from the phenolic ligand **1** (64%). Anal. Calc. for C₁₄H₁₄N₂OBr₂Ni (444.78): C, 37.81; H, 3.17; N, 6.30%. Found: C, 37.02; H, 3.06; N, 5.92%. IR (KBr): ν 1624 cm⁻¹ (m.), 1589 cm⁻¹ (m., C=N), 1560 cm⁻¹ (w.). MS (ESI+ in CH₃CN): *m/z*: 406 [M - Br + CH₃CN]⁺, 225 [2c - H]⁺.

G1-[(ONNMe₂)NiBr₂]₄ (7): Yellow paramagnetic solid (43%). Anal. Calc. for C₇₆H₁₀₀N₈O₄Si₅Br₈Ni₄ (2204.11): C, 41.42; H, 4.57; N, 5.08%. Found: C, 40.83; H, 5.06; N, 4.88%. IR (Nujol/CsI): ν 1626 cm⁻¹ (w.), 1595 cm⁻¹ (vs., C=N), 1570 cm⁻¹ (w.).

G2-[(ONNMe₂)NiBr₂]₈ (8): Yellow paramagnetic solid. (75%). Anal. Calc. for C₁₆₈H₂₃₆N₁₆O₈Si₁₃Ni₈Br₁₆ (4720.95): C, 42.74; H, 5.04; N, 4.75%. Found: C, 41.73; H, 5.32; N, 4.06%. IR (KBr): ν 1625 cm⁻¹ (m.), 1597 cm⁻¹ (vs., C=N), 1567 cm⁻¹ (w.).

G3-[(ONNMe₂)NiBr₂]₁₆ (9): Solid [NiBr₂(DME)] (115 mg, 0.37 mmol) suspended in dichloromethane (50 ml) was added to a solution of compound **G3-(ONNMe₂)₁₆ (5)** (147 mg, 0.023 mmol) in the same solvent (50 ml) and the mixture was stirred at room temperature for 3 days. A brownish orange solid precipitated out of the mixture, which was separated by filtration and washed

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with CH₂Cl₂ (3 × 10 ml) and hexane (3 × 10 ml) to give **9** as an orange paramagnetic solid (46%) scarcely soluble in CH₂Cl₂ and THF as solvents. Anal. Calc. for C₃₅₂H₅₀₈N₃₂O₁₆Si₂₉Ni₁₆Br₃₂ (9754.61): C, 43.34; H, 5.25; N, 4.59%. Found: C, 41.89; H, 5.64; N, 4.08%. IR (KBr): ν 1625 cm⁻¹ (m.), 1599 cm⁻¹ (vs., C=N), 1578 cm⁻¹ (w.).

General procedure for ethylene catalytic reactions.

The corresponding catalyst precursor was weighed (5-10 mg) into 250 ml screw-capped glass pressure reactor equipped with a mechanical stirrer. The reactor was capped and sealed with a septum, purged with argon, charged with toluene (50 ml), and flushed with ethylene gas fed at constant pressure (2 bars). PMAO-IP in toluene (Al/Ni = 1000) was added 10 min later with vigorous stirring. After a desired time interval the ethylene pressure was released, the polymerization reactions quenched with acidified methanol (2 % HCl) and the mixture stirred overnight. The polymer was filtered, washed with methanol, and dried. The reaction filtrate was washed with water, treated with MgSO₄, and the volatiles removed in a rotary evaporator. In order to minimize experimental error, the polymerization data represent the average of a number of runs disregarding the data from those with yields deviations above 7%. The obtained oligomers were analyzed by GC in pentane as a solvent. The integrated areas of heavier oligomers (from C₁₆ to C₃₀) were used to calculate the Schulz-Flory α parameter,⁴ and lower olefins lost during workup were calculated using that α constant. The microstructure of these materials was also determined by ¹H NMR (oligomers, r.t., CDCl₃) or ¹³C{¹H} NMR (polymers, 100 °C, 20% v/v benzene-*d*₆/TCB).

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