

## \*\*\*Supplementary Information\*\*\*

### High activity ethylene trimerisation catalysts based on diphosphine ligands

Anthea Carter,<sup>a</sup> Steven A. Cohen,<sup>b</sup> Neil A. Cooley,<sup>a</sup> Aden Murphy,<sup>a</sup> James Scutt<sup>a</sup> and Duncan F. Wass<sup>a\*</sup>

<sup>a</sup> BP, Chemicals Stream, Sunbury on Thames, Middlesex, U.K. E-mail: wassdf@bp.com

<sup>b</sup> BP, Chemicals Stream, Naperville, Illinois, U.S.A.

---

#### Experimental details for trimerisation experiments

*General*:- All manipulations were performed under anaerobic conditions. Solvents and gases were dried and degassed by standard procedures. Chemicals were purchased from the Aldrich Chemical Company unless stated otherwise. Methyl alumoxane (MAO) and modified methyl alumoxane (MMAO) were purchased from Witco as 10% w/w solutions in toluene or heptanes respectively. Ligands **1-7** were synthesized according to literature procedures or slight modifications thereof.<sup>1</sup> Reaction products were analysed by GCMS using 50m × 0.3mm id, CP sil. CBS-MS, df=0.4µm columns, an initial temperature of -30°C, hold 1 min, ramp rate 7 °C/min, final temperature 280°C and final hold of 5 mins. Molar quantities of catalyst are based upon the molar quantity of chromium source used in their preparation.

*Experiments at low pressure (runs 1, 7, 8, 10, 11, 14-19)*:- Details are given here for run1; other runs followed the same basic procedure only reagents were changed as indicated in Table 1 in the main text. A Schlenk tube was charged with CrCl<sub>3</sub>(THF)<sub>3</sub> (8 mg, 0.02 mmol) and **1** (10 mg, 0.02 mmol), 10ml THF was added and the solution stirred for 2 hours. After this time, solvent was removed under reduced pressure and the resultant solid suspended in 50 ml toluene. MAO (4.2 ml, 6.0mmol, 300 equivalents) was added and an immediately a green solution was observed. The solution placed under an ethylene atmosphere (1 bar). An immediate exotherm was observed. The reaction was run for 60 minutes during which time the vessel was left open to a supply of ethylene at 1 bar. The catalyst was then destroyed by addition of 50ml dilute aqueous HCl (Caution! vigorous reaction of MAO residues with water), the organic layer separated and dried over MgSO<sub>4</sub>. The product mass was recorded by weighing the mass gain of the Schlenk reaction vessel.

*Experiments at higher pressure (runs 2-6, 9, 12, 13)*:- Details for run 3 are described here; other runs followed the same basic procedure only conditions were changed as indicated in Table 1 in the main text. A Schlenk vessel was charged with CrCl<sub>3</sub>(THF)<sub>3</sub> (4 mg, 0.01 mmol) and **1** (5 mg, 0.01 mmol), 10 ml THF was added and the solution stirred for 2 hours. After this time, solvent was removed under reduced pressure, the resultant solid suspended in 10 ml toluene and MAO (2.1 ml, 3.0 mmol, 300 equivalents) added. This solution was then injected into an autoclave, previously charged with 500ml toluene, pressurised to 8 bar ethylene partial pressure and heated to 80°C. The reaction was run for 60 minutes during which time gas was fed on demand to maintain 8 bar ethylene partial pressure and the autoclave was cooled to maintain a temperature of 80°C. After this time, the ethylene feed was stopped, the autoclave cooled to ca. 0°C and ethylene gas carefully vented. The reaction products were worked up as described above.

*Preparation of MAO on silica*:- Toluene (200 ml) was added to a vessel containing silica (prepared according to procedures described in WO 99/12981 example 37.1. Silica was supplied by Crosfield as grade ES70X), calcined at 200°C overnight, 20.5g after calcination) under an inert atmosphere. The slurry was mechanically stirred and MAO (1.5 M, 62.1 mmol, 41.4 ml) was added via syringe. The mixture was stirred for 1 hour at 80°C before removing excess toluene and drying under vacuum to obtain 15% w/w MAO on silica in quantitative yield.

*Preparation of supported catalyst*:- A Schlenk vessel was charged with CrCl<sub>3</sub>(THF)<sub>3</sub> (4 mg, 0.01 mmol) and **1** (5mg, 0.01 mmol), 10ml THF was added and the solution stirred for 2 hours. After this time, solvent was removed under reduced pressure and the resultant solid suspended in 20 ml toluene. MAO (0.7 ml, 1mmol, 100 equivalents) was added and an immediately a green solution was observed. This solution was then transferred via canula to a Schlenk tube containing a slurry of 15% w/w MAO on silica (prepared as described above) in toluene (1g of MAO/Silica in 30 ml toluene). The green

colour of the solution was quickly transferred onto the silica/MAO and a colourless supernatant remained. This slurry was transferred as appropriate by wide-bore canula.

## References

- 1 N.A. Cooley, S.M. Green, D.F. Wass, K. Heslop, A.G. Orpen and P.G. Pringle, *Organometallics*, 2001, **20**, 4769.

---

### Typical ethylene uptake profile (run 3):

