

Supplementary Information

**Ethylene trimerisation and tetramerisation catalysts with polar-substituted
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. Methylaluminoxane (MAO) was obtained from Crompton GmbH. 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 required. Ethylene oligomerisation products were analysed by GC-MS and GC-FID. All solvents were percolated under nitrogen 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 R₂R₃PCl 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.

R₂R₃PCl + R₄R₅PCl + R₁NH₂ → R₂R₃PN(R₁)PR₄R₅			
Ligand	Amine: (R₁NH₂)	Phosphorus Chloride:	PNP - ³¹P NMR (ppm)
1	Methylamine	R ₂₋₅ = 2-Methoxyphenyl	51.8 (s)
2	Methylamine	R ₂₋₅ = 3-Methoxyphenyl	74.6 (s)
3	Methylamine	R ₂₋₅ = 4-Methoxyphenyl	70.5 (s)
4	Methylamine	R ₂₋₅ = Phenyl	74.2 (s)
5	Isopropylamine	R ₂₋₅ = 4-Methoxyphenyl	46.1 (br s)
6	Isopropylamine	R ₂₋₅ = Phenyl	50.1 (br s)
7	Isopropylamine	R _{2,5} = 1-Methoxyphenyl; R _{3,4} = Phenyl	50.0 – 25.0 (br m) (conformers)
8	Isopropylamine	R ₂ = 1-Methoxyphenyl; R ₃₋₅ = Phenyl	55.0 (br s), 22.0 (br m)
9	Isopropylamine	R ₂ = 1-Ethylphenyl; R ₃₋₅ = Phenyl	52.1 (br s), 35.0 (br m)

Example 1. Preparation of (4-methoxyphenyl)₂PN(isopropyl)P(4-methoxyphenyl)₂ (5)

1a) Preparation of N,N-Diisopropylphosphoramidate dichloride

Diisopropylamine (70 ml, 0.50 mol) in toluene (80 ml) was added to a solution of PCl₃ (21.87 ml, 0.25 mol) in toluene (80 ml) at -10 °C. The mixture was stirred for two hours and then allowed to warm to room temperature. The solution was stirred for a further hour after which it was filtered through a pad of celite. The product (35 g, 68 %) was obtained after removal of the solvent. ³¹P {H} NMR: 170 ppm

1b) Preparation of Bis(4-methoxyphenyl) phosphorus chloride/bromide

Magnesium turnings (9.11 g, 0.375 mol) were treated with 4-bromoanisole (9.39 ml, 75 mmol) in THF (100 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 a solution of 4-methoxyphenyl magnesium bromide. This Grignard reagent was added to N,N-diisopropylphosphoramidate dichloride (6.64 ml, 36 mmol) in THF (100 ml) at 0 °C. After stirring at room temperature overnight the mixture was diluted with cyclohexane (200 ml) and dry HCl gas was bubbled through the solution for 0.5 hours. After removal of the precipitate by filtration, the solvent was removed to give a mixture of the phosphine chloride and bromide in an 80% yield. This material was used without characterisation in the next step.

1c) Preparation of (4-methoxyphenyl)₂PN(isopropyl)P(4-methoxyphenyl)₂

To a solution of the crude bis(4-methoxyphenyl) phosphorus chloride (28.8 mmol calculated from crude reaction mixture) in dichloromethane (80 ml) and triethylamine (15 ml) at 0 °C was added isopropylamine (1.11 ml, 13 mmol). 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 by-product. The product was isolated after crystallisation from ethanol in 77 % yield.

Example 2. Ethylene tetramerisation reaction with 5

A solution of **5** (9.8 mg, 0.018 mmol) in toluene (10ml) was added to a solution of Cr(THF)₃Cl₃ (5.6 mg, 0.015 mmol) in toluene (10ml). 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 (4.5 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 bar. 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 10°C. After releasing the excess ethylene from the autoclave, the liquid contained 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 wax/polymeric products. These solid products were dried overnight in an oven at 60°C and then weighed to yield 1.0g of polyethylene. The GC analyses indicated that the reaction mixture contained 42.72 g of soluble oligomers.