Supplementary Material for Chemical Communications

Supplementary data

"Yttrium alkyl complexes with a sterically demanding benzamidinate ligand: synthesis, structure and catalytic ethene polymerisation"

By : Sergio Bambirra, Daan van Leusen, Auke Meetsma, Bart Hessen* and Jan H. Teuben

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, diethyl ether 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 and THF-d_8 were dried over Na/K alloy and vacuum transferred before use. Bromobenzene-d_5 was degassed and dried over 4Å molecular sieves. $Y(CH_2SiMe_3)_3(thf)_2$ was prepared according to literature procedures (a description of the specific procedure used can be found in the supporting material of reference 3 of the paper). *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 $^{i}Bu_3Al$ (Witco) in toluene, as described in reference 12 of the paper. For the polymerisation 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 N,N'*-Bis-(2,6-diisopropylphenyl)benzamidine (1).** A stirred mixture of P_2O_5 (1.5 g, 10.5 mmol), hexamethyldisiloxane (3.35 mL, 16 mmol) and dichloromethane (3 mL) was refluxed for 30 minutes. The volatiles were distilled off by heating the mixture to 160 °C. Benzoic acid (0.152 g, 1.25 mmol) and 2,6-diisopropylaniline (0.47 mL, 2.5 mmol) were added to the viscous syrup and this mixture was heated at 170 °C for 6 hours. The mixture was poured into a 1 M KOH solution (50 mL), producing an oil that solidified in the course of two days. The solid was washed with water, then crystallized from ethanol/water to give 0.3 g (54%) of the amidine product. Mp 128 °C; IR (Nujol) 3362 (NH), 1611 cm^{-1} (C=N). ^{1}H NMR ($CDCl_3$): δ 6.8-7.4 (m, 11H), 5.70 (s, 1H), 3.12-3.38 (m, 4H), 1.35 (d, *J* = 7.1 Hz, 6H), 1.23 (d, *J* = 6.8 Hz, 6H), 0.98 (d, *J* = 6.8 Hz, 6H), 0.84 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, APT): δ 153.5, 145.0, 139.2, 134.8, (-)129.0, (-)128.6, (-)127.6, (-)127.4, (-)123.5, (-)123.3, (-)123.1, (-)28.3, (-)28.1, (-)24.9, (-)24.2, (-)22.2, (-)22.1. MS (EI); *m/z* (%) = 440 [M^+] (15.6), 264 (100). HRMS: calcd.for $C_{31}H_{40}N_2$: 444.319; found 440.318. Alternatively, the compound was prepared from the corresponding imidoyl chloride and 2,6-diisopropyl aniline. A solution of 2,6-diisopropylaniline (0.885 g, 5 mmol), triethylamine (2.5 mL), and *N*-2,6-diisopropylbenzimidoyl chloride (1.50 g, 5 mmol) in 10 mL of toluene was refluxed for 24 h.The mixture was washed with water, dried (Na_2SO_4) and concentrated. After one crystallization from ethanol/water, 1.88 g (85%) of the benzamidine was obtained, identical to the compound described above as seen by mp and NMR spectroscopy.

Synthesis of [PhC(N-2,6-Pr$^i_2$C$_6$H$_3$)$_2$]Y(CH$_2$SiMe$_3$)$_2$(THF) (3). A solution of $(Me_3SiCH_2)_3Y(THF)_2$ (**2**, 0.31 g, 0.63 mmol) in pentane (30 ml) was reacted with [PhC(N-2,6-$Pr^i_2C_6H_3)_2$]H (**1**, 0.27 g, 0.63 mmol) at room temperature. The reaction mixture was stirred for 3 hours, after which the volatiles were removed *in vacuo*. Residual THF was removed from the remaining sticky solid by stirring with pentane (5 ml), which was subsequently removed *in vacuo*. Extraction with pentane (2 x 20 ml), concentrating and cooling the extract to – 30 ºC gives the crystalline product (0.40 g, 0.51 mmol, 64 %). The identity of the product was confirmed by single crystal X-ray diffraction. ^{1}H NMR (300 MHz, C_6D_6): δ 7.11-7.08 (m, 2 H, *Ar*-Pr^i_2), 7.00 (m, 5 H, Ph), 6.65-6.61 (m, 4 H, *Ar*-Pr^i_2), 3.69 (m, 4 H α-THF), 3.61 (sept, $^3J_{HH}$ = 6.6 Hz, 4 H, C*H*Me$_2$), 1.37 (d, $^3J_{HH}$ = 6.6 Hz, 12 H, CH*Me*$_2$), 1.14 (m, 4 H β-

THF), 1.01 (d, $^3J_{HH}$ = 6.6 Hz, 12 H, CH*Me*$_2$), 0.29 (s, 18H, CH_2Si*Me*$_3$), -0.11 (d, $^2J_{YH}$ = 3.0 Hz, 4 H, C*H*$_2$SiMe$_3$). ^{13}C NMR (75.4 MHz, C_6D_6): δ 174.8 (N*C*N), 143.2 (*ipso*-Ph), 142.2 (*ipso*-C_6H_3), 132.2 (C_6H_3 C), 130.4 (d, $^1J_{CH}$ = 159.8 Hz, Ar CH), 129.2 (d, $^1J_{CH}$ = 161.1 Hz, Ar CH), 127.0 (d, $^1J_{CH}$ = 158.6 Hz, Ar CH), 124.7 (d, $^1J_{CH}$ = 158.6 Hz, Ar CH), 123.9 (d, $^1J_{CH}$ = 150.0 Hz, Ar CH), 70.7 (t, $^1J_{CH}$ = 147.6 Hz, α-THF), 39.5 (dt, $^1J_{YC}$ = 40.3 Hz, $^1J_{CH}$ = 100.1 Hz, Y*C*H$_2$SiMe$_3$), 28.6 (d, $^1J_{CH}$ = 126.9 Hz, *C*HMe$_2$), (q, $^1J_{CH}$ = 126.9 Hz, CH*Me*$_2$), 24.9 (t, $^1J_{CH}$ = 124.4 Hz, β-THF), 23.5 (q, $^1J_{CH}$ = 125.7 Hz, CH*Me*$_2$), 4.2 (q, J_{CH} = 117.2 Hz, YCH$_2$Si*Me*$_3$). Anal. [$C_{43}H_{69}N_2OSi_2Y$] (775.11) calcd: C, 66.63; H, 8.97; N, 3.61; Y, 11.47. Found: C, 66.16; H, 8.95; N, 3.54; Y, 11.32.

Synthesis of [PhC(N-2,6-Pr$^i_2$C$_6$H$_3$)$_2$]Y(CH$_2$SiMe$_3$)$_2$(THF)$_2$ (4). A solution of $(Me_3SiCH_2)_3Y(THF)_2$ (0.30 g, 0.60 mmol) in pentane (30 ml) was reacted with [PhC(N-2,6-Pr$^i_2$C$_6$H$_3$)$_2$]H (0.26 g, 0.60 mmol) at room temperature. The reaction mixture was stirred for 3 hours, after which the volume of the solution was reduced to 10 ml. Cooling to – 30 ºC gives the product (0.36 g, 0.43 mmol, 72 %). The identity of the product was corroborated by single crystal X-ray diffraction. ^{1}H NMR (500 MHz, C_6D_6, δ): 7.10 (m, 2 H, *Ar*), 6.99 (m, 6 H, *Ar*), 6.63-6.61 (m, 3 H, *Ar*), 3.64 (m, 8 H α-THF), 3.61 (sept, $^3J_{HH}$ = 6.5 Hz, 8 H, C*H*Me$_2$), 1.37 (d, $^3J_{HH}$ = 6.5 Hz, 12 H, CH*Me*$_2$), 1.26 (m, 8 H β-THF), 1.00 (d, $^3J_{HH}$ = 6.5 Hz, 12 H, CH*Me*$_3$), 0.28 (s, 18H, CH_2Si*Me*$_3$), -0.13 (d, $^2J_{YH}$ = 2.5 Hz, 4 H, C*H*$_2$SiMe$_3$). ^{13}C NMR (125.7 MHz, C_6D_6, δ): 174.8 (NN*C*Ph), 143.3 (Ph *ipso*-C), 142.2 (C_6H_3 *ipso*-C), 132.2 (C_6H_3 C), 130.4 (d, $^1J_{CH}$ = 157.9 Hz, C_6H_3), 129.2 (d, $^1J_{CH}$ = 159.6 Hz, Ph), 127.1 (d, $^1J_{CH}$ = 159.6 Hz, Ph), 124.8 (d, $^1J_{CH}$ = 159.6 Hz, Ph), 123.9 (d, $^1J_{CH}$ = 154.4 Hz, C_6H_3), 69.55 (t, $^1J_{CH}$ = 147.4 Hz, α-THF), 39.0 (dt, $^1J_{YC}$ = 40.3 Hz, $^1J_{CH}$ = 101.8 Hz, Y*C*H$_2$SiMe$_3$), 28.6 (d, $^1J_{CH}$ = 128.1 Hz, *C*HMe$_2$), 25.8 (q, $^1J_{CH}$ = 126.3 Hz, CH*Me*$_2$), 25.3 (t, $^1J_{CH}$ = 124.4 Hz, β-THF), 23.5 (q, $^1J_{CH}$ = 126.3 Hz, CH*Me*$_2$), 4.3 (q, J_{CH} = 115.8 Hz, YCH$_2$Si*Me*$_3$). [$C_{47}H_{77}N_2O_2Si_2Y$] 847.21, cal: C: 66.63 H: 9.16 N: 3.31 Y: 10.49. found: C: 66.50 H: 8.83 N: 3.29 Y: 11.28.

Reaction of [PhC(N-2,6-Pr$^i_2$C$_6$H$_3$)$_2$]Y(CH$_2$SiMe$_3$)$_2$(THF) with [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$]. A solution of [PhC(N-2,6-Pr$^i_2$C$_6$H$_3$)$_2$]Y(CH$_2$SiMe$_3$)$_2$(THF) (**3**, 23 mg, 30.0 μmol) in THF-*d*$_8$ (0.6 ml) was reacted with [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] (24 mg, 30.0 μmol). The obtained solution was transferred to an NMR tube and analyzed by NMR spectroscopy, which showed full conversion to the cationic species {[PhC(N-2,6-Pr$^i_2$C$_6$H$_3$)$_2$]Y(CH$_2$SiMe$_3$)(THF-*d*$_8$)$_n$}[B(C$_6$F$_5$)$_4$], $SiMe_4$ and free $PhNMe_2$. ^{1}H NMR (500 MHz, THF-*d*$_8$): δ 7.12-7.09 (m, 2 H, *Ar*-Pr$^i_2$), 7.06 (m, 5 H, Ph), 6.96-6.94 (m, 4 H, *Ar*-

Pr^i_2), 3.33 (sept, $^3J_{HH}$ = 6.50 Hz, 4 H, C*H*Me$_2$), 1.24 (d, $^3J_{HH}$ = 6.5 Hz, 12 H, CH*Me*$_2$), 0.86 (d, $^3J_{HH}$ = 6.5 Hz, 12 H, CH*Me*$_2$), -0.02 (s, 9 H, CH$_2$Si*Me*$_3$), -0.15 (d, $^2J_{YH}$ = 3.0 Hz, 2 H, C*H*$_2$SiMe$_3$). PhNMe$_2$: 6.96 (d, $^3J_{HH}$ = 8.50 Hz, 4 H, Me$_2$N*Ph*), 6.67 (d, $^3J_{HH}$ = 8.00 Hz, 2 H, Me$_2$N*Ph*), 6.58 (t, $^3J_{HH}$ = 7.00 Hz, 1 H, Me$_2$N*Ph*), 2.87 (s, 6H, *Me*$_2$NPh). $^{13}C\{^1H\}$ NMR (125.7MHz, THF-d_8): δ 179.3 (N*C*N), 144.4 (*ipso*-Ar), 143.5 (*ipso*-Ar), 132.5 (Ar), 132.2 (Ar) 131.8 (Ar), 130.4 (Ar), 128.7 (Ar), 127.1 (Ar), 126.7 (Ar), 42.3 (d, $^1J_{YC}$ = 42.73 Hz, Y*C*H$_2$SiMe$_3$), 29.7 (*C*HMe$_3$), 26.0 (CH*Me*$_3$), 25.9 (m, β-THF), 24.5 (CH*Me*$_3$), 4.8 (YCH$_2$Si*Me*$_3$). ^{19}F NMR (188.15 MHz, 20 °C, C_6D_5Br) δ: -133.89 (o-CF), -165.98 (p-CF), -169.48 (m-CF).

Ethylene polymerization with {PhC(N-2,6-$Pr^i_2C_6H_3)_2$}Y($CH_2SiMe_3)_2$(THF) (3) and [$HNMe_2Ph$][$B(C_6F_5)_4$]. In a drybox, solutions were made of [PhC(N-2,6-$Pr^i_2C_6H_3)_2$]Y($CH_2SiMe_3)_2$(THF) (**3**, 10 μmol) and [$HNMe_2Ph$][$B(C_6F_5)_4$] (10 μmol), each in 5 ml of toluene in separate vials sealed with a serum cap. 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 50 °C and pressurized with ethene (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 [PhC(N-2,6-$Pr^i_2C_6H_3)_2$]Y($CH_2SiMe_3)_2$(THF) solution. The ethylene pressure was kept constant during the reaction by replenishing flow. The reactor was stirred for the required reaction time, and then vented. The polymer was repeatedly rinsed with methanol and dried in a vacuum oven.

Ethylene polymerization with [PhC(N-2,6-$Pr^i_2C_6H_3)_2$]Y($CH_2SiMe_3)_2(THF)_2$ (4) with [$HNMe_2Ph$][$B(C_6F_5)_4$] activator and TIBAO. In a drybox, a solution was made of the appropriate yttrium dialkyl (10 μmol) in 5 ml toluene. [$HNMe_2Ph$][$B(C_6F_5)_4$] (10 μmol) and partially hydrolyzed tris(isobutyl)aluminum (TIBAO, 100 μmol) were mixed together in 10 ml toluene. The two solutions were each placed in a vial sealed with a serum cap. Ethylene polymerization was performed in a stainless steel 1.0L autoclave, pre-dried and flushed with nitrogen, charged with 200 ml of dry toluene, equilibrated at the desired reaction temperature, and pressurized with ethene (5 bar). The solution of [$HNMe_2Ph$][$B(C_6F_5)_4$]/TIBAO was injected first into the reactor (using a pneumatically operated injector), and the reaction was started by injecting the solution of the yttrium dialkyl. The ethylene pressure was kept constant during the reaction by replenishing flow. The reactor was stirred for the specified reaction time,

after which the reactor was vented. The polymer was rinsed repeatedly with methanol and subsequently dried in a vacuum oven.