Supporting Material to

Mono(amidinate) Yttrium Alkyl Complexes: the Effect of Ligand Variation on Ethene Polymerization Catalysis

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Experimental Section

General. All experiments were carried out under an inert atmosphere of purified dinitrogen using standard Schlenk and glove-box techniques, unless mentioned otherwise. Toluene, pentane and THF were distilled from Na or Na/K alloy before use or purified by percolation under nitrogen atmosphere over columns of alumina, molecular sieves and supported copper oxygen scavenger (BASF R3-11). Benzene-d_6, Toluene-d_8 and THF-d_8 were dried over Na/K alloy and vacuum transferred before use. Bromobenzene-d_5 was degassed and dried over CaH_2. *N*-2,6-diisopropylbenzimidoyl chloride was prepared according to T. Ugi et al., *Chem. Ber.* 95 (1965) 126. Hexamethyldisiloxane, benzoic acid, 2,6-diisopropylaniline, dichloromethane, triethyl amine and $[PhNMe_2H][B(C_6F_5)_4]$ were used as purchased. TiBAO was prepared by careful partial hydrolysis of iBu$_3$Al (Witco) in toluene. For the polymerization experiments, the toluene solvent (Aldrich anhydrous, 99.5%) as well as the ethene (AGA, polymer grade) were passed over columns of oxygen scavenger (BASF R3-11) and molecular sieves (4Å) before being passed to the reactor. NMR spectra were recorded on Varian Unity 500, VXR 300 and Gemini 200 spectrometers. Gel permeation chromatography (GPC) analysis of the polyethenes was carried out by A. Jekel (University of Groningen) on a Polymer Laboratories Ltd. (PL-GPC210) chromatograph using 1,2,4-trichlorobenzene (TCB) as the mobile phase at 150 °C. The samples were prepared by dissolving the polymer in the mobile phase solvent in an external oven at 0.1% (weight/volume) and were run without filtration (column: 4PL-Gel Mixed A). The molecular weight was referenced to polystyrene (Mw = 65500, PDI = 1.02) standards. The polystyrene was used for column calibration – single point calibration for Triple Detector (RI + Visco + LS, 90°) (VISCOTEK®, Software: TRISEC®). Elemental analyses were performed at the Microanalytical Department of the University of Groningen. All reported values are the average of at least two independent determinations.

Synthesis of $Y(CH_2SiMe_3)_3(THF)_2$

$LiCH_2SiMe_3$ (1.41 g, 15.00 mmol) was added to a suspension of $YCl_3 \cdot THF_{3.5}$ (2.24 g, 5.00 mmol) in hexanes (100 ml) at 0 °C. The reaction mixture was stirred for 3 hours. After which time the suspension was filtrated. Removal of the solvent leaves the title compound as a white microcrystalline solid (1.77 g, 3.60 mmol, 72 %). The product was pure by NMR spectroscopy.

^{1}H NMR (300 MHz, C_6D_6, δ): 3.83 (m, 8H, α-THF), 1.32 (m, 8H, β-THF), 0.29 (s, 27H, $CH_2Si\mathit{Me}_3$), –0.69 (d, $^2J_{YH}$ = 2.4 Hz, 6H, $C\mathit{H}_2SiMe_3$). ^{13}C NMR (75.4 MHz, C_6D_6, δ): 69.8 (t, $^1J_{CH}$ = 150.1 Hz, α-THF), 33.8 (d, $^1J_{YC}$ = 34.18 Hz; t, $^1J_{CH}$ = 100.0 Hz, $\mathit{C}H_2SiMe_3$), 25.2 (t, $^1J_{CH}$ = 134.2 Hz, β-THF), 4.5 (q, $^1J_{CH}$ = 117.0 Hz, $CH_2Si\mathit{Me}_3$).

Synthesis of N,N'-Bis-(2,6-diisopropylphenyl)-pentafluorobenzamidine (L2H)

A stirred mixture of P_2O_5 (10.65 g, 37.5 mmol), hexamethyldisiloxane (17 mL, 80 mmol) and dichloromethane (15 mL) was refluxed for 30 minutes. The volatiles were distilled off by heating the mixture to 160 °C. Pentafluorobenzoic acid (1.26 g, 6.25 mmol) and 2,6-diisopropylphenylamine (2.5 mL, 13.3 mmol) were added to the viscous syrup, and this mixture was heated at 160 °C for 19 hours. The mixture was poured into a 1 M KOH solution (200 mL), and this was extracted with ether (100, 100 and 50 mL). The combined extracts were concentrated and the concentrate was filtered through a layer of alumina (3 cm cross section). The filtrate was concentrated and crystallized from ethanol/water to give 1.65 g (50%) of the amidine, MP 166-168 °C.

IR (Nujol) 3376 (NH), 1636 cm^{-1} (C=N).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.0 Hz, 2H, *o*-Ar), 7.10 (ps. t, 2 H total, *p*-Ar), 6.94 (d, *J* = 7.7 Hz, 2H, *o*-Ar), 5.78 (s, 1H, NH), 3.28 and 3.19 (overlapping sept, 4H total, $C\mathit{H}Me_2$), 1.33 (d, *J* = 7.0 Hz, 6H, $CH\mathit{Me}_2$), 1.15 (d, *J* = 7.0 Hz, 6H, $CH\mathit{Me}_2$), 1.08 (d, *J* = 6.6 Hz, 6H, $CH\mathit{Me}_2$), 0.84 (d, *J* = 6.6 Hz, 6H, $CH\mathit{Me}_2$). ^{13}C NMR (75.4 MHz, $CDCl_3$, APT) δ 147.0 (Ar ipso-C), 144.9 (d, $^1J_{CF}$ = 249.5 Hz, CF), 138.2 (d, $^1J_{CF}$ = 242.2 Hz, CF), 139.1 (Ar ipso-C), 137.9 (d, $^1J_{CF}$ = 256.3 Hz, CF), 131.6 (Ar C), 128.7 (Ar C), 125.9, 122.0, 121.0, and 120.8 (Ar CH), 25.9 and 25.5 ($\mathit{C}HMe_2$), 23.2, 21.9, 19.7 and 19.0 ($CH\mathit{Me}_2$). ^{19}F NMR (376.3 MHz, $CDCl_3$) δ –138.7 (d, $^3J_{FF}$ = 22 Hz, o-CF), –153.0 (t, $^3J_{FF}$ = 21 Hz, p-CF), –161.7 (d, $^3J_{FF}$ = 22 Hz, m-CF). MS (EI); *m/*z (%) = 530 [M^+] (31), 354 (100). HRMS: calcd. for $C_{31}H_{35}N_2F_5$: 530.272; found 530.271. Anal. [$C_{31}H_{35}N_2F_5$] (530.27) calcd: C, 70.17; H, 6.65; N, 5.28. Found: C, 70.15; H, 6.60; N, 5.27.

Synthesis of *N*-(2,6-diisopropyl)phenyl-*N'*-(2-dimethylaminoethyl)benzamidine (L3H)

To a solution of *N*,*N*-dimethylethylenediamine (1.1 mL, 10 mmol) in toluene (10mL) was added *N*-(2,6-diisopropyl)phenylbenzimidoylchloride (1.5 g, 5 mmol). After one hour of reflux, the mixture was cooled and 2N KOH (25 mL) was added. The organic phase was washed with water, dried (Na_2SO_4) and concentrated. The concentrate was Kugelrohr-distilled (0.02 mmHg, at 200 °C) to give 1.74 g (99%) of a pale yellow slowly solidifying oil. IR (neat) 3416 (NH), 1630, 1588 cm $^{-1}$ (C=N); ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.7-7.9 (m, overlapping 8H, Ar), 4.8-5.2 (br, 1H, NH), 3.16 (br, 2H, C*H*Me_2) 2.21, 1.8 (m, overlapping 10H, NMe_2, NCH_2), 1.1-1.4 (m, 12H, CH*Me*$_2$). ^{13}C NMR (125.8 MHz, $CDCl_3$): MS (CI); for $C_{23}H_{33}N_3$ *m/*z 352 $(M+H)^+$.

***N*-(2,6-diisopropyl)phenylbenzimidoylchloride**

A mixture of *N*-(2,6-diisopropyl)phenylbenzanilide (8.04 g, 28.6 mmol) and thionyl chloride (6.6 mL, 90 mmol) was refluxed for 1 hour. The remainder was distilled, using a Kugelrohr (oven ca 200 ^{o}C, 0.02 mmHg), to give 7.3 g (99%) of a yellow solidifying oil (mp 65 ^{o}C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.26 (d, *J* = 5.2 Hz, 2 H, Ar), 7.61–7.50 (m, 3 H, Ar), 7.24 (s, 3 H, Ar), 2.88 (sept, *J* = 4.4 Hz, 2 H, *i*Pr-CH), 1.27 (d, *J* = 4.4 Hz, 6 H, *i*Pr-CH_3), 1.21 (d, *J* = 4.4 Hz, 6 H, *i*Pr- CH_3).

Synthesis of $[C_6F_5C(N\text{-}2,6\text{-}iPr_2C_6H_3)_2]Y(CH_2SiMe_3)_2(THF)$

A solution of $(Me_3SiCH_2)_3Y(THF)_2$ (0.49 g, 1.00 mmol) in pentane (30 ml) was reacted with **L2**H (0.27 g, 0.53 mmol) at room temperature. The reaction mixture was stirred for 3 hours, after which the volatiles were removed under vacuum. Residual THF was removed from the remaining sticky solid by stirring with pentane (5 ml), which was subsequently removed under vacuum. Extracting with pentane (3 x 20 ml) and concentrating and cooling the extract to -30 ºC gave the product (0.60 g, 0.70 mmol, 70 %).

^{1}H NMR (300 MHz, C_6D_6): δ 6.98-6.89 (m, 6 H, C_6H_3), 3.59 (sept, $^3J_{HH}$ = 6.6 Hz, 4 H, C*H*Me_2), 3.55 (m, 4 H α-THF), 1.30 (d, $^3J_{HH}$ = 6.6 Hz, 12 H, CH*Me*$_2$), 1.19 (d, $^3J_{HH}$ = 6.6 Hz, 12 H, CH*Me*$_2$), 1.14 (m, 4 H β-THF), 0.28 (s, 18H, CH_2Si*Me*$_3$), -0.05 (d, $^2J_{YH}$ = 3.0 Hz, 4 H, C*H*$_2$SiMe$_3$). ^{13}C NMR (75.4 MHz, C_6D_6): δ 165.7 (N*C*N), 143.6 (C_6H_3 *ipso*-C), 143.1 (d, $^1J_{CF}$ = 250.2 Hz, CF), 141.1 (C_6F_5, *ipso*-C), 138.1 (d, $^1J_{CF}$ = 245.8 Hz, CF), 137. (d, $^1J_{CF}$ = 254.9 Hz, CF), 128.7 (C_6H_3 *ipso*-C), 125.7 (d, $^1J_{CH}$ = 159.8 Hz, C_6H_3), 123.8 (d, $^1J_{CH}$ = 156.2 Hz, C_6H_3), 69.7 (t, $^1J_{CH}$ = 152.5 Hz, α-THF), 41.2 (dt, $^1J_{CH}$ = 101.3 Hz, $^1J_{YC}$ = 41.5 Hz, Y*C*H_2SiMe$_3$), 28.3 (d, $^1J_{CH}$ = 126.9 Hz, *C*HMe$_2$), 26.9 (q, $^1J_{CH}$ = 125.7 Hz, CH*Me*$_2$), 25.0 (t, $^1J_{CH}$ = 135.4 Hz, β-THF), 23.0 (q, $^1J_{CH}$ = 126.9 Hz, CH*Me*$_2$), 4.2 (q, J_{CH} = 118.4 Hz, YCH$_2$Si*Me*$_3$).

^{19}F NMR (188.15 MHz, 20 °C, C_6D_6) δ: –132.41 (d, $^3J_{FF}$ = 19 Hz, o-CF), –151.35 (t, $^3J_{FF}$ = 21 Hz, p-CF), –161.77 (d, $^3J_{FF}$ = 17 Hz, m-CF).

^{1}H NMR (300 MHz, THF-d_8): δ 6.99-6.92 (m, 6 H, C_6H_3), 3.40 (sept, $^3J_{HH}$ = 6.6 Hz, 4 H, C*H*Me$_2$), 1.18 (d, $^3J_{HH}$ = 6.6 Hz, 12 H, CH*Me*$_2$), 1.06 (d, $^3J_{HH}$ = 6.6 Hz, 12 H, CH*Me*$_2$), –0.12 (s, 18H, CH$_2$Si*Me*$_3$), –0.62 (d, $^2J_{YH}$ = 2.8 Hz, 4 H, C*H*$_2$SiMe$_3$).

^{13}C NMR (75.4 MHz, THF-d_8): δ 166.0 (N*C*N), 145.4 (C_6H_3 *ipso*-C), 143.2 (d, $^1J_{CH}$ = 252.0 Hz, C_6F_5), 143.1 (C_6F_5, *ipso*-C), 138.1 (d, $^1J_{CH}$ = 248.3 Hz, C_6F_5), 137.0 (d, $^1J_{CH}$ = 254.9 Hz, C_6F_5), 131.3 (C_6H_3 *ipso*-C), 126.8 (d, $^1J_{CH}$ = 156.8 Hz, C_6H_3), 125.4 (d, $^1J_{CH}$ = 152.1 Hz, C_6H_3), 37.9 (dt, $^1J_{CH}$ = 102.1 Hz, $^1J_{YC}$ = 39.1 Hz, Y*C*H$_2$SiMe$_3$), 29.2 (d, $^1J_{CH}$ = 127.8 Hz, *C*HMe$_2$), 28.1 (q, $^1J_{CH}$ = 125.8 Hz, CH*Me*$_2$), 24.7 (q, $^1J_{CH}$ = 126.0 Hz, CH*Me*$_2$), 5.5 (q, J_{CH} = 118.4 Hz, YCH$_2$Si*Me*$_3$).

Anal. [$C_{43}H_{64}F_5N_2OSi_2Y$] (865.06) calcd: C, 59.70; H, 7.46; N, 3.24; Y, 10.28. Found: C, 60.72; H, 7.68; N, 3.41; Y, 10.07.

Reaction of [C_6F_5C(N-2,6-*i*Pr$_2C_6H_3$)$_2$]Y(CH$_2$SiMe$_3$)$_2$(THF) with [HNMe$_2$Ph][B(C_6F_5)$_4$]

Solid [C_6F_5C(N-2,6-*i*Pr$_2C_6H_3$)$_2$]Y(CH$_2$SiMe$_3$)$_2$(THF) (31.1 mg, 36 μmol) and [HNMe$_2$Ph][B(C_6F_5)$_4$] (28.8 mg, 36 μmol) were mixed THF-d_8 (0.6 ml) was added. The obtained solution was transferred to an NMR tube and analyzed by NMR spectroscopy, which showed full conversion to the ionic species {[C_6F_5C(N-2,6-*i*Pr$_2C_6H_3$)$_2$]Y(CH$_2$SiMe$_3$)(THF-d_8)$_n$}[B(C_6F_5)$_4$], SiMe$_4$, and free PhNMe$_2$.

^{1}H NMR (300 MHz, THF-d_8): δ 7.13-7.01 (m, 6H, C_6H_3), 6.89 (t, $^3J_{HH}$ = 8.5 Hz, 2 H, m-Ph), 6.64 (d, $^3J_{HH}$ = 8.5 Hz, 2 H, o-Ph), 6.58 (t, $^3J_{HH}$ = 8.0 Hz, 1 H, p-Ph), 3.37 (sept, $^3J_{HH}$ = 6.6 Hz, 4 H, C*H*Me$_2$), 2.85 (s, 6H, *Me*$_2$NPh), 1.17 (d, $^3J_{HH}$ = 6.6 Hz, 12 H, CH*Me*$_2$), 1.10 (d, $^3J_{HH}$ = 6.6 Hz, 12 H, CH*Me*$_2$), – 0.04 (s, 9 H, CH$_2$Si*Me*$_3$), –0.56 (d, $^3J_{YH}$ = 2.9 Hz, 2 H, C*H*$_2$SiMe$_3$).

^{13}C NMR (75.4 MHz, THF-d_8,): δ 170.4 (N*C*N), 150.1 (d, $^1J_{CF}$ = 241.5 Hz, BC_6F_5), 145.5 (C_6H_3 *ipso*-C), 144.3 (d, $^1J_{CF}$ = 251.6 Hz, C_6F_5), 141.7(C_6F_5, *ipso*-C), 143.9 (d, $^1J_{CF}$ = 251.6 Hz, BC_6F_5), 140.0 (d, $^1J_{CF}$ = 251.0 Hz, BC_6F_5), 139.4 (d, $^1J_{CF}$ = 241.5 Hz, C_6F_5), 139.0 (d, $^1J_{CF}$ = 246.5 Hz, C_6F_5), 138.3 (d, $^1J_{CF}$ = 249.6 Hz, BC_6F_5), 130.4 (C_6H_3, *ipso*-C), 128.1 (d, $^1J_{CH}$ = 154.2 Hz, C_6H_3), 126.3 (d, $^1J_{CH}$ = 156.5 Hz, C_6H_3), 45.2 (dt, $^1J_{CH}$ = 95.2 Hz, $^1J_{YC}$ = 43.1 Hz, Y*C*H$_2$SiMe$_3$), 29.3 (d, $^1J_{CH}$ = 128.4 Hz, *C*HMe$_2$), 27.8 (q, $^1J_{CH}$ = 124.6 Hz, CH*Me*$_2$), 24.8 (q, $^1J_{CH}$ = 125.8 Hz, CH*Me*$_2$), 4.7 (q, $^1J_{CH}$ = 116.2 Hz, YCH$_2$Si*Me*$_3$).

^{19}F NMR (188.15 MHz, 20 °C, C_6D_6) δ: –128.4 (d, $^3J_{FF}$ = 19 Hz, o-CF, C_6F_5), –133.1 (d, $^3J_{FF}$ = 10 Hz, o-CF, B(C_6F_5)$_4$), –142.8 (t, $^3J_{FF}$ = 21 Hz, p-CF, C_6F_5), –162.7 (t, $^3J_{FF}$ = 21 Hz, p-CF, B(C_6F_5)$_4$), –160.1 (d, $^3J_{FF}$ = 17 Hz, m-CF, C_6F_5), –160.1 (d, $^3J_{FF}$ = 18 Hz, m-CF, B(C_6F_5)$_4$).

Synthesis of $[C_6F_5C(N\text{-}2,6\text{-}Pr^i_2C_6H_3)_2]Y(CH_2SiMe_3)_2(THF)_2$

A solution of $(Me_3SiCH_2)_3Y(THF)_2$ (0.27 g, 0.54 mmol) in pentane (30 ml) was reacted with $[C_6F_5C(N\text{-}2,6\text{-}Pr^i_2C_6H_3)_2]H$ (0.29 g, 0.54 mmol) at room temperature. The reaction mixture was stirred for 3 hours, after which the volume of the solution was reduced to 10 ml and cooled to -30 ºC affording the product (0.32 g, 0.35 mmol, 65 %).

^{1}H NMR (300 MHz, C_6D_6, δ): 7.02-6.90 (m, 6 H, C_6H_3), 3.53 (sept, $^3J_{HH}$ = 6.6 Hz, 4 H, $CHMe_2$), 3.51 (m, 8 H α-THF), 1.29 (d, $^3J_{HH}$ = 6.6 Hz, 12 H, $CHMe_2$), 1.16 (d, $^3J_{HH}$ = 6.6 Hz, 12 H, $CHMe_2$), 1.10 (m, 8 H β-THF), 0.24 (s, 18H, CH_2SiMe_3), -0.05 (d, $^2J_{YH}$ = 3.3 Hz, 4 H, CH_2SiMe_3). ^{19}F NMR (188.15 MHz, 20 °C, C_6D_6) δ: -132.9 (d, $^3J_{FF}$ = 19.19 Hz, o-CF), -151.8 (t, $^3J_{FF}$ = 21.26 Hz, p-CF), -162.7 (d, $^3J_{FF}$ = 17.43 Hz, m-CF).

Preparation of $[\{PhC(N(CH_2)_2NMe_2)(N\text{-}2,6\text{-}iPr_2C_6H_3)\}Y(CH_2SiMe_3)_2(THF)]$

A solution of $[(Me_3SiCH_2)_3Y(THF)_2]$ (0.22 g, 0.44 mmol) in pentane (30 ml) was reacted with **L3**H (0.15 g, 0.44 mmol) at room temperature. The reaction mixture was stirred for 3 hours, after which time the volatiles were removed *in vacuum* and the remainder sticky solid stripped with pentane (5 ml). Extraction with pentane (2 x 20 ml) and cooling to – 30 ºC gives the product (0.40 g, 0.51 mmol, 64 %).

^{1}H NMR (300 MHz, C_6D_6,): δ 7.14 (d, $^3J_{HH}$ = 7.7 Hz, m, 2 H, C_6H_3), 6.95 (m, 5 H, Ph), 6.88 (d, $^3J_{HH}$ = 7.7 Hz, m, 1 H, C_6H_3), 3.71 (m, 4 H α-THF), 3.41 (sept, $^3J_{HH}$ = 6.9 Hz, 2 H, C*H*Me$_2$), 3.05 (t, $^3J_{HH}$ = 6.3 Hz, 2 H, NC*H*$_2$CH$_2$NMe$_2$), 2.41 (t, $^3J_{HH}$ = 6.3 Hz, 2 H, NCH$_2$C*H*$_2$NMe$_2$), 2.28 (s, 6H, N*Me*$_2$), 1.32 (m, 4 H β-THF), 1.26 (d, $^3J_{HH}$ = 6.9 Hz, 6 H, CH*Me*$_2$), 0.98 (d, $^3J_{HH}$ = 6.6 Hz, 6 H, CH*Me*$_2$), 0.37 (s, 18H, CH$_2$Si*Me*$_3$), –0.55 (d, $^2J_{YH}$ = 2.7 Hz, 4 H, YC*H*$_2$SiMe$_3$).

^{13}C NMR (75.4 MHz, C_6D_6,): δ 175.0 (NCN), 145.2(Ph, *ipso*-C), 142.2 (Ar, *ipso*-C), 133.4 (C_6H_3, C), 129.4 (d, $^1J_{CH}$ = 167.1 Hz, Ar), 129.1 (d, $^1J_{CH}$ = 169.6 Hz, Ar), 128.3 (d, $^1J_{CH}$ = 158.5 Hz, Ar), 127.8 (d, $^1J_{CH}$ = 161.1 Hz, Ar) 123.8 (d, $^1J_{CH}$ = 158.6 Hz, Ar), 69.1 (t, $^1J_{CH}$ = 145.1 Hz, α-THF), 61.34 (t, J_{CH} = 135.4 Hz, NC*H*$_2$CH$_2$NMe$_2$), 45.8 (t, J_{CH} = 135.4 Hz, NCH$_2$C*H*$_2$NMe$_2$), 45.6 (q, J_{CH} = 134.2 Hz, N*Me*$_2$), 30.0 (dt, J_{CH} = 101.3 Hz, J_{YC} = 37.8 Hz, YC*H*$_2$SiMe$_3$), 28.0 (d, $^1J_{CH}$ = 130.59 Hz, C*H*Me$_2$), 25.3 (t, $^1J_{CH}$ = 132.93 Hz, β-THF), 25.4 (q, J_{CH} = 125.7 Hz, CH*Me*$_2$), 23.8 (q, J_{CH} = 125.0 Hz, CH*Me*$_2$), 5.0 (q, J_{CH} = 118.4 Hz, YCH$_2$Si*Me*$_3$).

^{1}H NMR (300 MHz, THF-d_8,): δ 7.10 (m, 5 H, Ph), 6.80 (superimposed, 3 H, C_6H_3), 3.23 (sept, $^3J_{HH}$ = 6.7 Hz, 2 H, C*H*Me$_3$), 3.22 (t, $^3J_{HH}$ = 6.2 Hz, 2 H, NC*H*$_2$CH$_2$NMe$_2$), 2.73 (t, $^3J_{HH}$ = 6.2 Hz, 2 H, NCH$_2$C*H*$_2$NMe$_2$), 2.48 (s, 6H, N*Me*$_2$), 1.05 (d, $^3J_{HH}$ = 6.7 Hz, 6 H, CH*Me*$_2$), 0.81 (d, $^3J_{HH}$ = 6.7 Hz, 6 H, CH*Me*$_2$), –0.07 (s, 18H, CH$_2$Si*Me*$_3$), –0.91 (d, $^2J_{YH}$ = 2.95 Hz, 4 H, YC*H*$_2$SiMe$_3$).

^{13}C NMR (75.4 MHz, C_6D_6,): δ 176.6 (NCN), 146.8 (Ar, *ipso*-C), 143.7 (Ar, *ipso*-C), 135.2 (C_6H_3, C), 131.0 (d, $^1J_{CH}$ = 158.2 Hz, Ar), 130.7 (d, $^1J_{CH}$ = 163.0 Hz, Ar), 129.3 (d, $^1J_{CH}$ = 158.5 Hz, Ar), 125.0 (d, $^1J_{CH}$ = 158.6 Hz, Ar), 124.9 (d, $^1J_{CH}$ = 154.2 Hz, Ar), 63.2 (t, J_{CH} = 136.2 Hz, N*C*H_2CH$_2$NMe$_2$), 47.6 (t, J_{CH} = 135.8 Hz, NCH$_2$*C*H_2NMe$_2$), 47.2 (q, J_{CH} = 134.2 Hz, N*Me*$_2$), 31.6 (dt, J_{CH} = 95.5 Hz, J_{YC} = 38.7 Hz, Y*C*H_2SiMe$_3$), 29.5 (d, $^1J_{CH}$ = 130.4 Hz, *C*HMe$_2$), 26.5 (q, J_{CH} = 126.1 Hz, CH*Me*$_2$), 25.2 (q, J_{CH} = 125.7 Hz, CH*Me*$_2$), 6.0 (q, J_{CH} = 117.6 Hz, YCH$_2$Si*Me*$_3$).

[$C_{35}H_{62}N_3OSi_2Y$] 685.97, calcd C: 61.28 H: 9.11 N: 6.13 Y: 12.96. Found: C: 61.40 H: 9.00 N: 6.20 Y: 12.88

Reaction of [{PhC(N(CH$_2$)$_2$NMe$_2$)(N-2,6-*i*Pr$_2$C$_6$H$_3$)}Y(CH$_2$SiMe$_3$)$_2$(THF)] with [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] in THF-*d*$_8$.

Solid [{PhC(N(CH$_2$)$_2$NMe$_2$)(N-2,6-*i*Pr$_2$C$_6$H$_3$)}Y(CH$_2$SiMe$_3$)$_2$(THF)] (27.0 mg, 40 µmol) and [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] (32.0 mg, 40 µmol) were mixed and THF-*d*$_8$ (0.6 ml) was added. The obtained solution was transferred to an NMR tube and analyzed by NMR spectroscopy, which showed full conversion to the cationic species [{PhC(N(CH$_2$)$_2$NMe$_2$)(N-2,6-*i*Pr$_2$C$_6$H$_3$)}Y(CH$_2$SiMe$_3$)(THF-*d*$_8$)$_n$}[B(C$_6$F$_5$)$_4$], SiMe$_4$, and free PhNMe$_2$.

^{1}H NMR (300 MHz, THF-*d*$_8$): δ 7.30 (d, $^3J_{HH}$ = 7.3 Hz, 2 H, C_6H_3), 7.20 (t, $^3J_{HH}$ = 7.3 Hz, 1 H, C_6H_3), 6.95 (m, 5 H, Ph), 3.49 (t, $^3J_{HH}$ = 6.9 Hz, 2 H, NC*H*$_2$CH$_2$NMe$_2$), 2.88 (t, $^3J_{HH}$ = 6.6 Hz, 2 H, C*H*Me$_3$), 2.74 (t, $^3J_{HH}$ = 6.9 Hz, 2 H, NCH$_2$C*H*$_2$NMe$_2$), 2.28 (s, 6H, N*Me*$_2$), 1.12 (d, $^3J_{HH}$ = 6.6 Hz, 6 H, CH*Me*$_3$), 0.80 (d, $^3J_{HH}$ = 6.6 Hz, 6 H, CH*Me*$_3$), –0.07 (s, 9H, CH$_2$Si*Me*$_3$), –0.69 (d, $^2J_{YH}$ = 2.9 Hz, 4 H, YC*H*$_2$SiMe$_3$).

^{13}C NMR (75.4 MHz, C_6D_6,): δ 178.0 (NCN), 144.1 (Ar, *ipso*-C), 143.7 (Ar, *ipso*-C), 132.6 (C_6H_3, C), 130.8 (d, $^1J_{CH}$ = 158.2 Hz, Ar), 130.5 (d, $^1J_{CH}$ = 161.4 Hz, Ar), 129.3 (d, $^1J_{CH}$ = 156.5 Hz, Ar), 126.4 (d, $^1J_{CH}$ = 161.0 Hz, Ar), 125.6 (d, $^1J_{CH}$ = 157.4 Hz, Ar), 65.3 (t, J_{CH} = 134.3 Hz, N*C*H$_2$CH$_2$NMe$_2$), 47.8 (q, J_{CH} = 135.2 Hz, N*Me*$_2$), 47.2 (t, J_{CH} = 135.8 Hz, NCH$_2$*C*H$_2$NMe$_2$), 35.0 (dt, J_{CH} = 93.4 Hz, J_{YC} = 41.7 Hz, Y*C*H$_2$SiMe$_3$), 29.1 (d, $^1J_{CH}$ = 131.1 Hz, *C*HMe$_3$), 27.0 (q, J_{CH} = 125.3 Hz, CH*Me*$_3$), 25.6 (q, J_{CH} = 125.1 Hz, CH*Me*$_3$), 5.4 (q, J_{CH} = 118.5 Hz, YCH$_2$Si*Me*$_3$).

Reaction of [{PhC(N(CH$_2$)$_2$NMe$_2$)(N-2,6-*i*Pr$_2$C$_6$H$_3$)}Y(CH$_2$SiMe$_3$)$_2$(THF)] with [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] in C$_6$D$_5$Br.

Solid **3** (6.8 mg, 10 µmol) and [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] (8.0 mg, 10 µmol) were mixed and C_6D_5Br (0.6 ml) was added. The obtained solution was transferred to an NMR tube and analyzed by NMR spectroscopy, which showed conversion to the cationic species [{PhC(N(CH$_2$)$_2$NMe$_2$)(N-2,6-*i*Pr$_2$C$_6$H$_3$)}Y(CH$_2$SiMe$_3$)(THF)}][B(C$_6$F$_5$)$_4$], SiMe$_4$, and free

$PhNMe_2$. A small amount of another species is present that appears to be associated with thermal decomposition of the initial product. Full assignment of the initial product was accomplished by 2D-NMR (COSY and HSQC).

^{1}H NMR (500 MHz, –25 °C, C_6D_5Br) δ 7.07 (d, $^3J_{HH}$ = 7.6 Hz, 1 H, *m*-H Ar), 6.98. (t, $^3J_{HH}$ = 7.6, *p*-H Ar), 6.85 (t, $^3J_{HH}$ = 7.5 Hz, 1 H, *m*-H Ph), 6.80 (d, $^3J_{HH}$ = 7.6 Hz, 2 H, *m*-H Ar), 6.48 (t, $^3J_{HH}$ = 7.5 Hz, 1 H, *p*-H Ph), 6.36 (t, $^3J_{HH}$ = 7.5 Hz, 2 H, *o*-H Ph), 3.80 (br, 4 H, THF), 3.36 (superimposed 2 H, C*H*Me_2, NC*H*H'CH_2NMe_2), 2.82 (superimposed, 2 H, $NCH_2CHH'NMe_2$, $NCHH'CH_2NMe_2$), 2.65 (C*H*Me_2, overlapped), 2.63 ($PhNMe_2$), 2.18 (s, 3H, NMe_2), 2.03 (s, 3H, NMe_2), 1.90 (m, 1H, $NCH_2CHH'NMe_2$), 1.60 (br, 4 H, THF), 1.40 (d, $^3J_{HH}$ = 6.5 Hz, 3 H, CH*Me*$_2$), 1.26 (d, $^3J_{HH}$ = 6.5 Hz, 3 H, CH*Me*$_2$), 1.12 (d, $^3J_{HH}$ = 6.5 Hz, 3 H, CH*Me*$_2$), 0.37 (d, $^3J_{HH}$ = 6.5 Hz, 3 H, CH*Me*$_3$), –0.03 (s, 9H, CH_2SiMe_3), –0.87 (d, $^2J_{HH}$ = 11.2 Hz, 2 H, YC*H*$_2$SiMe$_3$), –1.08 (d, $^2J_{HH}$ = 11.2 Hz, 2 H, YC*H*$_2$SiMe$_3$).

^{13}C NMR (125.7 MHz, –25 °C, C_6D_5Br) δ 177.8 (N*C*N), 152.0, 141.9, 141.8 and 141.1 (s, Ar *ipso*-C, Ph *ipso*-C, and 2 Ar *m*-C), 132.8 (d, overlapped, Ph *m*-CH), 111.7 (d, $^1J_{CH}$ = 164 Hz, Ph *p*-CH), 111.6 (d, $^1J_{CH}$ = 164 Hz, Ph *o*-CH), 73.1 (t, $^1J_{CH}$ = 152 Hz, α-THF), 62.0 (t, $^1J_{CH}$ = 138 Hz, N*C*$H_2CH_2NMe_2$), 46.6 (N*Me*$_2$), 44.5 ($NCH_2CH_2NMe_2$), 43.0 (N*Me*$_2$), 36.3 (d, J_{YC} = 48.6 Hz, Y*C*H_2SiMe_3), 27.6 (*C*HMe_2), 27.5 (*C*HMe_2), 27.0 (CH*Me*$_2$), 25.7 (CH*Me*$_2$), 25.0 (β-THF), 24.6 (CH*Me*$_2$), 24.0 (CH*Me*$_2$), 4.1 (YCH_2SiMe_3).

Ethylene polymerization with [C_6F_5C(N-2,6-*i*$Pr_2C_6H_3)_2$]Y($CH_2SiMe_3)_2$(THF) (2) and [$HNMe_2Ph$][$B(C_6F_5)_4$].

In a drybox, solutions of **2** (10 μmol) and [$HNMe_2Ph$][$B(C_6F_5)_4$] (10 μmol), each in 10 ml of toluene were prepared. These were stored in separate serum-capped vials. Polymerization was performed in a pre-dried stainless steel 0.5L autoclave, charged with 150 ml of dry toluene, equilibrated at the desired reaction temperature (polymerization experiments were run at 30, 50, 80 and 100 °C), and pressurized with ethylene (5 bar). The solution of [$HNMe_2Ph$][$B(C_6F_5)_4$] was injected into the reactor first (using a pneumatically operated injector), and the reaction was started by subsequently injecting the solution of **2**. The ethylene pressure was kept constant during the reaction by providing a replenishing flow. The reactor was stirred for the required reaction time and then vented. The polymer (where obtained) was repeatedly rinsed with methanol and dried in a vacuum oven.

Ethylene polymerization with [C_6F_5C(N-2,6-*i*$Pr_2C_6H_3)_2$]Y($CH_2SiMe_3)_2$(THF) (2) , [$HNMe_2Ph$][$B(C_6F_5)_4$] and $B(C_6F_5)_3$

In a drybox, solutions were made of **2** (10 μmol), [$HNMe_2Ph$][$B(C_6F_5)_4$] (10 μmol) and $B(C_6F_5)_3$ (10 μmol), each in 10 ml of toluene. These solutions were prepared in separate vials

sealed with a serum cap. Ethylene polymerization was performed in a stainless steel 0.5L autoclave, pre-dried and flushed with nitrogen, charged with 150 ml of dry toluene, equilibrated at the desired reaction temperature, and pressurized with ethylene (5 bar). The solution of $[HNMe_2Ph][B(C_6F_5)_4]$ was injected first into the reactor (using a pneumatically operated injector), and then the solution of **2** was injected. The reaction was started by subsequently injecting the $B(C_6F_5)_3$ solution. The ethylene pressure was kept constant during the reaction by providing a replenishing flow. The reactor was stirred for 20 minutes, after which the reactor was vented. The polymer was rinsed repeatedly with methanol and subsequently dried in a vacuum oven.

Ethylene polymerization with $[C_6F_5C(N\text{-}2,6\text{-}i\mathbf{Pr}_2C_6H_3)_2]Y(CH_2SiMe_3)_2(THF)_2$, $[HNMe_2Ph][B(C_6F_5)_4]$ and TiBAO

In a drybox, solutions were made of $[C_6F_5C(N\text{-}2,6\text{-}i\mathrm{Pr}_2C_6H_3)_2]Y(CH_2SiMe_3)_2(THF)_2$ (10 μmol) in 10 ml toluene, solid $[HNMe_2Ph][B(C_6F_5)_4]$ (10 μmol) and TiBAO (100 μmol Al) were mixed together in 10 ml toluene. Each solution was prepared in a vial sealed with a serum cap. Ethylene polymerization was performed in a stainless steel 1.0 L autoclave, pre-dried and flushed with nitrogen, charged with 200 ml of dry toluene, equilibrated at the desired reaction temperature, and pressurized with ethylene (5 bar). The solution of $[HNMe_2Ph][B(C_6F_5)_4]$/TiBAO was injected first into the reactor (using a pneumatically operated injector), then the solution of $[C_6F_5C(N\text{-}2,6\text{-}i\mathrm{Pr}_2C_6H_3)_2]Y(CH_2SiMe_3)_2(THF)_2$ was added. The ethylene pressure was kept constant during the reaction by providing a replenishing flow. The reactor was stirred for 20 minutes, after which the reactor was vented. The polymer was rinsed repeatedly with methanol and subsequently dried in a vacuum oven.