

Bis(benzimidazole)amine Vanadium Catalysts for Olefin Polymerisation and  
Co-polymerisation: Thermally Robust, Single-Site Catalysts Activated by  
Simple Alkylaluminium Reagents

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**Supporting Information**

**Synthetic Procedures**

Synthesis of [*N,N*-bis(1*H*-benzimidazol-2-ylmethyl)-*N*-methylamine]trichlorovanadium(III)  
(**2**)

A slurry of *N,N*-bis(1*H*-benzimidazol-2-ylmethyl)-*N*-methylamine (12.00 g, 41.2 mmol) and  $\text{VCl}_3(\text{THF})_3$  (15.4 g, 41.2 mmol) in 120 mL THF was stirred at reflux for 30 min. The reaction mixture was then allowed to cool to room temperature and stirred for a further 4 hours. The resultant yellow-green solid was filtered, washed with THF (4 x 70 mL) and dried under reduced pressure. Yield 17.8 g (96.2%). Microanalysis, %: Calc'd for  $\text{C}_{17}\text{H}_{17}\text{N}_5\text{VCl}_3$ : C 45.51, H 3.82, N 15.61. Found C 45.39, H 3.62, N 15.41. IR (KBr),  $\text{cm}^{-1}$ : 3244, 1596, 1210, 1049, 1003, 982, 944, 752, 701, 653, 621, 518, 475, 455, 432, 416.  $\mu_{\text{eff}} = 2.89$  BM.

Synthesis of [*N,N*-bis(1*H*-benzimidazol-2-ylmethyl)-*N*-methylamine]dipropoxy-  
oxovanadium(V) (**3**)

To a cold (-78°C) slurry of *N,N*-bis(1*H*-benzimidazol-2-ylmethyl)-*N*-methylamine (0.50 g, 1.72 mmol) in THF (20 mL) was added a THF (10 mL) solution of tripropoxyoxovanadium (0.42 g, 1.72 mmol) cooled to -78°C. The mixture was allowed to warm to room temperature and stirred for 30 min. The orange-red solution was filtered to remove excess *N,N*-bis(1*H*-benzimidazol-2-ylmethyl)-*N*-methylamine and the filtrate then evaporated to ca. 5 mL. Addition of pentane (50 mL) resulted in the formation of an orange solid which was filtered, washed with pentane (2 x 5 mL) and dried under reduced pressure. Yield 0.72g (88.0%). Microanalysis, %: Calc'd for C<sub>23</sub>H<sub>30</sub>N<sub>5</sub>O<sub>3</sub>V: C 58.10, H 6.36, N 14.73. Found: C 57.93, H 6.26, N 14.77. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ=0.85 (t, J(H,H)=14.7 Hz, 6H; CH<sub>3</sub>-CH<sub>2</sub>-), 1.62 (m, 4H, -CH<sub>2</sub>-CH<sub>2</sub>), 2.85 (s, 3H; CH<sub>3</sub>-N), 3.08 (d, J(H,H)=15.9 Hz, 2H; CH<sub>2</sub>-N), 4.02 (d, J(H,H)=16.2 Hz, 2H; CH<sub>2</sub>-N), 4.88 (dt, J(H,H)=13.4, 11.6 Hz, 2H; CH<sub>2</sub>-O), 5.34 (dt, J(H,H)=12.5, 11.3 Hz, 2H; CH<sub>2</sub>-O), 7.14 (m, 4H; Ar-H), 7.42 (m, 2H; Ar-H), 8.05 (m, 2H; Ar-H). <sup>13</sup>C NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ=154.9 (N=CH-N), 140.9, 138.8, 128.4, 122.4, 122.1 (C<sub>Ar-5</sub>, C<sub>Ar-6</sub>), 116.5 (C<sub>Ar-4</sub>), 114.1 (C<sub>Ar-7</sub>), 86.2 (CH<sub>2</sub>-O), 59.3 (CH<sub>2</sub>-N), 49.5 (CH<sub>3</sub>-N), 26.6 (O-CH<sub>2</sub>-CH<sub>2</sub>-), 10.8 (CH<sub>3</sub>-CH<sub>2</sub>-). <sup>51</sup>V NMR (131 MHz, V(O)Cl<sub>3</sub>, CD<sub>2</sub>Cl<sub>2</sub>): δ=-560.2. IR (KBr), cm<sup>-1</sup>: 3435(w), 2959(w), 2919(w), 1608(w), 1474(m), 1450(m), 1345(w), 1270(m), 1092(w), 1063(m), 971(vs), 913(w), 883(w), 787(w), 749(m), 641(m), 624(m), 514(w), 435(w).

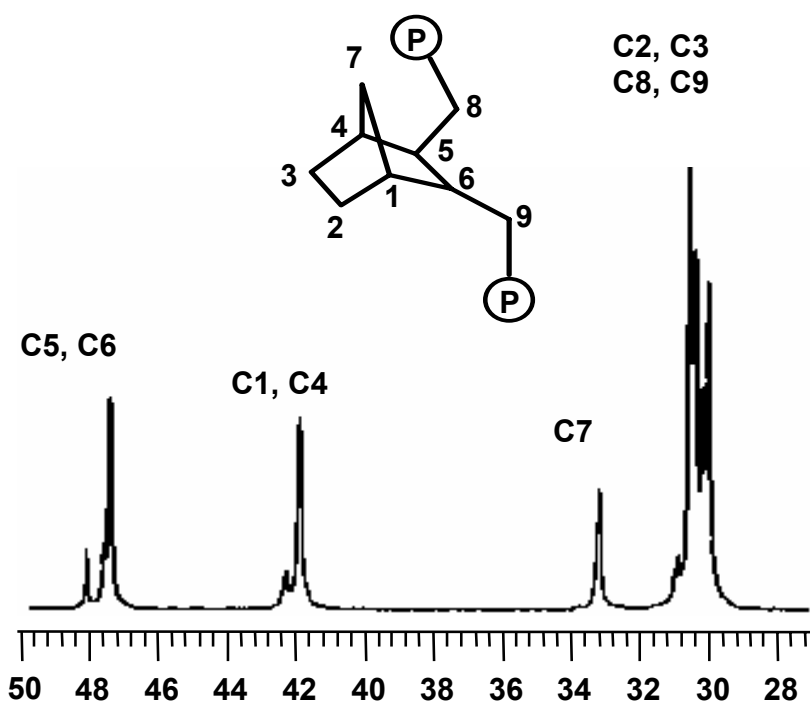
#### Ethylene homo- and co-polymerization procedure

*A. Preparation of activated catalyst solution.* The required amount of catalyst precursor (0.5-5.0 mg) was suspended or dissolved in toluene (20-100 mL) followed by addition of the co-catalyst (Me<sub>2</sub>AlCl, 0.01-2.00 mmol). Thus prepared, the solution can be stored at 0°C for several days.

*B. Polymerization.*

Ethylene homo- and co-polymerization reactions were carried out either in a 400 ml Fischer-Porter glass reactor or in a 1L stainless steel autoclave equipped with a gas inlet, a catalyst inlet, a mechanical stirrer, a digital thermometer and a temperature / pressure control system. An aliquot of catalyst solution (1-5 mL) was added to the reactor containing 200-400 mL solvent (toluene or heptane), 0.1-1.0 mmol scavenger (usually  $\text{Me}_2\text{AlCl}$ ), 0.01-0.50 mmol promoter (usually ethyl trichloroacetate) and the required amount of comonomer. Ethylene was introduced either before (stainless steel reactor) or after (Fischer-Porter glass reactor) addition of the catalyst. The polymerizations were typically carried out over 10-120 min (usually 60 min) and terminated by venting off ethylene. For polymerizations carried out in toluene, the reactor contents were poured into a beaker containing methanol (400 mL) and a few drops of 2M HCl. The precipitated polymer was filtered, washed with methanol and dried at 60°C in a vacuum oven. In the case of heptane, the polymer was filtered, washed with heptane and dried at 60°C under vacuum.

$^{13}\text{C}$  NMR spectrum of poly(ethylene-*co*-norbornene), containing 15.5 mol% norbornene, prepared by catalyst **3**.



Kinetic profile for ethylene polymerization using **3** ( $\rho_{\text{O}_2}$  9);  $\zeta = 0.1 \mu\text{mol}$

