

Supplementary Information

**Highly selective chromium-based ethylene trimerisation catalysts with bulky
diphosphinoamine ligands**

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In the examples that follow all procedures were carried out under inert conditions, using pre-dried reagents. Chemicals were obtained from Sigma-Aldrich or Strem Chemicals unless stated otherwise. All trialkylaluminium and aluminoxane compounds and solutions thereof were obtained from Crompton GmbH, Akzo Nobel and Albemarle Corporation. In all the examples, the molar mass of methylaluminoxane (MAO) was taken to be 58.016 g/mol, corresponding to the (CH₃-Al-O) unit, in order to calculate the molar quantities of MAO used in the preparation of the catalysts described in the examples below. Similarly the molar mass of ethylaluminoxane (EAO) was taken as 72.042 g/mol, corresponding to the (CH₃CH₂-Al-O) building block, and that of modified methylaluminoxane prepared from a 70:30 mixture of trimethylaluminium and tri-isobutylaluminium as 70.7 g/mol corresponding to the (Me_{0.70}isonBu_{0.30}-Al-O) unit. Ethylene oligomerisation products were analysed by GC-MS and GC-FID. All solvents were percolated through neutral, activated alumina prior to use. NMR spectra were recorded on a Varian Mercury, 400 MHz spectrometer, with samples made up in CDCl₃.

The mixed heteroatomic PNP ligands were synthesised by reacting the amine and phosphine chlorides R₂PCl as described in S.J. Dossett, A. Gillon, A.G. Orpen, J.S. Fleming, P.G. Pringle, D.F. Wass and M.D. Jones, *Chem. Commun.*, 2001, 699; M.S. Balakrishna, T.K. Prakasha and S.S. Krishnamurthy, *J. Organomet. Chem.*, 1990, **390**, 2, 203; N.A. Cooley, S.M. Green, D.F. Wass, K. Heslop, A.G. Orpen and P. Pringle, *Organometallics*, 2001, **20**, 4769. The respective phosphine chlorides R₂PCl were prepared as described by T.V. Rajanbabu, T.A. Ayers, G.A. Halliday, K.K. You and J.C. Calabrese, *J. Org. Chem.*, 1997, **62**, 17, 6012. The ligands were all fully characterized; ³¹P NMR shifts (ppm) are given in Table 1

Table 1			
$R_1R_2PCl + R_3R_4PCl + R_5NH_2 \rightarrow R_1R_2PN(R_5)PR_3R_4$			
Ligand	Amine: (R'NH ₂)	Phosphorus Chloride: R=	PNP - ³¹ P NMR (ppm)
1	Methylamine	R _{1,4} = 2-Methylphenyl	58.3 (s)
2	Methylamine	R _{1,4} = 2-Ethylphenyl	57.4 (s)
3	Methylamine	R _{1,4} = 2-Isopropylphenyl	53.8 (s)
4	Methylamine	R ₁ = Phenyl, R _{2,4} = 2-Methylphenyl	64.8 (d), 57.8(d) J= 309 Hz
5	Methylamine	R _{1,2} = Phenyl; R _{3,4} = 2-Methylphenyl	71.9 (d), 58.1 (d) J = 294 Hz
6	Methylamine	R _{1,3} = Phenyl; R _{2,4} = 2-Methylphenyl	65.8 (s), 65.3 (s) conformers
7	Methylamine	R _{1,3} = Phenyl; R _{2,4} = 2-Ethylphenyl	64.5 (s), 64.3 (s) conformers

8	Isopropylamine	R _{1,3} = Phenyl; R _{2,4} = 2-Ethylphenyl	39.6 (br s)
9	Isopropylamine	R ₁₋₃ = Phenyl; R ₄ = 2-Ethylphenyl	52.1 (br m), 35.0 (br m)

Example 1 : Preparation of the (o-Ethylphenyl)₂PN(methyl)P(o-Ethylphenyl)₂ ligand

Magnesium turnings (9.11 g, 0.375 mol) were treated with the 1-bromo-2-ethyl-benzene (10.37 ml, 0.075 mol) in THF (200 ml). A vigorous reaction ensued which was cooled in an ice bath. Once the reaction had dissipated, the reaction mixture was heated under reflux for 2 hours yielding the Grignard reagent.

The Grignard reagent was added dropwise over 2 hours with stirring to a solution of PCl₃ (2.62 ml, 0.03 mol) in THF (200 ml) at -78 °C. After complete addition the dry ice/acetone bath was removed and the reaction was allowed to warm to room temperature. The reaction was left stirring overnight and the solvent removed *in vacuo*. The crude product was found to be a mixture of (Br:Cl)-phosphines and was used without purification in the next step.

The Bis(o-ethylphenyl) phosphorus chloride (30 mmol from the crude reaction mixture) was added to a solution of methylamine (2.0 M sol. in THF, 6.5 ml, 13.0 mmol) in DCM (80 ml) and triethylamine (15 ml) at 0 °C. The reaction was stirred for 30 min after which the ice bath was removed. After stirring for a total of 14 hrs the solution was filtered to remove the triethylammonium salt formed. The product was isolated after crystallisation from ethanol in 85 % yield.

Example 2: Ethylene trimerisation reaction using Cr(III) acetylacetonate, (o-ethylphenyl)₂PN(methyl)P(o-ethylphenyl)₂ and MAO

A solution of 33.7 mg of (o-ethylphenyl)₂PN(methyl)P(o-ethylphenyl)₂ (0.066 mmol) in 5 ml of toluene was added to a solution of 11.5 mg Cr(III) acetylacetonate (0.033 mmol) in 15 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 4.95 mmol) at 45°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was kept at 45 barg. Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 10 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 20°C. After releasing the excess ethylene from the autoclave, the reaction mixture in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield the mass of polyethylene.

Example 3: Ethylene trimerisation reaction using CrCl₃.(Tetrahydrofuran)₃, (o-ethylphenyl)₂PN(methyl)P(o-ethylphenyl)₂ and MAO

A solution of 33.7 mg of *(o*-ethylphenyl)₂PN(methyl)P(*o*-ethylphenyl)₂ (0.066 mmol) in 5 ml of toluene was added to a solution of 12.4 mg CrCl₃·(Tetrahydrofuran)₃ (0.033 mmol) in 15 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 9.9 mmol) at 35°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was allowed to gradually increase to 45 barg over a period of 15 minutes. Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 15 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 20°C. After releasing the excess ethylene from the autoclave, the reaction mixture in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield the mass of polyethylene.

Example 4: Ethylene trimerisation reaction using Cr(III) (2-ethylhexanoate), (*o*-ethylphenyl)₂PN(methyl)P(*o*-ethylphenyl)₂ and MAO

A solution of 33.7 mg of *(o*-ethylphenyl)₂PN(methyl)P(*o*-ethylphenyl)₂ (0.066 mmol) in 5 ml of toluene was added to a solution of 22.7 mg Cr(III) (2-ethylhexanoate) (70 mass % in mineral oil, 0.033 mmol) in 15 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 9.9 mmol) at 35°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was kept at 45 barg. Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 10 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 20°C. After releasing the excess ethylene from the autoclave, the reaction mixture in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield the mass of polyethylene.

Example 5: Ethylene trimerisation reaction using Cr(III) acetylacetonate, (*o*-ethylphenyl)₂PN(methyl)P(*o*-ethylphenyl)₂ and MMAO-3A

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A solution of 6.9 mg of (*o*-ethylphenyl)₂PN(methyl)P(*o*-ethylphenyl)₂ (0.0135 mmol) in 10 ml of toluene was added to a solution of 3.5 mg Cr(acac)₃ (0.01 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (77ml) and MMAO-3A (modified methylaluminoxane, Akzo Nobel, 3.0 mmol) at 35°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was kept at 45 barg. Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 30 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 20°C. After releasing the excess ethylene from the autoclave, the reaction mixture in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield the mass of polyethylene.

Example 6: Ethylene trimerisation reaction using Cr(III) acetylacetonate, (*o*-ethylphenyl)₂PN(methyl)P(*o*-ethylphenyl)₂ and EAO/TMA

A solution of 33.7 mg of (*o*-ethylphenyl)₂PN(methyl)P(*o*-ethylphenyl)₂ (0.066 mmol) in 10 ml of toluene was added to a solution of 11.5 mg Cr(acac)₃ (0.033 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml), EAO (ethylaluminoxane, 33 mmol) and TMA (trimethylaluminium, 0.80ml, 8.3 mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was kept at 45 barg. Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 46 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 20°C. After releasing the excess ethylene from the autoclave, the reaction mixture in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield the mass of polyethylene.

Example 7: Ethylene trimerisation reaction using Cr(III) acetylacetonate, (*o*-ethylphenyl)₂PN(methyl)P(*o*-ethylphenyl)₂ and MAO in cyclohexane as solvent

A solution of 33.9 mg of (*o*-ethylphenyl)₂PN(methyl)P(*o*-ethylphenyl)₂ (0.066 mmol) in 5 ml of cyclohexane was added to a solution of 11.7 mg Cr(III) acetylacetonate (0.033 mmol) in 15 ml

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cyclohexane in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of cyclohexane (71ml) and MAO (methylaluminoxane, 9.9 mmol) in toluene (9 ml) at 45°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was kept at 45 barg. Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 10 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 20°C. After releasing the excess ethylene from the autoclave, the reaction mixture in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield the mass of polyethylene.