Supporting Information

Synthesis of Ti(IV) complexes of donor-functionalised phenoxy-imine tridentates and their evaluation in ethylene oligomerisation and polymerisation

James A. Suttil, Miranda F. Shaw, David S. McGuinness,* Michael G. Gardiner, and Stephen J. Evans

X-Ray Structure of S1:

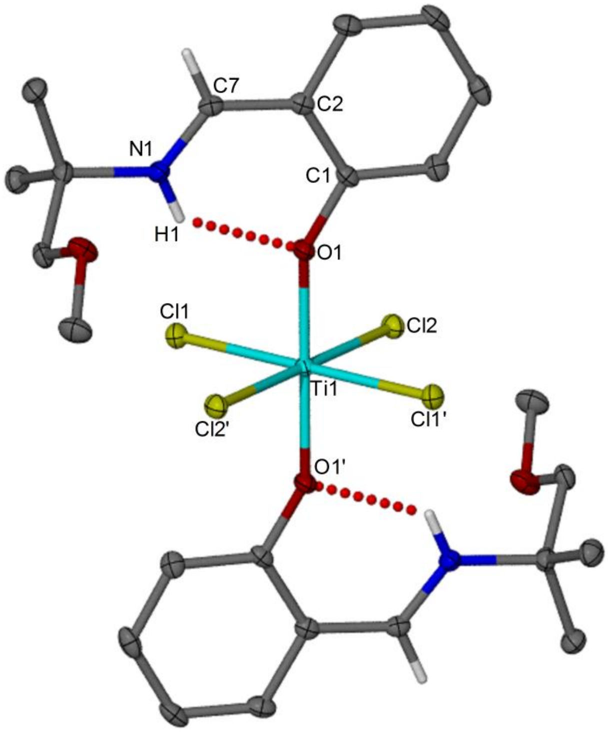

Fig. S1. Molecular structure of **S1** (' denotes symmetry operator 1-*x*, -*y*, -*z*). Thermal ellipsoids are shown at the 50% probability level. Diffuse lattice solvent was removed in the refinement. All methyl and aromatic-ring hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°):Ti1-O1,Cl1,Cl2 1.8936(12), 2.3768(5), 2.3563(5), C2-C7 1.431(3), C7-N1 1.288(3), N1-H1 0.84(2), Cl1-Ti1-Cl2,Cl2' 90.487(17), 89.513(18), O1-Ti1-Cl 88.70(4)-91.30(4), C1-O1-Ti1 148.68(13), C2-C7-N1 126.68(17).

Preparation of 2-(OH)C_6H_4C=N(C(CH_3)$_2$$CH_2$OMe):

2-methyl-3-methoxypropyl-2-amine (0.29 g, in dimethylformamide, 2.84 mmol) was taken up in 10 ml of diethyl ether and added to salicylaldehyde (0.38 g, 3.12 mmol) in 10 mL of diethyl ether with stirring on molecular sieves. The resulting yellow solution was stirred overnight. The supernatant was removed via canula filtration and the residue washed with 3 × 8 ml of diethyl ether. The supernatant and washings were combined and concentrated to yield a yellow oil which was heated at 65 °C under vacuum to give a black residue. The residue was extracted with 12 mL of petroleum spirits to give pure 2-(OH)C_6H_4C=N(C(CH_3)$_2$$CH_2$OMe) in 76 % yield (0.45 g, 2.16 mmol). ^{1}H NMR (CD_2Cl_2, 299.89 MHz): δ 14.04 (s, 1H, O*H*), 8.40 (s, 1H, N=C*H*), 7.26 – 7.32 (m, 2H, *aryl-H*), 6.84 – 6.91 (m, 2H, *aryl-H*), 3.37 (s, 2H, CH_2-O-CH_3), 3.34 (s, 2H, CH_2-O-CH_3), 1.31 (s, 6H, C(CH_3)). ^{13}C NMR (CD_2Cl_2, 75.41 MHz): δ 162.3 (N=*C*H), 119.6, 162.2 (*aryl-C$_{ipso}$*), 117.4, 118.8, 132.1, 132.5 (*aryl-C*), 81.2 (*C*H_2-O-CH_3), 60.5 (*C*(CH_3)), 59.7 (CH_2-O-*C*H_3), 24.7 (C(*C*H_3)). MS (electron ionisation): *m/z* 207 [M]$^+$.

Preparation of S1:

$2\text{-}(OH)C_6H_4C{=}N(C(CH_3)_2CH_2OMe)$ (0.20 g, 0.97 mmol) was taken up in 20 mL of toluene and added to $TiCl_4$ (0.12 mL, 1.07 mmol) in 2 mL of toluene over 20 minutes at – 95 °C with stirring. The resulting dark red solution was stirred overnight generating a brick red suspension. The supernatant was removed by canula filtration and the remaining red solid was washed with 3 × 10 mL of petroleum spirits. The resulting solid was dried *in vacuo* for 40 minutes to yield **S1** as a dark brown solid in quantitative yield (0.29 g, 0.48 mmol). Crystals suitable for X-ray diffraction were grown by reverse vapour diffusion of dichloromethane into toluene. ^1H NMR (CD_2Cl_2, 299.89 MHz): δ 11.70 (bs, 2H, $N^+\text{-}H\text{-}O^-$), 8.31 (d, J = 16.79 Hz, 2H, N=C*H*), 7.83 (m, 2H, *aryl-C*), 7.55 (m, 2H, *aryl-C*), 7.14 – 7.24 (m, 4H, *aryl-C*), 3.60 (s, 4H, $CH_2\text{-}O\text{-}CH_3$), 3.40 (s, 6H, $CH_2\text{-}O\text{-}CH_3$), 1.65 (s, 12H, $C(CH_3)$). ^{13}C NMR (CD_2Cl_2, 75.41 MHz): δ 166.6 (N=*C*H), 115.0, 162.3 (*aryl-C$_{ipso}$*), 123.9, 126.3, 136.4, 140.5 (*aryl-C*), 77.3 ($CH_2\text{-}O\text{-}CH_3$), 63.6 ($C(CH_3)$), 59.7 ($CH_2\text{-}O\text{-}CH_3$), 23.9 ($C(CH_3)$).