Supplementary material to:

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Ethylene Trimerization over Supported SNS and PNP Chromium Catalysts,

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Supplementary Information

Ethylene Trimerisation over Supported SNS and PNP Chromium Catalysts

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1. Catalyst preparation

1.1. Ligand preparation (S, N, P tridentate ligands)

1.1.1. Synthesis of bis [2-(ethylsulfanyl)ethyl]amine (L1)

A solution of bis(2-chloroethyl)amine hydrochloride (2.0 g, 11.20 mmol) in ethanol (23 mL) was added to a solution of NaOH (1.4 g, 33.6 mmol) and ethanethiol (2.1 g, 33.7 mmol) in ethanol (37 mL) at 0 °C. The mixture was stirred at 0 °C for 2 h, and then at RT overnight. The mixture was then filtered, and the filtrate evaporated to dryness. The residue was taken up in cold diethyl ether (2 x 40 mL) and filtered again. The solvent was then removed under reduced pressure. The product (1.4 g, 65%) remained as a colourless-pale yellow semi-solid material. ^{1}H NMR δ_H($CDCl_3$):1.22 (6H, t, J($_{HH}$) 7.4 Hz, C*H*$_3$), 2.14 (1H, bs, N*H*), 2.42 (4H, q, J($_{HH}$) 7.4 Hz, SC*H*$_2$CH$_3$), 2.59 (4H, t, J($_{HH}$) 7.4 Hz, SC*H*$_2$) and 2.74 (4H, t, J($_{HH}$) 7.4 Hz, NC*H*$_2$); δ_C($CDCl_3$): 14.9(***C***H$_3$), 25.38 (***C***H$_2$), 31.8(***C***H$_2$) and 48.3(***C***H$_2$).

1.1.2. Synthesis of bis[2-(ethylsulfanyl)decyl]amine (L2)

Ligand **L2** was prepared in the similar manner as **L1**. This ligand was synthesised using a solution of bis(2-chloroethyl)amine hydrochloride (1.1 g, 6.25 mmol) in ethanol, and a solution of decanethiol (3.9 mL , 18.8 mmol) and NaOH (0.75 g, 18.6 mmol) in ethanol. Yield (2.53 g, 96.8%).^{1}H NMR δ_H 0.88 (6H, t, J($_{HH}$) 7.4Hz, CH$_3$), 1.25-1.40 (28H, m, SCH$_2$CH$_2$(C***H$_2$***)$_7$, 1.60 (4H, m, SCH$_2$C***H$_2$***(CH$_2$)$_7$, 1.89 (1H, bs, N*H*), 2.49 (4H, t, SCH$_2$(CH$_2$)$_8$), 2.70 (4H, t, J($_{HH}$) 7.2 Hz, SC*H*$_2$CH$_2$NH) and 2.85 (4H, t, J($_{HH}$) 7.4 Hz NC***H$_2$***); δ_C($CDCl_3$):14.1 (CH$_3$), 22.7 (CH$_3$*C*H$_2$), 28.5 (S(CH$_2$)$_2$*C*H$_2$), 28.9 (CH$_3$(CH$_2$)$_4$(*C*H$_2$), 29.3 (CH$_3$(CH$_2$)$_2$*C*H$_2$), 29.6 (CH$_3$(CH$_2$)$_3$(*C*H$_2$), 30.6 (S(CH$_2$*C*H$_2$CH$_2$), 31.8 (CH$_3$CH$_2$*C*H$_2$), 32.5 (S*C*H$_2$CH$_2$NH) 32.9 (S*C*H$_2$) and 50.8 (SCH$_2$*C*H$_2$NH).

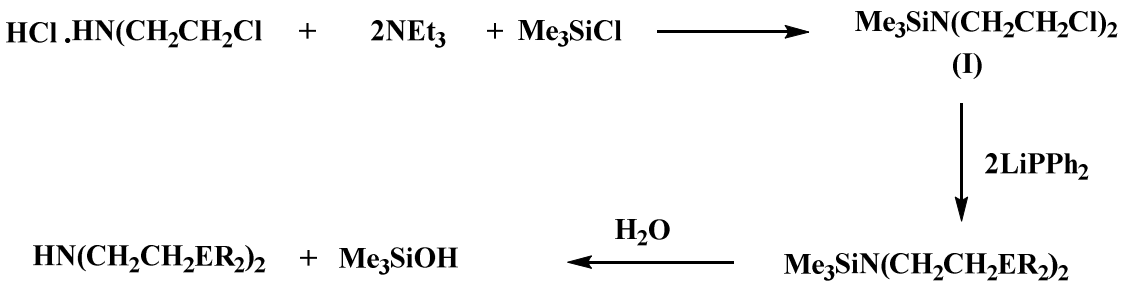
1.1.3. Synthesis of bis[(2-diphenylphosphino)ethyl]amine (2)

Method 1 (2a)

Ammonia (200 mL) was condensed at -78 ˚C in a Schlenk tube. Sodium (1.5 g, 65.2 mmol) pre-washed in hexane was added to the ammonia. An intense blue solution formed immediately

and the resultant ammonia/sodium mixture was stirred at -78 °C for 1 h. Triphenylphosphine (5.66 g, 21.58 mmol) was added slowly over a period of ca. 15 min and the solution was stirred for a further 2 h. Ammonium chloride (1.10 g, 20.57 mmol) was added to the solution. A solution of bis(2-chloroethyl)amine hydrochloride (2.2 g, 12.52 mmol) in THF (50 mL) was added to the mixture. Upon the addition of this solution the intensely blue mixture turned white. The solution was then left to stir overnight. The white solution was then cooled to 0 °C and degassed H_2O (50 mL) was added dropwise. Upon the addition of the water the solution became clear. The solution was taken up in Et_2O (50 mL) and the organic phase removed under reduced pressure. The product was washed with ethanol and a white fluffy material was formed. The white product was then dried under reduced pressure. Yield (1.59 g, 60%).

Method 2 (2b)



Scheme S2 Synthetic pathway to PNP ligands using trimethyl protecting group (Method 2)

Step 1: Bis(2-chloroethyl)amine hydrochloride (2.00 g, 11.20 mmol) was suspended in a mixture of triethyl amine (20 mL), trimethylsilyl chloride (8 mL) and DMSO (0.25 mL) and the mixture was refluxed for 16 h under nitrogen with magnetic stirring. The mixture gave a yellowish thick precipitate. It was then cooled to RT. The suspension was filtered and the remaining volatiles removed under reduced pressure. A yellow-orange oil remained. Yield (0.94 g, 40%). ^{1}H NMR $\delta_H(CDCl_3)$: 0.03 (12H, s), 2.95 (2H, t, $J_{(HH)}$ 7.9 Hz, CH_2CH_2) and 3.61 (2H, t, $J_{(HH)}$ 8.0 Hz, CH_2CH_2). This yellow-orange oil obtained was used without further purification for the synthesis of **2b**.

Step 2 : To a solution of the product from step 1 (0.94 g, 4.39 mmol) in THF (50 mL) was added at -40 °C with stirring a solution of PPh_2Li made by reacting Li (0.17 g, 2.45 mmol) and a solution of PPh_3 (3.00 g, 1.14 mmol) in THF (50 mL). This addition was done slowly over a period of 0.5 h at room temperature. After completion of the addition, the mixture was

allowed to warm to room temperature and heated under reflux for 8 h. The solution was then cooled to RT and hydrolysed by addition of 18 mL H_2O. It was then allowed to heat under reflux for a further hour at 100 °C. The two-phase mixture was separated and the aqueous phase extracted with Et_2O (3 x 50 mL). The combined organic phases were dried over anhydrous $MgSO_4$ and the solvent was removed under vacuum. Yield (0.67 g, 71%).

1.1.4. Synthesis of bis[(2-diphenylphosphino)ethyl]amine·HCl (PNP)

Under a stream of nitrogen, lithium metal sheets (0.38 g, 54.76 mmol) were added into a stirred solution of triphenylphosphine (6.25 g, 23.83 mmol) in THF (50 mL) in an ice-bath. Most of the lithium dissolved within 5 h to yield a deep red solution. Water was carefully added to the solution (6 mL, drop wise and 12 mL added at once). Deoxygenated diethyl ether (25 mL) was added to the solution and stirred vigorously. The organic phase was dried over anhydrous Na_2SO_4. After filtration, the volatiles were removed under reduced pressure. Diphenylphosphine (4.17 g, 22.40 mmol) was added to a suspension of potassium *tert*-butoxide (3.93 g, 35.09 mmol) in dry THF (80 mL) under nitrogen. The resulting red solution was stirred for 5 min and bis(2-chloroethyl)amine hydrochloride (2.00 g, 11.20 mmol) was added as a coarse powder. The mixture was then heated under reflux for 16h, poured into hexane (115 mL) and washed in succession with 45 mL portions of 10% aqueous NaOH and saturated NaCl solutions. The organic layer was separated, filtered and stirred vigorously with 100 mL of 2N aqueous hydrochloric acid giving a white dense precipitate. Recrystallisation from boiling acetonitrile afforded a fine white needle-like material.
Yield (0.81 g, 90%). Mp 173.5-174.5 ˚C. ^{1}H NMR δ_H ($CDCl_3$): 2.3- 3.3 (8*H*, m), 7.0- 7.6 (20 *H*, m), 9.8 (2*H*, s). ^{13}C NMR ($CDCl_3$): 23.8 (d, CH_2-PPh_2), 45.9 (d, CH_2CH_2-PPh_2), aromatic C, 128.8, 129.2, 132.5. ^{31}P NMR ($CDCl_3$) :-10 (P-Ph). Elemental Analysis (EA): $C_{28}H_{30}ClNP_2$; C, 70.36; H, 6.33; N, 2.93. Found: C, 70.69, H, 6.03; N, 3.02.

1.1.5. Synthesis of bis(2-diphenylphosphinoethyl)phenylphosphine (L3)

In a sealed Schlenk tube, a mixture of divinylphenylphosphine (0.165 g, 1.02 mmol), diphenylphosphine (0.38 g, 2.04 mmol) and AIBN (100 mg) were irradiated using a 350W Hg Arc lamp at room temperature for 48 h. The resulting white solid was washed with *n*-pentane and the excess volatiles were removed under reduced pressure. Yield (0.49 g, 90.7%). ^{1}H NMR δ_H($CDCl_3$): 1.4-1.6 (8*H*, m), 7.2- 7.6 (25 *H*, m) ^{13}C NMR δ_C ($CDCl_3$): 25.2 (CH_2CH_2-PPh_2)

aromatic C (128-132). ^{31}P NMR ($CDCl_3$): 20 d (P-P). Mp 129-130 °C. Elemental Analysis (EA): $C_{34}H_{33}P_3$; C, 76.39; H, 6.22. Found C, 76.36; H, 6.34.

1.2. Cr(III) complex preparation

1.2.1. Synthesis of $CrCl_3$(bis-(2-ethylsulfanyl-ethyl))-amine (1)

A solution of bis [2-(ethylsulfanyl) ethyl] amine (0.24 g, 1.24 mmol) in THF (4.5 mL) was added to (0.43 g, 1.14 mmol) of $CrCl_3(THF)_3$ in THF (11.5 mL) at room temperature. The solution turned blue-green immediately and was stirred for ten minutes at room temperature. The solvent was removed under vacuum until ≈ 7 mL remained. A further aliquot of diethyl ether (12 mL) was added, the solution was filtered and the solid was washed with a mixture of diethyl ether and THF (12 mL) each and then with a further diethyl ether (12 mL). The solid was dried under vacuum. Yield (0.29 g, 72%). IR (ATR) cm^{-1}: N-H 3220 (s); Cr-S 123 (s); Cr-N 498 (w), 364 (s); Cr-Cl 447. Elemental Analysis = $C_8H_{19}Cl_3CrNS_2$: C, 27.32; H, 5.44; N, 3.98; S, 18.23. Found: C, 27.41; H, 5.38; N, 3.88; S, 17.99.

1.2.2. Synthesis of $CrCl_3$ (bis-(2-decylsulfanyl-ethyl))-amine (2)

This complex was prepared in a similar manner as the ethyl complex analogue in **2.4.2.1**. Yield (0.35 g, 74%). IR (KBr) $cm^{-1:}$ N-H 2955 (s); Cr-S 123 (s); Cr-N 381 (m), 360 (s); Cr-Cl 447.13. EA= $C_{24}H_{51}Cl_3CrNS_2$: C, 50.03; H, 8.92; N, 2.43; S, 11.13. Found: C, 49.95; H, 8.74; N, 2.39; S, 12.00.

1.2.3. Synthesis of $CrCl_3$ (bis-(2-diphenylphosphinoethyl))-amine (Cr-PNP)

$CrCl_3(THF)_3$ (0.563 g, 1.51 mmol) was taken up in THF (10 mL) and a solution of bis[(2-diphenylphosphino)ethyl]amine (0.67 g, 1.52 mmol) in THF (5 mL) added. The solution was stirred for 20 minutes, over which time a green precipitate formed. The solvent was evaporated to about half the original volume and 10 mL Et_2O was added. The precipitated product was collected by filtration, washed with further 10 mL ether and dried under vacuum. Yield (0.55 g, 60.7%). IR (KBr) cm^{-1} = N-H 3374 (m); Cr-P 694 (m); Cr-Cl 502 (m). EA= $C_{28}H_{29}Cl_3CrNP_2$: C, 56.06; H, 4.87; N, 2.34. Found C, 55.90, H, 4.72; N, 2.06.

1.2.4. Synthesis of $CrCl_3$(bis(2-diphenylphosphinoethyl)phenyl)phosphine (3)

$CrCl_3(THF)_3$ (0.372 g, 1 mmol) was dissolved in dichloromethane and filtered. Bis (2-diphenylphosphinoethyl)phenylphosphine (0.535 g, 1 mmol) was dissolved in dichloromethane (40 mL) and added to the filtrate under nitrogen. The solution was then stirred at room temperature. The solvent was removed under reduced pressure and the solid product was left stirring overnight in petroleum ether. The blue solid was isolated by filtration. Yield (0.275 g, 45.8%). IR (KBr) cm^{-1} = P-C 1133 (s); Cr-P 688 (s); Cr-Cl 478 (m). EA= $C_{34}H_{33}Cl_3CrP_3$: C, 58.94; H, 4.80. Found C, 58.76; H, 4.75.

1.3. Supported catalyst preparation

1.3.1. Incipient wetness impregnation method (Supported complexes-SC) (Method I) (Catalysts SC1 – SC3)

Silica was pre-calcined in a stream of dry N_2 at 600 °C for 24 h. A pre-determined amount of the support (SiO_2) was placed in a round bottomed flask and solvent (toluene) added. After warming to ~100 °C, to give a Cr loading of ~1% an amount of the chromium catalyst complex in solution was added to the support and the two were mixed at ~115 °C. After stirring for 2 h, the toluene was removed in vacuo at 120-130 °C under reduced pressure. The catalysts were obtained as bright green and bright blue powders depending on the complexes supported. The sulphur-based complexes gave green powders and phosphorus-based complexes gave blue powders. The catalysts were left to dry at 40 °C overnight.

1.3.2. Two-step incipient wetness impregnation method *(Supported ligands-SL)* (Catalysts SL1 – SL3)

The silica was firstly impregnated with the solution of the ligand (in toluene) of a known concentration. The silica and the ligand were mixed and stirred at ~100 °C for 2 h. This mixture was then dried (solvent evaporated) at ~115 °C. The dried solid product was then impregnated for the second time with a solution of a chromium precursor, $CrCl_3(THF)_3$ (to obtain a 1.0 wt %) chromium loading. These were stirred again for 2 h at ~115 °C. The solvent was then removed under reduced pressure at 120-130 °C. The catalysts were obtained as light green and bright green powders. The catalysts powders were dried at 40 °C overnight.

1.4. Catalyst characterisation

The supported catalysts were characterised by Fourier Transformer Infra-Red (FT-IR), BET (Surface Area Measurements), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray (EDX) and X-ray fluorescence (XRF).

1.4.1. Fourier Transformer Infra-Red (FT-IR) and Attenuated total reflection (ATR)

FTIR spectra were recorded on a Nicolet 410 Impact Fourier-Transform Infrared spectrometer. The sample was introduced into a small quantity of KBr powder and pressed into a disc and analysed from 400 - 4000 cm^{-1}. IR spectra were also recorded on a Perkin Elmer 100 series Attenuated Total Reflectance spectrometer on a diamond crystal. The powdered sample was placed to completely cover the crystal. Then pressure was applied to the sample by tightening a pressure plate to ensure contact between the sample and crystal.

1.4.2. BET (Surface Area Measurements)

This method of surface area measurements is based on the non-specific physisorption of nitrogen onto the sample at -196 °C, the condensation temperature of the adsorbing nitrogen gas. Samples (~0.20 g) were degassed overnight under N_2 at 200 °C. The samples were then cooled to room temperature and re-weighed. The surface areas of the catalysts were determined using a Gemini Micromeretics instrument.

1.4.3. Scanning Electron Microscopy (SEM) and energy dispersive X-ray (EDX analysis

This technique was employed to understand the surface morphological structure of the catalysts. The elemental composition of the surface was determined by energy dispersive X-ray analysis. Samples were stuck onto metal stubs with double sided carbon tape and coated with gold in the Polaron SEM coating unit E5100 to prevent charging by the incident electron beam. The analysis was performed using a Leo 1450 scanning electron microscope fitted

with a Link ISIS energy dispersive X-ray analytical system and the software used to capture the images was a Leo-32 SEM.

1.4.4. X-ray fluorescence (XRF) Spectroscopy

The XRF analysis was done to determine the amount of Cr in wt % in the supported catalysts. Approximately 0.2-0.3 g of a sample was prepared in a norish fusion bed in a Ru tube. About 1.5 g of flux was applied to fuse the sample at 1000 °C in a Pt-Au crucible. The PW 1404 X-Ray Fluorescence instrument equipped with a flow counter detector was used for this analysis.