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# A survey of pendant donor-functionalised (N,O) phosphine ligands for Cr-catalysed ethylene tri- and tetramerisation†

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In this study three classes of ligands are explored for ethylene tri-/tetramerisation in conjunction with chromium and both triethylaluminium ($AlEt_3$) and methylaluminoxane (MAO) co-catalysts. Hydrazine based ligands containing an N–H functionality [PN(NH)P], analogous to Rosenthal's previously reported PNPNH system, show selectivity towards 1-hexene and 1-octene formation in conjunction with $AlEt_3$, and act as PNP tetramerisation analogues when MAO is employed. PNP ligands containing non-protic pendant donor moieties generally show poor activity and selectivity when $AlEt_3$ is employed as an activator, however when MAO is used good activities and selectivities are achieved. *n*-Propylcyclopentane and 2-propenylcyclopentane, and higher homologues, are produced during catalysis when oxygen is the donor atom. The formation of such products is discussed with respect to the generation of methylenecyclopentane and methylcyclopentane by PNP based tetramerisation catalysts. Simple phosphine ligands containing O–H functionalisation are also explored and it was shown that the catalyst selectivity is highly dependent on both the activator and structural features of the ligand employed.

## Introduction

While the production of linear alpha olefins (LAOs) is traditionally by full-range processes, these processes increasingly do not meet the market demand for short chain LAOs (1-butene, 1-hexene and 1-octene) which are important feedstocks for the production of linear low density polyethylene. Attempts to meet the high demand for these feedstocks may result in the over production of higher molecular weight fractions and as such there has been significant focus on developing alternate selective oligomerisation technologies for ethylene conversion which will circumvent this issue. A number of such technologies have been reported in both the patent and academic literature and have been the focus of a number of reviews in recent years.[1–7] Investigation of the mechanistic aspects of this reaction also continues to receive interest.[8–11] While a number of systems are known for the selective trimerisation of ethylene to 1-hexene, there are fewer known systems with high activity and selectivity for ethylene tetramerisation.

In 2004, researchers from Sasol reported the first catalysts for the selective conversion of ethylene to 1-octene which consisted of a chromium source, methylaluminoxane and a PNP ligand (**I**).[12,13] In the initial reports activities of 591 000 g per g of Cr $h^{-1}$ and selectivities in excess of 70% 1-octene were achieved however in subsequent reports activities exceeding 3 000 000 g per g of Cr $h^{-1}$ have been reported.[12–14] Since their discovery, there has been numerous studies into the electronic and steric factors that govern the PNP ligands novel selectivity and excellent activity, as well the effects of the ligand backbone length and composition.[1,4,5] At the same time, new ligand structures which support tetramerisation catalysis continue to be developed.[15–18] A particularly interesting ligand, bearing marked similarity to Sasol's PNP system, was described in the patent literature in 2009.[19,20] The ligand (**II**) contains the PNP backbone and, when unactivated, binds to chromium in a similar fashion with coordination to the metal centre through both phosphorous atoms as a bidentate ligand.[13,21–23] In the original report it was stated that, in conjunction with a chromium source and MAO, the oligomer distribution consists of 1-hexene and 1-octene; a result that was later confirmed by Wass and co-workers.[20,22] Perhaps more interesting is that combinations of the ligand with triethylaluminium yield a catalyst capable of trimerising ethylene with high selectivity (87% 1-hexene) and with an activity of 72 500 g per g of Cr $h^{-1}$. Reduction of the ligand steric bulk (**III**) was shown to convert the catalyst from predominantly

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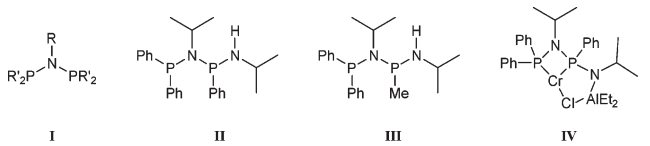
producing 1-hexene to mainly 1-octene (80%), however the activity was somewhat reduced (10 500 g per g of Cr $h^{-1}$).[19] The activation of the system with triethylaluminium is of industrial relevance as it replaces costly MAO as the co-catalysts.[24–30]



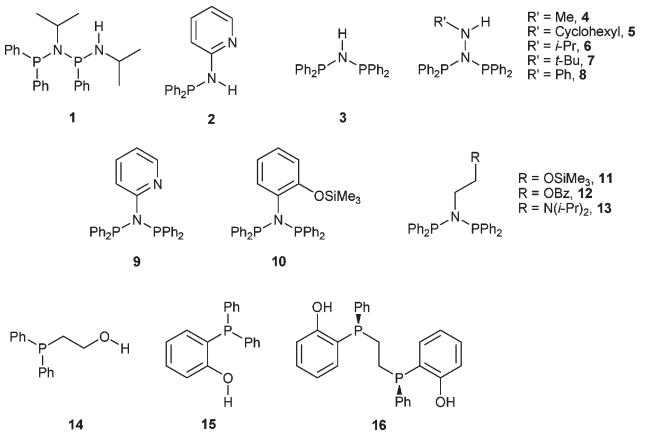
I II III IV

Since the development of this system there has been significant work to determine the extent of the interaction between the alkylaluminium co-catalyst, the chromium source and the ligand. Early studies showed that the ligand could readily coordinate to $AlR_3$, however an increase in temperature was required to deprotonate the PNPNH ligand backbone.[21,31–34] It was also demonstrated that further heating resulted in rearrangement of the ligand backbone to give an NPPN species which was shown to be inactive for ethylene oligomerisation and was speculated to be the mode by which the catalyst deactivated.[21,32] The catalyst's temperature dependence was also demonstrated in kinetic studies where it was shown that at lower temperatures an induction period of ~30 minutes is required before trimerisation commences. However, at temperatures above that which ligand deprotonation can occur, ethylene trimerisation commences with no induction period. Such kinetic studies have also demonstrated the catalyst's long lifetime with ethylene uptake and 1-hexene production shown to be continuous over a period of 2 hours.[35,36] In addition to this, supporting the ligand on a series of functionalised polystyrene resins was shown to be a viable method for preparing a recyclable catalyst material.[37,38] These studies demonstrated that a supported system could generate 1-hexene and that the catalyst material remained active for a period greater than 40 hours and through eight batch runs. In more recent reports Rosenthal and co-workers have demonstrated the beneficial effect of addition of a chloride source to the catalyst mixture.[39,40] A three-fold improvement in activity for some chloride additives in combination with $Cr(acac)_3$ was demonstrated compared to standard runs with $CrCl_3(thf)_3$. Interestingly, in this report combinations of $Cr(acac)_3$/PNPNH/$AlEt_3$ were shown to be completely inactive for catalysis, and as such the authors conclude that the active species most likely contains chloride; a result which is further supported by a subsequent structural study and is analogous to previously reported ethylene trimerisation systems.[33,34,41–44] However, while there is no doubt that addition of a chloride source to the reaction mixture yields a positive result, previous reports by Rosenthal and co-workers have also demonstrated that catalytic mixtures containing no chloride can readily give high trimerisation activity and selectivity and as such the exact role of chloro groups in the catalytic mechanism remains unclear.[19,23] At this stage most of the evidence points towards a coordination arrangement such as shown in **IV**, in which the chloro group attached to aluminium acts as a third weak donor. Such an arrangement has been demonstrated by Gambarotta and co-workers in the case of Cr/pyrrole/triethylaluminium (Phillips type) trimerisation catalysts,[42,43] as well as in other cases.[45]

The highly selective nature of the PNPNH systems in conjunction with their long catalyst lifetime and the low cost of the co-catalyst make them of interest to industry, while their well-defined nature make them ideal for structural and mechanistic studies. Given these previous studies, we were interested in investigating a series of PNP derivatives bearing either a protic nitrogen connected to the PNP nitrogen backbone, which could react with the alkylaluminium activator, or bearing donor functionalities, capable of forming a Lewis pair with alkylaluminium compounds. Additionally, it was off interest to see if this concept could be extended to the use of hydroxy moieties, both with bidentate phosphine ligands and simple monophosphine ligands. Herein we report the preparation of such ligands and their catalytic activity in conjunction with a chromium source and triethylaluminium or MAO.

## Results and discussion

The ligand motifs explored in this study are shown in Scheme 1. Ligand **1** is the PNPNH system reported by Rosenthal and co-workers, and is included in the study to provide a benchmark against which new catalysts could be compared.[21] The ligands upon which the present study is based fall into three general classes. Ligands **2–8** are potentially bidentate and contain an amine functionalisation either directly (**2**, **3**), or pendant to (**4–8**), the ligand backbone. With the exception of **2**, these ligands all contain the PNP ligand structure. They, therefore, probably bear the closest similarities to ligand **1** of the systems studied herein. The second class of ligands (**9–13**) contain a pendant donor group attached, *via* an aromatic (**9** and **10**) or an ethyl (**11–13**) bridge, to the central nitrogen of the PNP ligand. While this donor cannot be deprotonated, it is expected to be capable of coordinating to the aluminium cocatalyst,

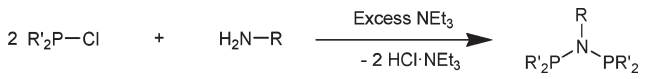



**Scheme 1** Ligand motifs surveyed for Cr-catalysed ethylene oligomerisation.

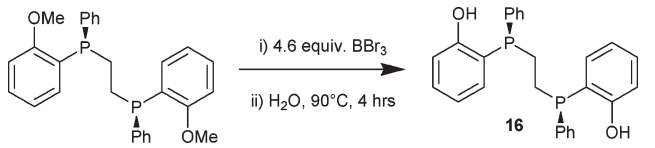
which could potentially lead to analogous behaviour to that observed with **1**. Finally, we were also interested in surveying some simple phosphines containing hydroxy functionalisation (**14–16**). In these cases the cocatalyst could deprotonate and interact with the hydroxyl group. Attempts to prepare ligands with hydroxy functionality pendant to the PNP structure have not been successful thus far, as discussed below.

### Ligand synthesis

Compounds **1–3**, **8**, **14** and **15** were either prepared *via* the literature procedures or purchased and used as received (see Experimental section).[21,46–48] Ligands **7** and **9** have been previously reported in the literature and prepared by other methods but were readily synthesised according to reaction (1).[49,50] An assortment of novel PNP ligands with protic nitrogen moieties (**4–6**) or bearing donor functionalities (**10–13**) were prepared according to reaction (1) and characterised by $^{1}H$, $^{13}C$ and $^{31}P$ NMR spectroscopy and either elemental analysis or mass spectrometry. Each of the ligands shows a single phosphorous resonance in the range of $\delta$ 60–70 which is consistent with previously reported PNP analogue.[14] Compound **10** shows peak broadening for the phosphine bound phenyl rings in the $^{1}H$ and $^{13}C$ NMR spectra, which is indicative of hindered rotation around the C–P bond on the NMR time scale, interestingly the analogous compound $Ph_2PN((o\text{-}CH_3)C_6H_4)PPh_2$ wherein the trimethylsilyl ether is replaced with a methyl ether shows no such restriction.[51] Demethylation of (*R*,*R*)-1,2-bis[(2-hydroxyphenyl)(phenylphosphino)]ethane, following a previously published analogous method, with boron tribromide furnished ligand **16** in 54% yield (reaction (2)) with a single phosphorous resonance at $\delta$ −40.37.[52]




(1)




(2)

Crystals of **4** and **13** suitable for X-ray diffraction were grown from saturated solutions in anhydrous ethanol. The solid state structure of **4** (Fig. 1) is broadly comparable to a series of substituted 2,2-bis(diphenylphosphino)hydrazines all of which contain a trigonal planar $P_2NN$ core; the core bond angles of compound **4** sum to 359.40° which is in agreement with the range of 356.7° to 359.9° for the analogous compounds.[50,53,54] The reported compound 1-*tert*-butyl-2-bis(diphenylphosphino)hydrazine shows the greatest structural similarity to **4** with good agreement between the N1–N2 (1.4443(13) Å/1.445(1) Å) and N2–H2N (0.903(18) Å/0.89(2) Å) bond lengths.[50] The solid state structure of ligand **13** (Fig. 2)

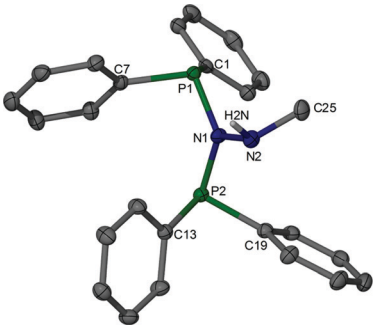



**Fig. 1** Molecular structure of ligand **4**. Thermal ellipsoids are shown at the 50% probability level. All methyl and aromatic-ring hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): N1–P1/2 1.7204(10), 1.7150(10), N1–N2 1.4443(13), P–C 1.8239(12)–1.8331(12), N2–H2N 0.903(18), C–P–C/N 101.23(5)–103.33(5), 102.02(5)–104.10(5), ∑(angles about $N_{P2N/CHN}$) 359.40, 326.7.

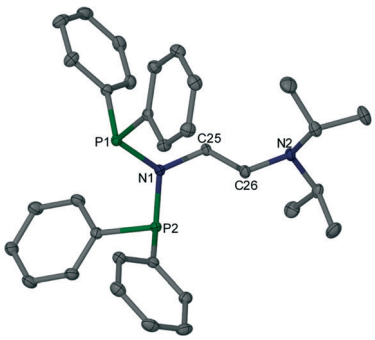



**Fig. 2** Molecular structure of ligand **13**. Thermal ellipsoids are shown at the 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): N1–P1/2 1.7088(10)–1.7181(11), P–C 1.8306(12)–1.8428(13), N–C 1.4743(14)–1.4862(14), C25–C26 1.5272(16), C–P–C/N 100.69(5)–107.66(6), ∑(angles about N1/2) 359.89, 339.67.

is consistent with the previously reported analogous compound *N*,*N*-bis(diphenylphosphino)-2-(diphenylphosphino)ethanamine. Compound **13** displays $sp^2$ hybridisation for the $P_2NC$ core with the sum of the bond angles in **13** equal to 359.89° compared to 360° for the analogous compound. Similarly the P–N1 (1.7088(10)–1.7181(11) Å/1.716(3)–1.718(3) Å), N1–C25 (1.4862(14) Å/1.472(4) Å) and C25–C26 (1.5272(16) Å/1.519(4) Å) bond lengths are in good agreement between the two compounds.[55] In both **4** and **13**, the pendant nitrogen donor and phosphines display trigonal pyramidal geometry indicating that the electron lone pairs are available for donation.

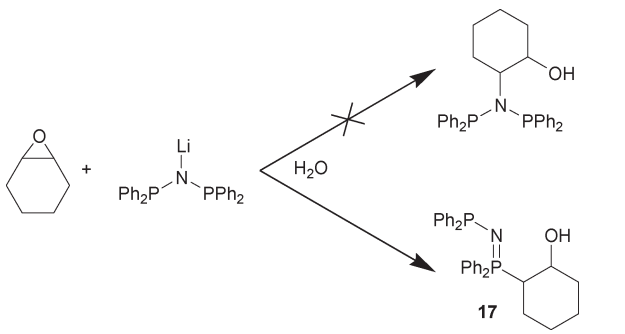
In addition to the preparation of a series of secondary amine substituted PNP ligands, attempts have been made to prepare PNP ligands bearing a hydroxyl moiety on the nitrogen backbone. While the target ligands have ultimately not been synthesised, we have investigated some interesting chemistry of the PNP ligands. Given that diphenylphosphine chloride reacts preferentially with alcohols rather than amines, standard synthetic methods could not be employed to prepare the desired ligands and as such other strategies

have been explored. Epoxide ring opening reactions were initially investigated as one means of introducing a hydroxyl functionality to the PNP ligands. Surprisingly, the reaction between bis(diphenylphosphino)amine and cyclohexene oxide did not lead to opening of the epoxide ring, even in refluxing tetrahydrofuran. Deprotonation of the PNP precursor with *n*-butyllithium, to generate the PNP derived lithium amide, followed by introduction of cyclohexene oxide (Scheme 2) did lead to ring opening, however rather than the desired N-functionalised compound, the reaction yielded **17** in moderate yields after hydrolytic work up. $^{31}$P NMR spectroscopy of **17** shows two sets of doublets with a $^{2}J_{pp}$ splitting of 94 Hz which is comparable with similarly reported compounds.[53,56] Crystals of **17** were grown from a saturated solution in hot methanol (Fig. 3) and structural analysis shows P═N–P bond lengths broadly comparable with those reported for the analogous compounds 7-($Ph_2$–N═$PPh_2$)-8-$NH_2$-quinoline and *P*,*P*-diphenyl-*N*-(1,1,2,2-tetraphenyl-1-diphosphanylidene)phosphinous amide.[53,57] Upon initial inspection, it is somewhat surprising that the ring opening reaction has occurred on a tertiary phosphorous atom rather than the secondary amine core. However, the PNP crystal structures reported herein (Fig. 1 and 2), as well as the crystal structure of lithium[bis(diphenylphosphino)amide], show an $sp^2$ hybridised nitrogen core (trigonal planar geometry) indicating a significant reduction in its basicity and hence a decrease in its capacity to react as a nucleophile in the epoxide ring opening reaction.[58] Examples of triarylphosphines undergoing epoxide ring opening reactions have previously been demonstrated in the literature and are typically facilitated by the presence of an acid to act as the alcohol proton source and the phosphorane counter anion.[59–61] In the case of PNP ligands it appears that no acid source is required as the phosphorane is stabilised by the amides anionic character while the lithium cation most likely generates a lithium alkoxide, upon ring opening, which is readily converted to the alcohol during hydrolytic work up.

The use of protecting group chemistry has also been employed in an attempt to prepare the desired derivatives. Attempts to cleave the benzyl functionality of **12** by hydrogenation with 5% palladium on carbon according to an analogous literature procedure yielded only starting material and a secondary product wherein one phosphorous/nitrogen bond had been cleaved; cleavage of the benzyl ether bond was not observed.[62] Similarly, no reaction of **12** was observed with other hydrogenation catalysts.

Silyl ethers have often been employed as alcohol protecting groups as they are easily and selectively prepared in the presence of amines and can be readily cleaved either with tetrabutylammonium fluoride (TBAF) and a proton source or by hydrolysis. Deprotection of **11** with TBAF gave only an intractable residue from which no species could be definitively identified while both **10** and **11** proved resistant to hydrolysis, even at elevated temperatures. It has previously been demonstrated that phenolic trimethylsilyl ethers can be readily cleaved by titanium(IV) chloride or its tetrahydrofuran adduct.[63] However, introduction of **10** and **11** to $TiCl_4$ in dichloromethane showed no cleavage of the silyl ether but rather a bidentate coordination of the ligand through the phosphorous donors (reaction (3)). The stability of the silyl ether is quite remarkable and somewhat unexpected given the oxophilic nature of titanium. Complex **18** has been characterised by $^{1}$H, $^{13}$C and $^{31}$P NMR spectroscopy and elemental analysis while crystals suitable for X-ray diffraction were grown from a hot dichloromethane–petroleum spirits solution (Fig. 4). Structural analysis shows a distorted octahedral arrangement of the ligands around the titanium atom. In an attempt to prepare crystals of **10** from a hot methanol solution it was found that, under these conditions, the ligand undergoes facile deprotection of the trimethylsilyl ether followed by a rapid intramolecular reaction to generate a monocyclic hydrophosphorane (**19**, reaction (4)). Compound **19** crystallises readily from saturated diethyl ether solutions to give colourless needles suitable for X-ray diffraction studies. The solid state structure of **19** (Fig. 5) shows a trigonal bipyramidinal arrangement of the ligands around the phosphorane core with the phenoxide moiety and proton occupying the axial positions. Several similar hydrophosphorane structures have been reported but, to the best of the authors' knowledge, this is the first example based on a PNP backbone.[64–70]




**Scheme 2** Reaction of cyclohexene oxide with lithium bis(diphenylphosphino)amide to afford compound **17**.

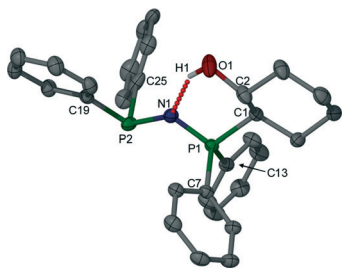



**Fig. 3** Molecular structure of **17**. Thermal ellipsoids are shown at the 50% probability level. Disorder in a phenyl ring (C25) is omitted for clarity. All methylene, methine and aromatic-ring hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): N1–P1,P2 1.5846(13), 1.6853(13), P–C 1.8092(15)–1.8413(18), O1–H1 0.91(4), N1···H1 1.90, C–P1–C 106.42(6)–108.37(7), N1–P1–$C_{Ph/Cy}$ 112.87(7)–114.66(7), 107.00(7), C–P2–C/N1 96.77(7)–102.16(8).

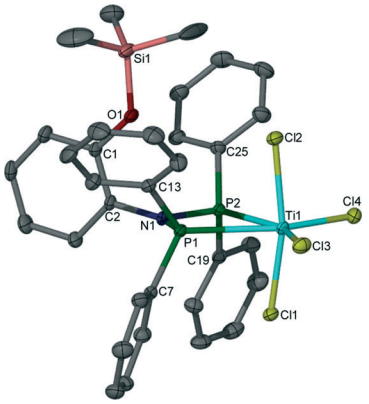



**Fig. 4** Molecular structure of **18**. Thermal ellipsoids are shown at the 50% probability level. A second molecule of similar geometry and a DCM lattice solvent molecule is not shown (geometries given below are for the range found in both molecules). All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ti–P 2.6314(11)–2.6393(12), Ti–$Cl_{trans\ P/trans\ Cl}$ 2.2796(8)–2.3022(8), 2.2360(14)–2.2694(12), N–P 1.711(4)–1.720(4), P–Ti–P 62.99(3), 63.38(3), Cl–Ti–$P_{cis/trans}$ 81.00(4)–91.47(5), 153.13(5)–154.65(4), Cl–Ti–Cl *cis* equat/*cis* axial/*trans* 114.77(4)–115.33(4),92.25(4)–94.95(4),164.40(3)–166.82(3), ∑(angles about N) 356.6–357.8.

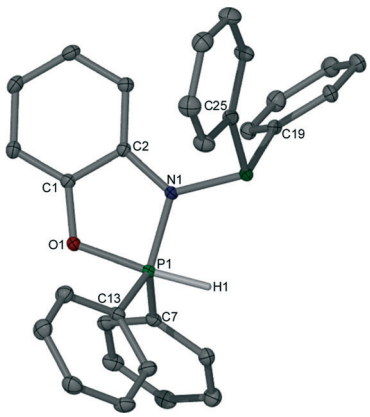
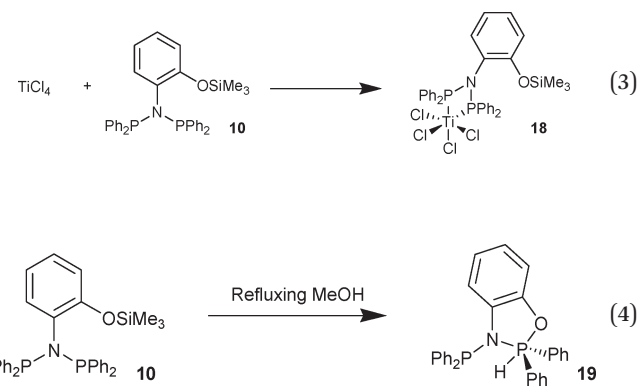



**Fig. 5** Molecular structure of **19**. Thermal ellipsoids are shown at the 50% probability level. All aromatic-ring hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): P1–N1,O1,C7,C13 1.7384(11), 1.7666(9), 1.8281(14), 1.8259(13), 1.337(18), H1–P1–O1,N1,C7, C13 175.1(8), 88.3(8), 90.4(8), 92.4(8), N1–P1–C7,C13 124.01(6)–124.18(6), C7–P1–C13 111.81(6).




## Ethylene oligomerisation and polymerisation

While there have been numerous ethylene trimerisation studies with **1** previously reported in the literature,[21–23,32–36,38,40] it was of interest to optimise the ligand under our conditions in order to determine a series of conditions with which to benchmark the novel ligand systems. The results of catalytic testing of **1**/Cr in conjunction with triethylaluminium are shown in Table 1. In accordance with the literature the catalyst shows stable selectivity across a range of temperatures and ethylene pressures yielding, in most cases, in excess of 95% $C_6$ isomers which consist almost exclusively of 1-hexene. We do note some differences in the relative amounts of the minor products when compared to other studies. In particular, less $C_4$ and $C_{10}$ products, and slightly more polymer. This might be related to different reaction solvents (cyclohexane *versus* toluene), but has not been explored further. As expected, increasing the ethylene pressure yields a corresponding increase in the activity of the system (*cf.* Table 1, entries 1–3) due to the first order dependence on ethylene.[35] More profound however is the effect of temperature on activity; an increase of 10 °C shows an almost doubling in activity (*cf.* Table 1, entries 3 and 4), which has previously been attributed to higher temperatures facilitating deprotonation of the nitrogen functionality by triethylaluminium.[21,32] It has also been reported that only moderate amounts of cocatalyst are required to generate an active trimerisation system and that lower catalyst loadings are beneficial to catalyst activity as they reduce the rate of ligand isomerisation to an inactive species.[35] While we were able to reproduce this trend (*cf.* Table 1, entries 4 and 5) for subsequent testing of new catalysts it was reasoned that a higher cocatalyst loading may be beneficial as an impurity scavenger. While the inclusion of chloro-containing modifiers can have a beneficial effect when used in conjunction with **1**, it has also been shown that employing chromium(III) chloride tetrahydrofuran adduct as the metal source is sufficient.[40]

Screening of the ligands **1–4** and **9–16** was undertaken (Table 2) employing the optimised conditions determined for ligand **1** and the behaviour of the different classes of ligand are discussed below.

**Ligands containing N–H functionality (2–8).** Ligand **2**, which is envisaged to be bidentate through the phosphine and pyridine nitrogen donors with a protic nitrogen bridge, shows poor oligomerisation selectivity in conjunction with triethylaluminium yielding a series of LAOs and a high degree of polymer (Table 2, entry 2). Ligands **3** and **4** are PNP analogues that contain amine moieties in their ligand structure which we envision could be deprotonated in a similar fashion to that reported by Rosenthal and co-workers.[21] Ligand **3** has previously been reported as an ineffective ethylene tri-/tetramerisation system in conjunction with MAO yielding a broad range of oligomeric products.[14] Similarly, when triethylaluminium is employed as the activator, **3** yields a broad range of oligomeric products (Table 2, entry 3); attempts to improve the selectivity and activity by varying both the temperature and cocatalyst loading (Table 2, entries 4 and 5)

**Table 1** Optimisation of **1**/Cr/$AlEt_3$ for ethylene trimerisation[a]

| Entry | Pressure (bar)/$T$ (°C) | Activity[b] | % $C_4$ | % $C_6$ (1-$C_6$) | % $C_8$ (1-$C_8$) | % Other | % PE |
|---|---|---|---|---|---|---|---|
| 1 | 30/50 | 19 970 | 0.1 | 95.1 (99.9) | 3.4 (3.4) | 0.4 | 1 |
| 2 | 45/50 | 22 270 | 0.1 | 95.4 (99.9) | 3.3 (5.5) | 0.4 | 0.9 |
| 3 | 50/50 | 24 150 | 0.1 | 94.6 (99.9) | 3.3 (5.6) | 0.4 | 1.6 |
| 4 | 50/60 | 44 380 | 0.2 | 95.6 (99.9) | 2.6 (5.0) | 0.3 | 1.3 |
| 5[c] | 50/60 | 50 260 | 0.0 | 95.4 (99.9) | 2.7 (4.6) | 0.3 | 1.5 |

[a] 17.5 μmol of ligand **1**, 10 μmol $CrCl_3(thf)_3$, 70 equiv. $AlEt_3$, 200 mL cyclohexane total volume, 30 min. [b] g product per g of Cr $h^{-1}$. [c] Run employed only 15 equivalents of $AlEt_3$.

**Table 2** Ethylene oligomerisation and polymerisation with ligands **1**–**4** and **9**–**16** in conjunction with Cr/$AlEt_3$[a]

| Entry | Catalyst | Activity[b] | % $C_4$ | % $C_6$ (1-$C_6$) | % $C_8$ (1-$C_8$) | % Other | % PE |
|---|---|---|---|---|---|---|---|
| 1 | **1** | 44 380 | 0.2 | 95.6 (99.9) | 2.6 (5.0) | 0.3 | 1.3 |
| 2 | **2** | 7630 | 0.3 | 1.5 (94.7) | 2.0 (34.8) | 10.5 | 85.7 |
| 3 | **3** | 2760 | 1.3 | 9.3 (88.2) | 8.2 (53.3) | 16.3 | 64.9 |
| 4[c] | **3** | 4550 | 0.9 | 1.6 (69.5) | 1.7 (75.9) | 2.6 | 93.1 |
| 5[d] | **3** | 3710 | 17.2 | 12.9 (92.8) | 6.9 (41.5) | 6.1 | 56.9 |
| 6 | **4** | 4590 | 1.6 | 11.1 (90.4) | 17.6 (85.7) | 7.0 | 62.7 |
| 7 | **9** | 3600 | 0.6 | 3.1 (94.4) | 4.1 (44.3) | 22.8 | 69.5 |
| 8[e] | **10** | — | Trace | Trace | — | — | — |
| 9[e] | **11** | — | Trace | Trace | — | — | — |
| 10[e] | **12** | — | Trace | Trace | — | — | — |
| 11 | **13** | 4280 | 2.8 | 28.8 (98.6) | 1.7 (75.4) | 3.4 | 63.3 |
| 12 | **14** | 3200 | 1.2 | 5.1 (96.4) | 5.1 (30.3) | 16.5 | 72.1 |
| 13 | **15** | 3280 | 1.4 | 38.3 (98.8) | 1.6 (75.3) | 0 | 58.7 |
| 14[e] | **16** | 910 | 3.3 | 17.7 (99.9) | 1.0 (50.0) | 1.8 | 76.2 |

[a] 17.5 μmol of ligand, 10 μmol $CrCl_3(thf)_3$, 70 equiv. $AlEt_3$, 200 mL cyclohexane total volume, 30 min, 50 bar ethylene pressure, 60 °C. [b] g product per g of Cr $h^{-1}$. [c] Run performed at 40 °C. [d] Run employed 300 equivalents of $AlEt_3$. [e] 17.5 μmol of ligand, 10 μmol $CrCl_3(thf)_3$, 70 equiv. $AlEt_3$, 50 mL cyclohexane total volume, 30 min, 50 bar ethylene pressure, 60 °C.

gave little improvement towards selective oligomerisation. Interestingly, the hydrazine derived ligand **4**, when activated with triethylaluminium, shows selectivity in the liquid phase towards both 1-hexene (overall 10%) and 1-octene (overall 15%, Table 2, entry 6, combined 1-$C_6$ and 1-$C_8$ represents 67% of liquid products). Such a liquid phase distribution is comparable with that observed for the Sasol PNP ligands, however in our case there is still a significant contribution from polymer formation. Work with **1** has shown that temperature and $AlEt_3$ concentration can have a profound effect on the activity and selectivity of the catalyst and as such it was of interest to attempt to improve our system by varying these factors (Table 3).[32,35] While reducing the temperature does indeed increase the activity it also significantly increases polymer formation (*cf.* Table 3, entries 1 and 2). However, increasing the temperature was also found to have a detrimental effect yielding a significant increase in the formation of higher oligomers (*cf.* Table 3, entries 2 and 4). These results are somewhat consistent with those reported for **1** wherein a narrow temperature range is required for the deprotonation of the amine by triethylaluminium to occur, generating an active trimerisation system, but excessive heating results in catalyst deactivation.[32] Increasing the loading of the cocatalyst (Table 3, entry 3) shows a slight increase in the selectivity towards 1-hexene however a significant amount of 1-butene is now formed, indicating that the ethylene oligomerisation has shifted from a somewhat selective distribution towards a Schulz–Flory type distribution.

Structural factors of the hydrazine derived PNP ligands and their effect on catalytic selectivity have also been investigated (Table 4). In all cases where a bulkier nitrogen substituent was

**Table 3** Optimisation of **4**/Cr/$AlEt_3$ for ethylene tri-/tetramerisation[a]

| Entry | Temperature (°C) | Activity[b] | % $C_4$ | % $C_6$ (1-$C_6$) | % $C_8$ (1-$C_8$) | % Other | % PE |
|---|---|---|---|---|---|---|---|
| 1 | 40 | 5970 | 1.3 | 3.5 (91.8) | 8.7 (92.0) | 3.0 | 83.5 |
| 2 | 60 | 4590 | 1.6 | 11.1 (90.4) | 17.6 (85.7) | 7.0 | 62.7 |
| 3[c] | 60 | 4057 | 13.7 | 14.6 (90.7) | 15.9 (76.4) | 8.9 | 46.9 |
| 4 | 75 | 4380 | 1.0 | 8.3 (93.0) | 10.9 (79.4) | 27.0 | 52.8 |

[a] 17.5 μmol of ligand, 10 μmol $CrCl_3(thf)_3$, 70 equiv. $AlEt_3$, 200 mL cyclohexane total volume, 30 min, 50 bar ethylene pressure, 60 °C. [b] g product per g of Cr $h^{-1}$. [c] Run employed 300 equivalents of $AlEt_3$.

Table 4 Ethylene oligomerisation and polymerisation with hydrazine derived ligands **4**–**8** in conjunction with $Cr/AlEt_3$[a]

| Entry | Catalyst | Activity[b] | % $C_4$ | % $C_6$ (1-$C_6$) | % $C_8$ (1-$C_8$) | % Other | % PE |
|---|---|---|---|---|---|---|---|
| 1 | **4** | 4590 | 1.6 | 11.1 (90.4) | 17.6 (85.7) | 7 | 62.7 |
| 2 | **5** | 2455 | 2.9 | 18.7 (93.2) | 12.9 (67.1) | 18.2 | 47.3 |
| 3 | **6** | 2310 | 2.5 | 18.6 (98.4) | 12.2 (60.3) | 16.7 | 50 |
| 4 | **7** | 2180 | 4.5 | 16.1 (96.5) | 11.2 (73.9) | 6.6 | 61.6 |
| 5 | **8** | 1130 | 9.1 | 32.8 (97.2) | 13.4 (66.9) | 10.8 | 33.9 |

[a] 17.5 μmol of ligand, 10 μmol $CrCl_3(thf)_3$, 70 equiv. $AlEt_3$, 200 mL cyclohexane total volume, 30 min, 50 bar ethylene pressure, 60 °C. [b] g product per g of Cr $h^{-1}$.

used the liquid phase selectivity shifts from predominantly 1-octene towards 1-hexene. Ligands **5**, **6** and **7** show overall 1-hexene selectivities of 17%, 18% and 16% respectively (Table 4, entries 2–4), however a significant amount of higher oligomers was also recorded for ligands **5** and **6**. Screening of ligand **8** resulted in the most selective trimerisation system of the series with an overall 1-hexene selectivity of 32%, albeit the activity of this ligand is also the lowest which might perhaps be attributed to its rearrangement, that has been known to occur upon deprotonation.[46] It is notable that, for ligands **4**, **7** and **8**, the combined 1-hexene and 1-octene selectivity within the liquid product fraction is reasonably high (62–67%), however the formation of polyethylene lowers the overall selectivity.

**PNP ligands containing pendant donor functionalities (9–13).** Previous structural studies of PNP ligands bearing pendant ether and thioether donor functionalities from the nitrogen backbone have shown that, for ethyl and propyl bridges between the nitrogen and donor atom, rather than the expected tridentate binding mode to chromium the ligands adopt a bidentate *P,P* coordination mode with the pendant donor remaining uncoordinated.[51,71] As such we envisaged that analogous pendant donor functionalised ligands may be able to form Lewis acid/base adducts with triethylaluminium through their donor moiety, bringing the aluminium cocatalyst into close proximity with the chromium metal centre and potentially generating an active tri-/tetramerisation system. This concept has been demonstrated by Rosenthal and co-workers for their ethylene trimerisation system **1** (structure IV).[21] Unfortunately the majority of pendant donor functionalised systems screened either led to poor liquid phase selectivity (Table 2, entry 7) or, in the case of the ether functionalised ligands, no catalytic activity was noted (Table 2, entries 8–10). However, ligand **13** shows good selectivity towards ethylene trimerisation in the liquid phase (Table 2, entry 11, overall 28% 1-hexene, 76% of liquid products), but again suffers from high polymer formation. The reason behind the lack of activity demonstrated by the ether functionalised systems in comparison to their amine functionalised counterparts is currently unclear.

**Phosphine ligands containing hydroxyl functionality (14–16).** Screening of the simple phosphine ligand **14** yielded approximately 28% liquid phase oligomers however the selectivity towards short chained linear alpha olefins was only moderate (Table 2, entry 12). Conversely, ligands **15** and **16**, where the hydroxyl/phosphine bridge is converted from a saturated alkane to an aromatic bridge, shows an improvement in selectivity towards 1-hexene yielding overall 38% and 17% 1-hexene respectively (Table 2, entries 13 and 14). Previous studies have shown the benefits of bidentate phosphine ligands for selective oligomerisation, and as such it was of interest to increase the ratio of **15** : chromium in an attempt to improve selectivity.[1,4–7] Increasing the ligand : Cr ratio from 1.75 : 1 to 2.2 : 1 yields a two-fold increase in overall 1-hexene selectivity from 37.8% to 75.3%, however a decrease in activity is also noted (*cf.* Table 5, entries 1 and 2). This indicates that the shift in selectivity results not from an increase in the production of 1-hexene but rather from a suppression of polymer formation. Interestingly, activation of **15**, regardless of the ligand ratio, with MAO yielded only a polymerisation catalyst (Table 5, entries 3 and 4). Ligands of the type **15** and **16**, in conjunction with triethylaluminium, are reminiscent of aryloxide systems first disclosed by IFP Energies Nouvelles with both systems (**15** and IFP's bis(2,6-diphenylphenoxy)isobutylaluminium) yielding comparable activities and selectivities.[72,73] Moreover, workers from Sasol Technology have demonstrated that combinations of a chromium source, triethylaluminium and certain phenols when combined *in situ* can yield effective ethylene

Table 5 Ethylene oligomerisation with **15**/Cr and $AlEt_3$ or MAO

| Entry | Ligand (μmol) | Activity[a] | % $C_4$ | % $C_6$ (1-$C_6$) | % $C_8$ (1-$C_8$) | % Other | % PE |
|---|---|---|---|---|---|---|---|
| 1[b] | 17.5 | 3280 | 1.4 | 38.3 (98.8) | 1.6 (75.3) | 0 | 58.7 |
| 2[b] | 22.0 | 2040 | 2.4 | 76.2 (98.8) | 2.5 (74.0) | 0 | 18.9 |
| 3[c] | 10.0 | 22 310 | — | — | — | — | 100 |
| 4[c] | 20.0 | 10 190 | — | — | — | — | 100 |

[a] g product per g of Cr $h^{-1}$. [b] 10 μmol $CrCl_3(thf)_3$, 70 equiv. $AlEt_3$, 200 mL cyclohexane total volume, 30 min, 50 bar ethylene pressure, 60 °C. [c] 10 μmol Cr $(acac)_3$, 500 equiv. MAO, 200 mL cyclohexane total volume, 30 min, 45 bar ethylene pressure, 50 °C.

trimerisation catalysts, however high ligand : chromium ratios are required.[74,75]

**Screening of 2 and 4–16 in conjunction with MAO activation.** While it is of industrial importance to attempt to replace MAO with significantly cheaper cocatalysts such as triethylaluminium, there is still significant interest in generating new catalytic systems for ethylene oligomerisation, and as such we have also tested our novel systems in conjunction with MAO (Table 6), which is known to facilitate selective ethylene oligomerisation. Ligands **1** and **3** in conjunction with MAO have been tested previously,[14,22] while ligand **15** has been discussed above (see Table 5).

Ligand **2** shows only low selectivity towards selective tri-/tetramerisation due to the significant degree to which higher LAOs were also formed (Table 6, entry 1). The hydrazine derived ligands (**4–8**) act as direct PNP analogues in conjunction with MAO, albeit with high polymer formation, displaying selectivity towards 1-hexene (overall between 7–12%) and 1-octene (overall 30–60%). Ligand **4**, which has the lowest steric bulk on the nitrogen backbone, again yields both the highest 1-octene selectivity and overall activity of hydrazine derived ligands. Interestingly, ligand **8** once again shows poor activity compared to the alkyl substituted species which is most likely due to its poor stability.[46]

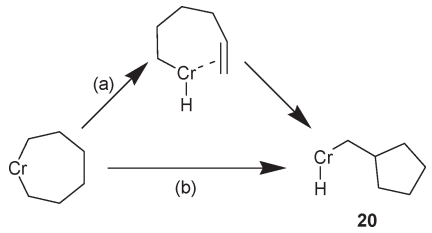
Activation of the pendant donor functionalised PNP ligands **9–13** with MAO yielded a series of selective oligomerisation systems. Ligand **9** displayed both the lowest activity and selectivity of the pendant donor functionalised systems screened (Table 6, entry 7), similar results have previously been demonstrated by Hor and co-workers for other pyridine functionalised PNP ligands.[71] Conversely, the amine donor functionalised ligand **13** yielded the most active system screened in conjunction with MAO, giving activities in excess of 420 000 g product per g of Cr $h^{-1}$ (Table 6, entry 11). While no direction comparison can be made, this system is beginning to approach the high activities known for other PNP derivatives. Similarly, this system displays good selectivity towards 1-octene; overall 55% of the total products.

The ether functionalised ligands **10–12** also show good activity and a high degree of selectivity towards 1-octene formation (Table 6, entries 8–10). Analogous ligands have previously been explored by Hor and co-workers and Bercaw and co-workers. Our results are generally in agreement with these studies.[51,71] It is noteworthy that in previous reports the longer chain oligomeric products are reported to be either $C_{11+}$ linear alpha olefins[71] or $C_{10}$ isomers (through the co-trimerisation of 1-hexene and ethylene) and $C_{12}$ isomers (through the co-trimerisation of 1-octene and ethylene),[51] however the co-trimeric isomers were not present in our catalytic mixtures. Detailed analysis of the liquid phase for ligands **10–12** in conjunction with MAO reveals some interesting features. Each oligomeric fraction consists of a distribution of four isomers; for example the $C_6$ oligomeric fraction from the catalytic mixture of ligand **10** comprises of 38.8% 1-hexene, 5.4% hexane, 23.9% methylcyclopentane and 31.9% methylenecyclopentane. Although the $C_8$ fraction is enriched in 1-octene (~95%), octane, *n*-propylcyclopentane and 2-propenylcyclopentane are also detected; while the higher oligomers ($C_{10+}$) show approximately equal portions of each of the four isomers. A previous investigation into the formation of methylcyclopentane and methylenecyclopentane by PNP based ethylene tetramerisation systems has proposed two possible mechanisms by which the species can form.[76] In that report the authors suggest that the readily formed chromacycloheptane can rearrange either *via* a concerted mechanism (Scheme 3, pathway a) or a formal β-hydride transfer to chromium and subsequent cyclisation of the 5-hexenyl moiety by reinsertion (Scheme 3, pathway b) to generate the cyclopentylmethylchromium intermediate **20**. This intermediate is proposed to decompose either *via* a

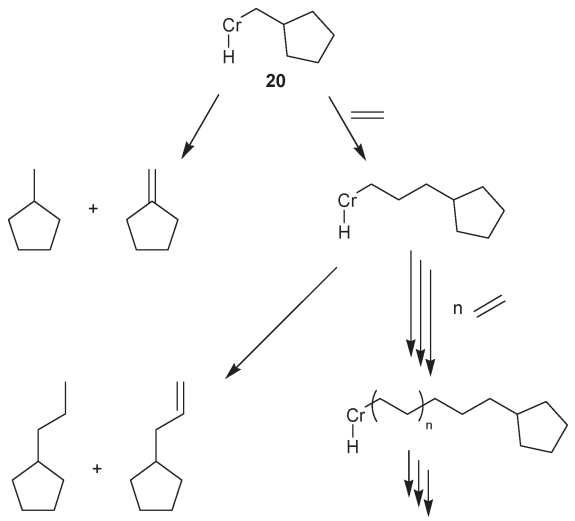
**Table 6** Ethylene oligomerisation and polymerisation with ligands **2** and **4–16** in conjunction with Cr/MAO[a]

| Entry | Catalyst | Activity[b] | % $C_4$ | % $C_6$ (1-$C_6$) | % $C_8$ (1-$C_8$) | % Other | % PE |
|---|---|---|---|---|---|---|---|
| 1 | **2** | 14 320 | 2.4 | 7.6 (60.6) | 13.2 (87.0) | 24.4 | 52.4 |
| 2 | **4** | 38 260 | 1.6 | 12.1 (62.4) | 62.6 (96.4) | 17.7 | 6.0 |
| 3 | **5** | 17 370 | 2.1 | 11.5 (64.8) | 46.2 (96.4) | 11.4 | 28.8 |
| 4 | **6** | 20 050 | 1.9 | 13.0 (67.6) | 52.4 (96.6) | 11.6 | 21.1 |
| 5 | **7** | 14 820 | 1.8 | 13.5 (86.3) | 39.5 (98.0) | 5 | 40.2 |
| 6 | **8** | 8880 | 3.3 | 13.6 (81.0) | 30.8 (96.0) | 9.1 | 43.2 |
| 7[c] | **9** | 5870 | 5.2 | 11.3 (55.2) | 10.0 (87.5) | 11.2 | 62.2 |
| 8[d] | **10** | 37 810 | 3.1 | 23.5 (38.8) | 55.1 (94.5) | 14.1 | 4.2 |
| 9[d] | **11** | 40 530 | 2.4 | 16.7 (35.4) | 52.8 (95.7) | 16.7 | 11.8 |
| 10[d] | **12** | 11 350 | 2.2 | 15.0 (41.1) | 41.7 (96.0) | 18.6 | 22.5 |
| 11 | **13** | 425 020 | 1.2 | 10.5 (57.1) | 58.0 (96.1) | 14.6 | 15.7 |
| 12[e] | **14** | 46 140 | 1.3 | 12.8 (73.2) | 55.2 (97.7) | 8.7 | 22.1 |
| 13 | **15** | 22 310 | — | — | — | — | 100 |
| 14[e] | **15** | 10 190 | — | — | — | — | 100 |
| 15[d] | **16** | 1460 | 1.2 | 1.3 (80.0) | 0.8 (86.1) | 2.9 | 93.8 |

[a] 10 μmol of ligand, 10 μmol $Cr(acac)_3$, 500 equiv. MAO, 200 mL cyclohexane total volume, 30 min, 45 bar ethylene pressure, 50 °C. [b] g product per g of Cr $h^{-1}$. [c] Run performed at 60 °C, 50 bar ethylene pressure. [d] 10 μmol of ligand, 10 μmol $Cr(acac)_3$, 500 equiv. MAO, 50 mL cyclohexane total volume, 30 min, 45 bar ethylene pressure, 50 °C. [e] 20 μmol of ligand employed.




**Scheme 3** Postulated mechanisms for the formation of cyclopentylmethylchromium intermediate **20**; (a) concerted, and (b) stepwise β-hydride transfer and reinsertion.




**Scheme 4** Ethylene insertion into intermediate **20** to yield higher *n*-alkylcyclopentanes and alkenylcyclopentanes.

disproportionation process (either mono- or bimetallic) or *via* cyclopentylmethyl radicals (although 5-hexen-1-yl radicals cannot be discounted); however experimental evidence disfavoured the latter mechanism.[76] The formation of the longer chained homologues of methylcyclopentane and methylenecyclopentane by ligands **10–12** is readily ratified by ethylene insertion (Cossee–Arlmann type chain growth) into the alkyl–Cr bond of intermediate **20** (Scheme 4) and subsequent decomposition *via* a disproportionation process; however the formation of such oligomers by radical intermediates seems unlikely. As such, the findings in this study are complimentary to the results previously published by Overett and co-workers.[76]

Somewhat surprisingly, ligand **14** which gave poor selectivity upon activation with triethylaluminium yields an active tri-/tetramerisation system when two ligand equivalents are employed with MAO (Table 6, entry 12), with good selectivity to 1-octene observed (overall 1-octene selectivity of 54%). To the best of the authors' knowledge this is the first report of this simple ligand motif for selective ethylene tri-/tetramerisation. Ligand **16**, which is structurally similar to SK Energy's bridged diphosphine ligands for ethylene tri-/tetramerisation, surprisingly yielded only poor short chain LAO selectivity with low activity (Table 6, entry 15).[77]

## Summary and conclusions

Herein we have prepared a series of ligands that fall into three general classes, each of which has been tested in conjunction with triethylaluminium and MAO. The first series contain an N–H functionality and are structurally similar to Rosenthal and co-worker's active PNPNH trimerisation system.[21] In conjunction with triethylaluminium, the hydrazine derived PNP ligands **4–8**, show selectivity towards 1-hexene and 1-octene formation. Unfortunately, this liquid phase selectivity is accompanied by a high degree of polymer formation, which ultimately could not be overcome. When MAO is employed as the activator these ligands act as PNP analogues yielding a high degree of selectivity towards 1-octene.

While our results with the hydrazine-based ligands do not match those achieved with the remarkable system of Rosenthal and co-workers, this new system does offer promise for MAO free tri- and tetramerisation, and provides directions for future development. The formation of two distinct product categories, short chain α-olefins and polyethylene, perhaps suggests that a number of different active species (and mechanisms) are formed upon activation. This is a behaviour we have observed previously with Ti-based catalysts.[78,79] The key to improving overall selectivity might therefore lie in controlling activation and such multi-mechanism behaviour, which is, unfortunately, unlikely to be a trivial matter.

The second class of catalysts consist of pendant donor functionalised PNP ligands. In the majority of cases activation with triethylaluminium leads to either low activity and poor selectivity or no activity at all. However, under the same conditions the amine functionalised ligand **13** shows selectivity towards 1-hexene. Broadly speaking, the pendant functionalised ligands, in conjunction with MAO, act as PNP derived tri-/tetramerisation systems and yield results consistent with previous studies. Ligand **13** shows the most remarkable activity (in excess of 425 000 g per g of Cr $h^{-1}$) of the systems screened in this study. The presence of *n*-propylcyclopentane and 2-propenylcyclopentane, and higher homologues, formed by the ether functionalised ligands **10–12** during catalysis, strongly supports the formation of such species *via* a cyclisation-chain growth-disproportionation mechanism rather than a radical based mechanism.

Screening of simple phosphine ligands containing an O–H functionality employing triethylaluminium as the cocatalyst has shown that with an aromatic bridge between the phosphine and hydroxyl moiety, the catalysts are effective for ethylene trimerisation and that polymerisation is suppressed at high ligand : chromium ratios. Such findings are consistent with previous work on aryloxy-chromium catalysts.[75] Conversely, in conjunction with MAO ligands **15** and **16** yield polymerisation systems, however **14** (aliphatic phosphine/hydroxyl bridge) shows selectivity for tetramerisation. As such, it is clear that both the choice of co-catalyst and ligand structure are important in determining the selectivity for this ligand motif.

# Experimental

## General considerations

(2-Hydroxyphenyl)diphenylphosphine (Sigma-Aldrich, 97%) and *N*,*N*-bis(diphenylphosphino)amine (Strem, 98%) were purchased and used as received. $Ph_2PN(i\text{-}Pr)P(Ph)N(i\text{-}Pr)H$ (**1**),[21] $Ph_2PN(2\text{-pyridinel})H$ (**2**),[48] $(Ph_2P)_2N\text{–}N(Ph)H$ (**8**) (ref. 46) and (2-hydroxyethyl)diphenylphosphine (**14**) (ref. 47) were prepared according to literature procedures. Syntheses involving air/moisture sensitive reactants or products were carried out under argon or nitrogen using standard Schlenk techniques, or in a glove box. Solvents were purified by passage through an Innovative Technologies purification system and, where appropriate, stored over a sodium mirror. MAO was supplied by Albemarle as a 10% solution in toluene and MMAO-3A was supplied by AkzoNobel as a 7% solution in heptane.

Nuclear magnetic resonance studies were performed using an Oxford AS400 or Varian Mercury 300Plus NMR spectrometer at room temperature. $^1$H NMR spectra were acquired at 400 MHz or 300 MHz, $^{13}$C NMR spectra at 100.5 MHz or 75 MHz and $^{31}$P NMR spectra at 161.8 MHz. $^1$H NMR spectra were internally referenced to the residual solvent peaks, and $^{13}$C NMR spectra to deuterated solvent resonances. $^{31}$P NMR spectra were referenced to triphenylphosphine standard.

The liquid products resulting from ethylene oligomerisation were analysed by GC on a Varian 3900 or a Shimadzu GC-2014 utilising helium carrier gas and FID detector. Quantification was achieved *via* addition of a known volume of cyclohexane or nonane internal standard upon completion of the catalytic run.

## Synthesis

**Preparation of $(Ph_2P)_2N\text{–}N(Me)H$ (4).** To 50 mL of stirred anhydrous tetrahydrofuran at 0 °C was added excess triethylamine (15 mL), methylhydrazine (0.53 g, 5.70 mmol) and diphenylphosphine chloride (1.06 mL, 5.70 mmol). The resulting suspension was stirred for 30 minutes and a second equivalent of diphenylphosphine chloride (1.06 mL, 5.70 mmol) was added dropwise. The mixture was stirred for 24 hours, solvent removed under vacuum, and the residue washed with 60 mL and 25 mL portions of degassed deionised water. The resulting oil was extracted with 2 × 5 mL portions of anhydrous ethanol which upon standing crystallised the title compound as small colourless cubes in 29% yield (0.14 g, 0.33 mmol). $^1$H NMR ($C_6D_6$, 400 MHz): $\delta$ 7.52–7.57 (m, 8H, aryl-*H*), 6.99–7.11 (m, 12H, aryl-*H*), 3.40 (bd, $J$ = 5.3 Hz, 1H, N*H*), 2.15 (d, $J$ = 4.5 Hz, 3H, NC$H_3$) $^{31}$P NMR ($C_6D_6$, 161.8 MHz): $\delta$ 65.85 (s). $^{13}$C NMR ($C_6D_6$, 100.5 MHz): $\delta$ 140.3 (t, $J$ = 5.7 Hz, aryl-$C_{ipso}$), 133.2 (t, $J$ = 11.1 Hz, aryl-*C*), 128.8 (s, aryl-*C*), 128.0 (s, aryl-*C*), 39.1 (t, $J$ = 5.6 Hz, N*C*$H_3$). Anal. calcd for $C_{25}H_{24}P_2N_2$: C 72.44, H 5.84, N 6.76. Found: C 73.02, H 5.87, N 6.76.

**Preparation of $(Ph_2P)_2N\text{–}N(cyclohexyl)H$ (5).** Cyclohexylhydrazine hydrochloride (0.30 g, 1.99 mmol) was suspended in 30 mL of anhydrous dichloromethane with stirring. Excess triethylamine (1.4 mL) was added, generating a colourless solution. Diphenylphosphine chloride (0.74 mL, 3.98 mmol) was added dropwise and the resulting pale yellow solution was stirred overnight. The solution was washed with 3 × 30 mL of degassed, deionised water, dried with sodium sulphate, filtered and the volatiles removed under reduced pressure to give a cream coloured residue. The residue was extracted with 8 mL of anhydrous ethanol from which the title compound crystallized overnight as a white solid in 21% yield (0.20 g, 0.42 mmol). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.42–7.48 (m, 8H, aryl-*H*), 7.21–7.31 (m, 12H, aryl-*H*), 3.78 (s, 1H, N*H*), 2.46 (t, $J$ = 10.5 Hz, 1H, NC*H*), 1.42 (m, 5H, cyclohexyl-*H*), 0.85 (m, 3H, cyclohexyl-*H*), 0.59 (m, 2H, cyclohexyl-*H*). $^{31}$P NMR ($CDCl_3$, 161.8 MHz): $\delta$ 69.60 (s). $^{13}$C NMR ($CDCl_3$, 100.5 MHz): $\delta$ 139.3 (t, $J$ = 6.2 Hz, aryl-$C_{ipso}$), 133.2 (t, $J$ = 11.6 Hz, aryl-*C*), 128.9 (s, aryl-*C*), 128.0 (t, $J$ = 2.9 Hz, aryl-*C*), 58.5 (t, $J$ = 3.8 Hz, N*C*H), 31.3 (s, cyclohexyl-*C*), 26.0 (s, cyclohexyl-*C*), 24.8 (s, cyclohexyl-*C*). Anal. calcd for $C_{30}H_{32}P_2N_2$: C 74.67, H 6.68, N 5.81. Found: C 74.95, H 6.93, N 6.10.

**Preparation of $(Ph_2P)_2N\text{–}N(i\text{-}Pr)H$ (6).** Compound **6** was prepared according to the procedure outlined for compound **5**, employing isopropylhydrazine hydrochloride (0.22 g, 1.99 mmol). Compound **6** was isolated as an off-white solid in 21% yield (0.19 g, 0.42 mmol). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.40–7.51 (m, 8H, aryl-*H*), 7.20–7.34 (m, 12H, aryl-*H*), 3.81 (d, $J$ = 2.0 Hz, 1H, N*H*), 2.94 (m, 1H, C*H*$(CH_3)_2$), 0.59 (d, $J$ = 6.3 Hz, 6H, CH(C$H_3)_2$). $^{31}$P NMR ($CDCl_3$, 161.8 MHz): $\delta$ 68.79 (s). $^{13}$C NMR ($CDCl_3$, 100.5 MHz): $\delta$ 139.4 (t, $J$ = 5.9 Hz, aryl-$C_{ipso}$), 133.3 (t, $J$ = 11.4 Hz, aryl-*C*), 128.9 (s, aryl-*C*), 128.0 (t, $J$ = 2.8 Hz, aryl-*C*), 50.1 (t, $J$ = 4.9 Hz, *C*H$(CH_3)_2$), 20.7 (s, CH$(CH_3)_2$). Anal. calcd for $C_{27}H_{28}P_2N_2$: C 73.29, H 6.38, N 6.33. Found: C 73.33, H 6.09, N 6.31.

**Preparation of $(Ph_2P)_2N\text{–}N(t\text{-}Bu)H$ (7).** Compound **7** was prepared according to the procedure outlined for compound **5**, employing *tert*-butylhydrazine hydrochloride (0.25 g, 2.01 mmol). Compound **7** was isolated as colourless plates in 25% yield (0.23 g, 0.51 mmol). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.45–7.51 (m, 8H, aryl-*H*), 7.19–7.25 (m, 12H, aryl-*H*), 3.76 (bs, 1H, N*H*), 0.73 (s, 9H, NC(C$H_3)_3$). $^{31}$P NMR ($CDCl_3$, 161.8 MHz): $\delta$ 71.21 (s). $^{13}$C NMR ($CDCl_3$, 100.5 MHz): $\delta$ 139.7 (d, $J$ = 14.0 Hz, aryl-$C_{ipso}$), 133.7 (d, $J$ = 23.5 Hz, aryl-*C*), 128.8 (s, aryl-*C*), 127.7 (d, $J$ = 6.4 Hz, aryl-*C*), 55.4 (s, N*C*$(CH_3)_3$), 28.9 (s, NC(*C*$H_3)_3$). Anal. calcd for $C_{28}H_{30}P_2N_2$: C 73.67, H 6.62, N 6.14. Found: C 73.42, H 6.51, N 5.98.

**Preparation of $Ph_2PN(2\text{-pyridine})PPh_2$ (9).** 2-Aminopyridine (0.25 g, 2.66 mmol) was dissolved into 30 mL of anhydrous dichloromethane, to which excess triethylamine (5 mL) was added. One equivalent of diphenylphosphine chloride (0.50 mL, 2.66 mmol) was added dropwise with stirring. The mixture was allowed to stir for 30 minutes and a second equivalent of diphenylphosphine chloride (0.50 mL, 2.66 mmol) was added, upon which the mixture was stirred for 3 days. The resulting precipitate was removed *via* cannula filtration and the filtrate passed through a 2 cm plug of neutral alumina. The volatiles were removed *in vacuo* to give a yellow residue which was washed with 3 × 5 mL portions of anhydrous ethanol to give the title compound as a white solid in 87% yield (1.11 g, 2.31 mmol). $^1$H NMR ($CDCl_3$, 400 MHz):

$\delta$ 8.18 (ddd, $J$ = 0.8, 2.1, 5.0 Hz, 1H, pyridine-*H*), 7.45–7.51 (m, 8H, aryl-*H*), 7.17–7.28 (m, 13H, aryl-*H*), 6.72–6.77 (m, 2H, pyridine-*H*). $^{31}$P NMR ($CDCl_3$, 161.8 MHz): $\delta$ 59.31 (s). $^{13}$C NMR ($CDCl_3$, 100.5 MHz): $\delta$ 159.5 (t, $J$ = 5.0 Hz, pyrindyl-$C_{ipso}$), 147.9 (s, pyrindyl-*C*), 138.1 (m, aryl-$C_{ipso}$), 136.2 (s, pyrindyl-*C*), 133.1 (d, $J$ = 22.6 Hz, aryl-*C*), 128.9 (s, aryl-*C*), 127.9 (t, $J$ = 2.4 Hz, aryl-*C*), 118.3 (s, pyrindyl-*C*), 117.9 (t, $J$ = 3.3 Hz, pyrindyl-*C*). Anal. calcd for $C_{29}H_{24}P_2N_2$: C 75.30, H 5.23, N 6.06. Found: C 75.02, H 5.07, N 6.09.

**Preparation of *O*-trimethylsilyl-2-aminophenol.** 2-Aminophenol (3.18 g, 29.1 mmol) was degassed with five vacuum/argon cycles and suspended in 60 mL of dichloromethane. Triethylamine (5 mL) was added and stirring was commenced. Trimethylsilyl chloride (4.85 mL, 38.4 mmol) was added as a stream and the resulting suspension was stirred for 1 hour. The resulting triethylamine hydrochloride was removed *via* cannula filtration and the yellow supernatant concentrated *in vacuo* to give a yellow liquid. The liquid was flash distilled at 95 °C under full pump vacuum to give the title compound as a pale yellow liquid in 43% yield (2.29 g, 12.6 mmol). $^1$H NMR ($CD_2Cl_2$, 299.89 MHz): $\delta$ 6.60–6.83 (m, 4H, aryl-*H*), 3.75 (bs, 2H, $NH_2$), 0.32 (s, 9H, $Si(CH_3)_3$). $^{13}$C NMR ($CD_2Cl_2$, 75.41 MHz): $\delta$ 142.9 (aryl-$C_{ipso}$), 138.9 (aryl-$C_{ipso}$), 115.7, 118.4, 119.0, 122.3 (aryl-*C*), 0.43 ($Si(CH_3)_3$). MS (electrospray): $m/z$ 182.0 $[M + H]^+$.

**Preparation of $(Ph_2P)_2N$(2-($Me_3SiO$)-phenyl) (10).** *O*-Trimethylsilyl-2-aminophenol (4.79 g, 32.9 mmol) was dissolved in 50 mL of anhydrous dichloromethane with stirring. To this was added diphenylphosphine chloride (4.64 mL, 25.2 mmol) dropwise. The resulting suspension was stirred overnight. The organic phase was then washed with 3 × 50 mL of degassed, deionised water, dried on magnesium sulphate and filtered before the volatiles were removed under reduced pressure. The resulting residue was washed with 2 × 10 mL portions of diethyl ether to give 7 as a white solid in 76% yield (5.29 g, 9.73 mmol). $^1$H NMR ($CD_2Cl_2$, 299.89 MHz): $\delta$ 7.20–7.40 (m, 20H, aryl-*H*), 7.00 (m, 1H, aryl-*H*), 6.78 (d, $J$ = 7.80 Hz, aryl-*H*), 6.54 (m, 2H, aryl-*H*), 0.09 (s, 9H, $Si(CH_3)_3$). $^{31}$P NMR ($CD_2Cl_2$, 161.8 MHz): $\delta$ 62.95 (s). $^{13}$C NMR ($CD_2Cl_2$, 75.41 MHz): $\delta$ 152.8 (s, aniline aryl-$C_{ipso}$), 140.6 (m, aryl-$C_{ipso}$), 139.1 (m, aniline aryl-$C_{ipso}$), 133.7 (broad m, aryl-*C*), 131.9 (m, aniline aryl-*C*), 127.8–129.8 (broad m, aryl-*C*), 126.8 (s, aniline aryl-*C*), 120.3 (s, aniline aryl-*C*), 118.4 (s, aniline aryl-*C*), 0.64 (s, $Si(CH_3)_3$). Anal. calcd for $C_{33}H_{33}P_2NSiO$: C 72.11, H 6.05, N 2.55. Found: C 72.02, H 5.98, N 2.37.

**Preparation of $(Ph_2P)_2NCH_2CH_2OSiMe_3$ (11).** Compound **11** was prepared according to the procedure outlined for compound **10**, employing *O*-trimethylsilyl-2-aminoethanol (1.68 g, 12.6 mmol). Compound **11** was isolated as a colourless liquid in 46% yield (2.92 g, 5.83 mmol) after washing with anhydrous methanol. $^1$H NMR ($CD_2Cl_2$, 299.89 MHz): $\delta$ 7.25–7.43 (m, 20H, aryl-*H*), 3.39 (m, 2H, $(Ph_2P)_2NCH_2$), 3.12 (t, $J$ = 2.81 Hz, 2H, $CH_2OSiMe_3$), 0.11 (s, 9H, $Si(CH_3)_3$). $^{31}$P NMR ($CD_2Cl_2$, 161.8 MHz): $\delta$ 62.83 (s). $^{13}$C NMR ($CD_2Cl_2$, 75.41 MHz): $\delta$ 139.9 (m, aryl-$C_{ipso}$), 133.1 (m, aryl-*C*), 128.2 (s, aryl-*C*), 128.5 (t, $J$ = 3.5 Hz, aryl-*C*), 61.9 (m, $(Ph_2P)_2NCH_2$), 46.6 (s, $CH_2OSiMe_3$), −0.66 (s, 9H, $Si(CH_3)_3$). MS (electrospray): $m/z$ 502 $[M + H]^+$.

**Preparation of $(Ph_2P)_2NCH_2CH_2OBz$ (12).** Compound **12** was prepared according to the procedure outlined for compound **10**, employing *O*-benzyl-2-aminoethanol (4.97 g, 32.9 mmol). Compound **12** was isolated as a colourless liquid in 20% yield (3.33 g, 6.42 mmol) after washing with anhydrous methanol. $^1$H NMR ($CD_2Cl_2$, 299.89 MHz): $\delta$ 7.11–7.43 (m, 25H, aryl-*H*), 4.14 (s, 2H, $OCH_2Ph$), 3.50 (m, 2H, $(Ph_2P)_2NCH_2$), 3.04 (t, $J$ = 6.90 Hz, 2H, $CH_2OBz$). $^{31}$P NMR ($CD_2Cl_2$, 161.8 MHz): $\delta$ 63.60 (s). $^{13}$C NMR ($CD_2Cl_2$, 75.41 MHz): $\delta$ 139.8 (m, aryl-$C_{ipso}$), 138.8 (m, aryl-$C_{ipso}$), 133.1 (m, aryl-*C*), 129.2 (s, aryl-*C*), 128.5 (m, aryl-*C*), 127.9 (s, aryl-*C*), 127.7 (s, aryl-*C*), 73.11 (s, $OCH_2Ph$), 70.1 (m, $(Ph_2P)_2NCH_2$), 51.84 (t, $J$ = 9.7 Hz, $CH_2OBz$). MS (electrospray): $m/z$ 520.1 $[M + H]^+$.

**Preparation of $(Ph_2P)_2NCH_2CH_2N$(i-Pr)$_2$ (13).** Compound **13** was prepared according to the procedure outlined for compound **4**, employing *N*,*N*-diisopropylethylenediamine (0.38 g, 2.64 mmol). Compound **13** was isolated as colourless plates in 24% yield (0.32 g, 0.63 mmol). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.35–7.44 (m, 8H, aryl-*H*), 7.26–7.31 (m, 12H, aryl-*H*), 3.26 (m, 2H, $(Ph_2P)_2NCH_2$), 2.67 (septet, $J$ = 6.6 Hz, 2H, $NCH(CH_3)_2$), 2.15 (m, 2H, $(i\text{-}Pr)_2NCH_2$), 0.73 (d, $J$ = 6.2 Hz, 12H, $NCH(CH_3)_2$). $^{31}$P NMR ($CDCl_3$, 161.8 MHz): $\delta$ 62.06 (s). $^{13}$C NMR ($CDCl_3$, 100.5 MHz): $\delta$ 139.7 (d, $J$ = 13.4 Hz, aryl-$C_{ipso}$), 132.8 (t, $J$ = 11.2 Hz, aryl-*C*), 128.7 (s, aryl-*C*), 128.1 (t, $J$ = 3.0 Hz, aryl-*C*), 54.3 (t, $J$ = 10.5 Hz, $(Ph_2P)_2NCH_2$), 48.9 (s, $NCH(CH_3)_2$), 46.4 (t, $J$ = 3.9 Hz, $(i\text{-}Pr)_2NCH_2$), 20.9 (s, $NCH(CH_3)_2$). Anal. calcd for $C_{32}H_{38}P_2N_2$: C 74.98, H 7.47, N 5.46. Found: C 74.78, H 7.77, N 5.55.

**Preparation of (*R*,*R*)-1,2-bis[(2-hydroxyphenyl)(phenylphosphino)]ethane (16).** *R*,*R*-DIPAMP (0.11 g, 0.24 mmol) was degassed with five vacuum/argon cycles before being dissolved in 5 mL of dichloromethane. The solution was cooled to −95 °C and boron tribromide (0.11 mL, 1.09 mmol) was added. The solution was allowed to return to room temperature and was stirred overnight. The volatiles were then removed under reduced pressure yielding a white solid which was suspended in 8 mL of degassed, deionised water and heated to 90 °C for four hours. Upon cooling, solid sodium hydrogen carbonate was added until a neutral pH was achieved. The aqueous solution was then extracted with 3 × 20 mL of diethyl ether and 1 × 20 mL of dichloromethane. The organic phases were combined, dried on magnesium sulphate, filtered and the solvent removed *in vacuo* to give the title product as a colourless solid in 54% yield (54.6 mg, 0.127 mmol). $^1$H NMR ($CD_2Cl_2$, 299.89 MHz): $\delta$ 7.25–7.32 (m, 12H, aryl-*H*), 7.07–7.11 (m, 2H, aryl-*H*), 6.86–6.91 (m, 4H, aryl-*H*), 6.60 (bs, 2H, O*H*), 2.17 (m, 4H, $CH_2$). $^{31}$P NMR ($CD_2Cl_2$, 161.8 MHz): $\delta$ −40.37 (s). $^{13}$C NMR ($CD_2Cl_2$, 75.41 MHz): $\delta$ 160.2 (t, $J$ = 9.7 Hz, aryl-$C_{ipso}$), 137.3 (m, aryl-$C_{ipso}$), 133.2, 131.8, 129.0, 121.4, 115.8 (s, aryl-*C*), 132.3 (t, $J$ = 9.1 Hz, aryl-*C*), 128.9 (t, $J$ = 3.4 Hz, aryl-*C*), 121.2 (m, aryl-$C_{ipso}$), 22.8 (m, $CH_2$). MS (electrospray): $m/z$ 431 $[M + H]^+$. Anal. calcd for $C_{26}H_{24}P_2O_2$: C 72.55, H 5.62. Found: C 71.64, H 5.39.

**Preparation of $Ph_2PN{=}P$(2-hydroxycyclohexyl)$Ph_2$ (17).** *N*,*N*-Bis(diphenylphosphino)amine (0.50 g, 1.30 mmol) was dissolved into 20 mL of tetrahydrofuran and cooled to −95 °C

with stirring. *n*-Butyllithium (0.66 mL, 1.05 mmol, 1.6 M in hexanes) was added dropwise to the solution. The resulting yellow solution was stirred for 30 minutes at −95 °C then allowed to return to room temperature where it was stirred for 5 hours. Cyclohexene oxide, freshly distilled from phosphorous pentoxide, was added and the mixture was heated to 67 °C for two days. The orange solution was then cooled to room temperature and quenched with 2 mL of degassed, deionised water. The volatiles were removed from the pale yellow solution to give a cream solid which was extracted with 2 × 10 mL of toluene. The organic extracts were combined, dried on sodium sulphate, filtered and then concentrated to give a colourless residue. The residue was washed with 3 × 5 mL portions of diethyl ether to give the title compound as a colourless powder in 44% yield (0.28 g, 0.58 mmol). Crystals suitable for X-ray diffraction were prepared by recrystallisation from hot methanol. $^1$H NMR ($CD_2Cl_2$, 299.89 MHz): $\delta$ 7.12–7.72 (m, 20H, aryl-*H*), 3.73 (m, 1H, C*H*-N), 2.72 (m, 1H, CH–OH), 2.03 (m, 1H, cyclohexyl-H), 1.16 (s, 1H, O*H*), 0.78–1.76 (m, 7H, cyclohexyl-H). $^{31}$P NMR ($CD_2Cl_2$, 161.8 MHz): $\delta$ 38.70 (d, $J$ = 94 Hz, *P*═N), 31.87 (d, $J$ = 94 Hz, *P*-N). $^{13}$C NMR ($CD_2Cl_2$, 75.41 MHz): $\delta$ 132.3 (dod, $J$ = 2.9, 9.1 Hz, aryl-*C*), 132.0 (dod, $J$ = 2.9, 9.1 Hz, aryl-*C*), 128.5 (d, $J$ = 4.0 Hz, aryl-*C*), 128.3 (d, $J$ = 4.0 Hz, aryl-*C*), 127.5, 128.0, 128.1, 128.7, 129.0, 129.1, 129.2, 129.8, 130.0, 130.9, 131.2, 134.0, 134.1 128.5 (aryl-*C*), 24.5, 25.9, 26.1, 26.3, 36.1, 36.3, 42.5, 43.6, 69.9, 70.0 (cyclohexyl-*C*). MS (electrospray): $m/z$ 484.1 $[M + H]^+$. Anal. calcd for $C_{30}H_{31}P_2NO$: C 74.51, H 6.47, N 2.90. Found: C 74.74, H 6.55, N 2.76.

**Preparation of $(Ph_2P)_2N$(2-($Me_3SiO$)-phenyl)titanium(IV)tetrachloride (18).** Compound **10** (0.25 g, 0.45 mmol) was taken up in 5 mL of dichloromethane and added slowly to $TiCl_4$ (0.06 mL, 0.50 mmol) in 10 mL of dichloromethane at −95 °C. The resulting red solution was allowed to return to room temperature and stirred overnight. The volatiles were removed *in vacuo* and the remaining red solid was washed with 10 mL of toluene to yield the title compound in 97% yield (0.33 g, 0.44 mmol). Crystals suitable for X-ray diffraction were grown from a hot solution of dichloromethane/petroleum spirits. $^1$H NMR ($CD_2Cl_2$, 299.89 MHz): $\delta$ 7.18–7.80 (m, 22H, aryl-*H*), 6.88 (dt, $J$ = 1.50, 8.55 Hz, 1H, aryl-*H*), 6.60 (dd, $J$ = 1.50, 8.10 Hz, 1H, aryl-*H*), −0.30 (s, 9H, Si($CH_3$)$_3$). $^{31}$P NMR (dichloromethane-$d_2$, 161.8 MHz): $\delta$ 61.38. $^{13}$C NMR (dichloromethane-$d_2$, 75.41 MHz): $\delta$ 119.4, 120.7, 128.4, 128.5, 128.6, 129.8, 130.6, 131.8, 131.9, 134.0, 154.2 (aryl-*C*), −0.00 (s, 9H, Si($CH_3$)$_3$). Anal. calcd for $C_{33}H_{33}P_2NSiOTiCl_4$(dichloromethane)$_{2/3}$: C 50.83, H 4.35, N 1.76. Found: C 50.95, H 4.42, N 1.75.

**Preparation of $(Ph_2P)$N(2-(O)-phenyl)$PHPh_2$ (19).** A portion of **10** (0.11 g, 0.20 mmol) was dissolved in hot methanol and stirred overnight. The volatiles were removed *in vacuo* and the resulting off-white solid was recrystallised from diethyl ether to give **19** in 50% yield (0.05 g, 0.10 mmol) as colourless needles suitable for X-ray diffraction. $^1$H NMR ($CD_2Cl_2$, 299.89 MHz): $\delta$ 6.31–8.14 (m, 24H, aryl-*H*), 3.65 (d, $J_{P,H}$ = 14.1 Hz, 1H, P-*H*). $^{31}$P NMR ($CD_2Cl_2$, 161.8 MHz): $\delta$ 37.52 (d, $J_{P,P}$ = 202 Hz, *P*(III)), −34.71 (d, $J_{P,P}$ = 202 Hz, *P*(V)). $^{13}$C NMR ($CD_2Cl_2$, 75.41 MHz): $\delta$ 110.1, 115.1, 118.0, 118.1, 119.2, 121.9, 123.8, 128.6, 128.8, 128.9, 129.0, 129.1, 129.4, 130.4, 130.7, 130.9, 131.2, 131.3, 131.4, 131.5, 131.6, 132.0, 134.6, 134.7 (aryl-*C*). MS (electrospray): $m/z$ 478 $[M + H]^+$. Anal. calcd for $C_{30}H_{25}P_2NO$: C 75.46, H 5.28, N 2.93. Found: C 75.25, H 5.23, N 2.80.

### Representative procedure for ethylene oligomerisation/polymerisation

A 0.45 L stainless steel Parr Reactor, fully temperature and pressure controlled and equipped with solvent/catalyst injection port and stirrer, was preheated to 120 °C and evacuated for a minimum of two hours before being purged with argon. The reactor was cooled to the appropriate temperature and charged with a total of 200 mL cyclohexane and the required amount of activator. Stirring was then commenced and the reactor charged with 4/5 the total required pressure of ethylene. The metal source and ligand solutions were then combined in the injection port and were injected into the reactor *via* a positive pressure gradient yielding the desired ethylene pressure. During the reaction, the pressure was kept constant with a replenishing flow of ethylene. Samples of the liquid phase were taken *via* an outlet every five minutes and immediately filtered and analysed by gas chromatography. After 30 minutes run time the replenishment of ethylene was ceased and the reactor cooled before purging of excess ethylene to atmospheric pressure. The solid and liquid phases were collected in a preweighed beaker and dried over night at 60 °C with reduced pressure (~50 mbar) to quantify non-volatile species.

### X-ray crystallography

Data for **4**, **13** and **17** were collected at −173 °C on crystals mounted on a Hampton Scientific cryoloop at the MX1 beamline of the Australian Synchrotron, while data for **18** and **19** were similarly collected on the MX2 beamline.[80] The structures were solved by direct methods with SHELXS-97, refined using full-matrix least-squares routines against $F^2$ with SHELXL-97,[81] and visualised using X-SEED.[82] All non-hydrogen atoms were refined anisotropically. Compound **17** featured disorder of a $PPh_2$ unit that was modelled as a two site complementary occupancy of the 5 remote carbon atoms of a phenyl ring and associated hydrogen atoms. Details of the disorder modelling are provided in the cif file. PH, NH and OH protons were located and positionally refined. Refinement for **18** is presented in $P2_1$, as $P2_1/m$ leads to disorder in the DCM lattice solvent across the mirror plane (not apparent in the $P2_1$ refinement) and significantly higher $R$ (>10%). All other hydrogen atoms were placed in calculated positions and refined using a riding model with fixed C–H distances of 0.95 Å ($sp^2$CH), 0.99 Å ($CH_2$), 0.98 Å ($CH_3$). The thermal parameters of all hydrogen atoms were estimated as $U_{iso}$(H) = 1.2$U_{eq}$(C) except for $CH_3$ where $U_{iso}$(H) = 1.5$U_{eq}$(C). A summary of crystallographic data is given below. CCDC 995241–995245.

Crystal data for **4**: $C_{25}H_{24}N_2P_2$, $M$ = 414.40, monoclinic, $a$ = 14.4930(3), $b$ = 10.3290(8), $c$ = 15.3920(3) Å, $\beta$ = 109.523(2)°, $U$ = 2171.68(18) Å$^3$, $T$ = 100 K, space group $P2_1/n$ (no. 14), $Z$ = 4, 35 591 reflections measured, 5447 unique ($R_{int}$ = 0.0421), 5163 > 4$\sigma(F)$, $R$ = 0.0366 (observed), $R_w$ = 0.0960 (all data). Crystal data for **13**: $C_{32}H_{38}N_2P_2$, $M$ = 512.58, triclinic, $a$ = 10.2160(7), $b$ = 10.3180(3), $c$ = 14.3790(6) Å, $\alpha$ = 79.664(2), $\beta$ = 76.635(2), $\gamma$ = 71.842(5)°, $U$ = 1391.70(12) Å$^3$, $T$ = 100 K, space group $P\bar{1}$ (no. 2), $Z$ = 2, 23 874 reflections measured, 6344 unique ($R_{int}$ = 0.0407), 5917 > 4$\sigma(F)$, $R$ = 0.0390 (observed), $R_w$ = 0.1072 (all data). Crystal data for **17**: $C_{30}H_{31}NOP_2$, $M$ = 483.50, monoclinic, $a$ = 8.6080(7), $b$ = 22.5050(8), $c$ = 13.7650(8) Å, $\beta$ = 106.913(2)°, $U$ = 2551.3(3) Å$^3$, $T$ = 100 K, space group $P\bar{2}_1/n$ (no. 14), $Z$ = 4, 41 516 reflections measured, 6283 unique ($R_{int}$ = 0.0328), 6184 > 4$\sigma(F)$, $R$ = 0.0475 (observed), $R_w$ = 0.1066 (all data). Crystal data for **18**: $C_{33}H_{33}Cl_4NOP_2SiTi{\cdot}0.5(CH_2Cl_2)$ $M$ = 781.80, monoclinic, $a$ = 11.5300(8), $b$ = 15.3370(7), $c$ = 20.8500(17) Å, $\beta$ = 103.737(3)°, $U$ = 3581.6(4) Å$^3$, $T$ = 100 K, space group $P\bar{2}_1$ (no. 4), $Z$ = 4, 77 400 reflections measured, 20 509 unique ($R_{int}$ = 0.0647), 18 238 > 4$\sigma(F)$, $R$ = 0.0450 (observed), $R_w$ = 0.1448 (all data). Crystal data for **19**: $C_{30}H_{25}NOP_2$, $M$ = 477.45, triclinic, $a$ = 8.701(2), $b$ = 10.6660(10), $c$ = 13.9380(13) Å, $\alpha$ = 70.2480(10), $\beta$ = 84.203(3), $\gamma$ = 81.578(3)°, $U$ = 1202.4(3) Å$^3$, $T$ = 100 K, space group $P\bar{1}$ (no. 2), $Z$ = 2, 25 361 reflections measured, 6695 unique ($R_{int}$ = 0.0370), 6170 > 4$\sigma(F)$, $R$ = 0.0435 (observed), $R_w$ = 0.1145 (all data).

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