Dendritic effects on ethylene polymerization promoted by peripheral nickel catalysts.

José M. Benito, Ernesto de Jesús, F. Javier de la Mata, Juan C. Flores and Rafael Gómez
Departamento de Química Inorgánica, Universidad de Alcalá,
Campus Universitario, 28871 Alcalá de Henares (Madrid), Spain.
E-mail: ernesto.dejesus@uah.es; juanc.flores@uah.es; Fax: +34 91 885 4683

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 [NiBr\(_2\)(DME)]\(^2\) and carbosilane dendrimers G\(_n\)-(Cl)\(_m\) (n = 1, m = 4; n = 2, m = 8; n = 3, m = 16) according to literature procedures.\(^3\) Pyridylimine dendritic ligands 3-5 where prepared similarly to 2, in reactions of 1 with the corresponding chlorosilane dendrimer G\(_n\)-(Cl)\(_m\). Nickel compounds 6-9 where obtained as illustrated below for 9. Chemical shifts (\(\delta\)) are reported in ppm referenced to SiMe\(_4\) for \(^1\)H, \(^{13}\)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, H⁷), 6.89 (s, 1H, H⁶), 7.33 (dd, 1H, JH,H= 7.5, 4.9 Hz, H¹¹), 7.79 (pt, 1H, H¹⁰), 8.22 (d, 1H, JH,H= 7.9 Hz, H⁹), 8.51 (s, 1H, H⁷), 8.67 (d, 1H, JH,H= 4.9 Hz, H¹²). ¹³C{¹H} NMR (CDCl₃): δ 15.6 and 17.5 (Me¹³,¹⁴), 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), 7.33 (dd, 1H, JH,H= 7.5, 4.9 Hz, H¹¹), 7.77 (pt, 1H, H¹⁰), 8.21 (d, 1H, JH,H= 7.9 Hz, H⁹), 8.51 (s, 1H, H⁷), 8.66 (d, 1H, JH,H= 4.9 Hz, H¹²). ¹³C{¹H} NMR (CDCl₃): δ 0.5 (SiMe₃), 16.3 and 17.6 (Me¹³,¹⁴), 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-rings). 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 –0.08 (s, 3H, SiMe), 0.22 (s, 12H, SiMe₂), 0.56 (m, 8H, SiCH₂), 0.81 (m, 2H, CH₂SiMe₂), 1.29 (m, 2H, CH₂CH₂CH₂), 1.42 (m, 2H, CH₂CH₂CH₂), 1.66 (m, 2H, CH₂CH₂CH₂), 2.13 (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, JH,H= 7.9 Hz, H⁹), 8.49 (s, 1H, H⁷), 8.65 (d, 1H, JH,H= 4.6 Hz, H¹²). ¹³C{¹H} NMR (CDCl₃): δ –1.2 (SiMe₂), 16.4 and 17.7 (Me¹³,¹⁴), 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=O), 1567 cm⁻¹ (vs. and s., py-rings). 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, JH,H= 7.7 Hz, H⁹), 8.48 (s, 1H, H⁷), 8.64 (d, 1H, JH,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 (CH_2), 119.6 (C_3), 120.7 (C_6), 121.3 (C_9), 124.5 (C_{11}), 126.8 (C_5), 131.7 (C_2), 136.4 (C_{10}), 142.9 (C_1), 149.4 (C_{12}), 152.7 (C_4), 155.4 (C_8), 157.4 (C_7).

^{29}Si{^1}H NMR (CDCl_3): \delta 18.4 (SiMe_2), 1.18 (SiMe), 0.5 (central Si). IR (Nujol/CsI): \nu 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-[ONNMe\(_2\)]\(_{16}\) (5): Brownish oil (91 %). Anal. Calc. for C\(_{352}\)H\(_{508}\)N\(_{32}\)O\(_{16}\)Si\(_{29}\) (6258.59): C, 67.55; H, 8.18; N, 7.16%. Found: C, 66.84; H, 8.23; N, 6.88%. \(^1\)H NMR (CDCl\(_3\)): \delta -0.09 (s, 9H, SiMe), 0.21 (s, 24H, SiMe\(_2\)), 0.53 (m, 20H, SiCH\(_2\)), 1.18 (s, 24H, SiMe\(_2\)), 0.80 (m, 8H, CH\(_2\)SiMe\(_2\)), 1.43 (m, 8H, CH\(_2\)CH\(_2\)CH\(_2\)), 2.13 (s, 12H, Me\(_{14}\)), 2.31 (m, 12H, Me\(_{13}\)), 6.60 (s, 1H, H\(_3\)), 6.87 (s, 1H, H\(_6\)), 7.28 (p, 1H, H\(_{11}\)), 7.73 (p, 1H, H\(_{10}\)), 8.19 (d, 1H, J\(_{H,H}= 7.0\) Hz, H\(_9\)), 8.48 (s, 1H, H\(_7\)), 8.64 (d, 1H, J\(_{H,H}= 4.5\) Hz, H\(_4\)). \(^{13}\)C{\(^1\)H\} NMR (CDCl\(_3\)): \delta -5.0 (SiMe, only one peak can be distinguished), -0.8 (SiMe\(_2\)), 16.5 and 17.7 (Me\(_{13,14}\)), 17.9, 18.6, 19.1 and 21.8 (CH\(_2\)), 119.6 (C\(_3\)), 120.6 (C\(_6\)), 121.2 (C\(_9\)), 124.5 (C\(_{11}\)), 126.8 (C\(_5\)), 131.6 (C\(_2\)), 136.4 (C\(_{10}\)), 142.7 (C\(_1\)), 149.3 (C\(_{12}\)), 152.6 (C\(_4\)), 155.1 (C\(_8\)), 157.3 (C\(_7\)). ^{29}Si{^{1}H} NMR (CDCl\(_3\)): \delta 18.1 (SiMe\(_2\)), 0.8 (outermost SiMe), 0.6 (SiMe), 0.1 (central Si). IR (Nujol/CsI): \nu 1627 cm\(^{-1}\) (s., C=N), 1598 (w., C=C), 1581 and 1568 cm \(^{-1}\) (s., py-ring).

G0-[(ONNMe\(_2\))NiBr\(_2\)] (6): Red paramagnetic solid (80%). Anal. Calc. for C\(_{17}\)H\(_{22}\)N\(_2\)OSiBr\(_2\)Ni (516.96): C, 39.50; H, 4.29; N, 5.42%. Found: C, 39.46; H, 4.09; N, 5.03%. IR (KBr): \nu 1630 cm\(^{-1}\) (w.), 1595 cm\(^{-1}\) (vs., C=N). MS (ESI+ in CH\(_3\)CN): m/z: 478 [M – Br + CH\(_3\)CN]^+.

H-[(ONNMe\(_2\))NiBr\(_2\)] (6\(^{0\text{th}}\)). Orange paramagnetic solid obtained as described below for 9 starting from the phenolic ligand 1 (64%). Anal. Calc. for C\(_{14}\)H\(_{14}\)N\(_2\)OBr\(_2\)Ni (444.78): C, 37.81; H, 3.17; N, 6.30%. Found: C, 37.02; H, 3.06; N, 5.92%. IR (KBr): \nu 1624 cm\(^{-1}\) (m.), 1589 cm\(^{-1}\) (m., C=N), 1560 cm\(^{-1}\) (w.). MS (ESI+ in CH\(_3\)CN): m/z: 406 [M – Br + CH\(_3\)CN]^+, 225 [2c – H]^+.

G1-[(ONNMe\(_2\))NiBr\(_2\)]\(_4\) (7): Yellow paramagnetic solid (43%). Anal. Calc. for C\(_{76}\)H\(_{100}\)N\(_8\)O\(_4\)Si\(_5\)Br\(_8\)Ni\(_4\) (2204.11): C, 41.42; H, 4.57; N, 5.08%. Found: C, 41.42; H, 4.57; N, 5.08%. IR (Nujol/CsI): \nu 1626 cm\(^{-1}\) (w.), 1595 cm\(^{-1}\) (vs., C=N), 1570 cm\(^{-1}\) (w.).

G2-[(ONNMe\(_2\))NiBr\(_2\)]\(_8\) (8). Yellow paramagnetic solid. (75%). Anal. Calc. for C\(_{168}\)H\(_{236}\)N\(_{16}\)O\(_8\)Si\(_{13}\)Ni\(_8\)Br\(_{16}\) (4720.95): C, 42.74; H, 5.04; N, 4.75%. Found: C, 41.73; H, 5.32; N, 4.06%. IR (KBr): \nu 1625 cm\(^{-1}\) (m.), 1597 cm\(^{-1}\) (vs., C=N), 1567 cm\(^{-1}\) (w.).

G3-[(ONNMe\(_2\))NiBr\(_2\)]\(_{16}\) (9). Solid [NiBr\(_2\)(DME)] (115 mg, 0.37 mmol) suspended in dichloromethane (50 ml) was added to a solution of compound G3-(ONNMe\(_2\))\(_{16}\) (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.
with CH$_2$Cl$_2$ (3 × 10 ml) and hexane (3 × 10 ml) to give 9 as an orange paramagnetic solid (46%) scarcely soluble in CH$_2$Cl$_2$ and THF as solvents. Anal. Calc. for C$_{352}$H$_{508}$N$_{32}$O$_{16}$Si$_{29}$Ni$_{16}$Br$_{32}$ (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 MgSO$_4$, 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 C$_{16}$ to C$_{30}$) 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 $^1$H NMR (oligomers, r.t., CDCl$_3$) or $^{13}$C{$^1$H} NMR (polymers, 100 ºC, 20% v/v bencene-d$_6$/TCB).


