Synthesis and characterization of amine-functionalized supported phosphine catalysts and their application in ethylene oligomerization

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ABSTRACT

A series of phosphorus and nitrogen-based ethylene oligomerization ligands of the type $Ph_2PN(X)PPh_2$ where X = i-propyl, n-butyl, ethylbenzene and cyclohexyl substituents are reported. These ligands were functionalized to enable tethering on amino-silica. The free ligands, amino-silica and the tethered ligands were characterized by BET, XRD, IR, TGA and NMR. The catalysts were tested for ethylene oligomerization using $Cr(acac)_3$ (acac = acetylacetonate) as the precursor and MMAO (modified methylaluminoxane) as the activator. The activity and selectivity of these catalysts to 1-octene was monitored at 45 bar ethylene in the temperature range of 45–100 °C. The activity of the supported catalysts was comparable to their homogeneous counterparts, surpassing them in some cases and selectivities to 1-octene in the C8 products were as high as 99 wt%. The steric effect of the substituent on the ligand as well as that of the support was found to influence the activity and product distribution.

INTRODUCTION

The drive in the oligomerization of ethylene to linear alpha olefins has been towards 1-hexene ($1-C_6$) and 1-octene ($1-C_8$). This is due to the increased demand and importance of these chemicals in the production of linear lower density polyethylene (LLDPE).[1-4] There has been a growing interest in a class of catalysts, namely single-site catalysts (SSC) in olefin transformations. A sub-class of these compounds, constrained-geometry catalysts (CGCs), have emerged as important catalysts in olefin polymerization in that they offer interesting combinations of environments around the metal centre, which result in polymers with desired qualities such as high molecular weight, tacticity and degree of branching. This is because of the open nature of their reactive centre. The supported analogues of these CGCs are known and the latter have been investigated for ethylene polymerization and titanium and zirconium CGCs (Figure 1) find the most application for this purpose.[5-7]

Surface organometallic chemistry employed by Basset et al.[8] produced a number of single-site catalysts on non-porous functionalized silica surfaces through residual silica pendant groups. The supported CGCs of this nature have been shown to exhibit good activity for ethylene polymerization which is mainly dependent on the nature of the support surface.[9] McKittrick and Jones reported a method for preparing an isolated titanium-centred polymerization catalyst on porous silica.[6, 10, 11] There are mainly three ways which have gained popular use for supporting organometallic compounds on silica in oligomerization catalysis viz. i) contacting the support with the co-catalyst, which in most cases has been methylaluminoxane (MAO); ii) the physisorption of the metal complex onto the support surface or a preformed complex that is designed to form covalent bonds between the ligand and the support surface and iii) immobilization of the complex via a covalent linkage between the ligand and the support using a multi-step grafting approach. The benefit of using this type of support has been reported to be that this method of supporting gives material that is less susceptible to the supported complex leaching due to MAO in the catalytic reaction.[6]

Amine-functionalized silica surfaces have been synthesized for a number of years for application in the fields of catalysis[12, 13] and adsorption chemistry[14–16]. These surfaces are of particular importance in catalysis because they create spatially isolated sites. This means that the amines on the surface can be strategically placed at minimum distances from each other, to avoid possible interactions that can occur between adjacent and neighbouring amines. The advantage of having these spatially isolated materials is that the amine sites, at relatively low loadings, behave as though they are isolated and uniform.[15] In this work, the synthesis, characterization and the novel application of the grafting approach to tether functionalized PNP ligands is reported. These supported ligands were used for ethylene oligomerization. The effect of the amine density on the silica material and its interaction with the catalyst and how it affects the overall selectivity and activity of the PNP catalysts, compared to their homogeneous counterparts, is also reported.

EXPERIMENTAL

Materials and instrumentation

Unless otherwise stated, all reactions were carried out using conventional Schlenk techniques under an inert atmosphere of pre-dried nitrogen. THF was dried using sodium and benzophenone and distilled under inert atmosphere. These chemicals were commercially available and they were used as received: 3,3,3-triphenylpropionic acid (Aldrich), 3-aminopropyltriethoxysilane (Aldrich), 1,1,1,3,3,3-hexamethyldisilizane (Aldrich), pyridinium dichromate (Fluka), Pluronic F-68 (Aldrich), sodium metasilicate (Aldrich), 3-iodobenzoic acid (Fluka), di-tertbutyl carbonate (Aldrich), 4-methylamino pyridine, chloro diphenylphosphine, 97% (Aldrich), lithium aluminium hydride, 1.0 M in THF (Aldrich), N- chloro succinamide, 97% (Aldrich), methylmagnesium chloride (Aldrich).

X-ray diffraction patterns were collected using a Phillips PW 1730/10 diffractometer, using Co Kα radiation on a long line focus operating with an amperage of 25 mA and a voltage of 40 kV. TEM images were obtained using a JEOL JEM 1010 and samples were placed on a copper micro grid. The samples were analyzed for porosity measurements on an Accelerated Surface Area and Porosity (ASAP 2020) instrument at 77 K. The samples were pre-treated by heating under N_2 at 90 °C

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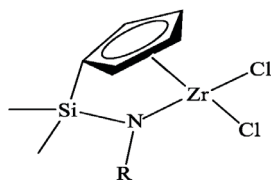Email: shozim2@ukzn.ac.za

Figure 1: An example of a constrained geometry zirconium complex[5]

for 1 h then at 350 °C for 4 h. Surface area measurements were done using a Micromeretics Gemini instrument. Prior to analysis, approximately 0.20 g of sample was degassed overnight under N_2 at 200 °C. Thermogravimetric analysis was performed on a Universal V4.5A TA SDT Q600 instrument. Samples were heated under air from 30 to 1000 °C at a rate of 10 °C min⁻¹. The organic loading was measured by determining the weight loss from 200 to 650 °C. Solution NMR spectra were recorded on a Bruker 400 MHz Ultrashield spectrometer. Solid-state NMR (CP-MAS) spectra were recorded on a Bruker DSX 600 MHz spectrometer. Samples were spun in 7-mm zirconia rotors at 5 kHz. Typical ^{13}C CP-MAS parameters were 10 000 scans, a 90° pulse length of 4 μs, and a delay of 4 s between scans. The ^{29}Si CP-MAS parameters were 2000 scans, a 90° pulse length of 5 μs, and a delay of 10 s between scans.

Ligand synthesis

Homogeneous ligands

The bis(diphenylphosphino)amine (PNP) ligands **1–4** were synthesized according to literature procedures or modification thereof.[17, 25] Full details are given in the supplementary information.

Heterogeneous ligands

Amino-functionalized SBA-15 was synthesized according to literature procedures.[10, 18] Prior to tethering the ligands onto the SBA-15, they were functionalized according to modification of literature procedures.[19] Full details are given in the supplementary information. The supported ligands are denoted as **S1–S4**.
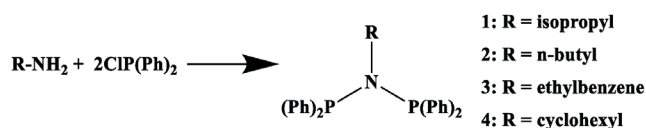
Catalyst testing

Prior to each run, a Parr® reactor was heated to the desired temperature. To eliminate water, oxygen and oxygenated impurities the reactor was evacuated using a high vacuum pump. The reactor was then filled with nitrogen. The reactor was then charged with solvent. The catalytic mixture (combination of Cr(acac)₃, MMAO-3A and ligand solutions) was then charged to the reactor. A constant flow of ethylene i.e. 45 bar was discharged and maintained through a pressure control flowmeter. After 30 minutes the ethylene flow was stopped and the reactor cooled to room temperature, followed by venting. The reaction was quenched using ethanol. Nonane was used as an internal standard in the liquid fraction. The liquid samples were analyzed using GC-FID equipped with a PONA column. The solid polyethylene obtained was dried in an oven at 110 °C overnight and then weighed.

RESULTS AND DISCUSSION

Synthesis and characterization of the ligands

Homogeneous ligands

The mixed heteroatomic PNP ligands were synthesized by reacting the amine and phosphine chlorides of the type Ph₂PCl (Scheme 1). This reaction takes place in basic medium in which triethylamine is used as a base. The resulting chloride salt is removed from the solution and the resulting ligands are purified. Table 1 shows the ^{13}C and ^{31}P NMR shifts of the prepared ligands.

Scheme 1: Synthesis of the PNP ligands

Table 1: The ^{13}C and ^{31}P NMR shifts for the synthesised PNP ligands

N substituent	^{13}C shift* (ppm)	^{31}P shift (ppm)
isopropyl (1)	24.3, 41.3	50.3
n-butyl (2)	13.8, 20.4, 33.3, 45.1	50.7
ethylbenzene (3)	53.3	73.0
cyclohexyl (4)	25.5, 25.8, 37.1, 56.0	50.8

*The ^{13}C shifts are for the alkyl/aryl substituents on the central nitrogen donor. All ligands showed the following ^{13}C shifts for the phenyl rings bonded to P: ~128, ~131 and ~140 ppm.

Heterogeneous ligands

Synthesis of SBA-15

Figure 2 shows the X-ray powder diffractogram of the synthesized SBA-15. The diffraction pattern shows three intense peaks 2θ values of 37, 53 and 78°. The XRD pattern obtained is characteristic of the 2D hexagonal structure as is reported in literature.[20] The physisorption measurements revealed that the SBA-15 had a surface area of 602 g m⁻², pore volume of 0.04 cm3 g⁻¹ and pore diameter of 153 nm, showing the material to be microporous.

Synthesis and characterization of site-isolated amine-functionalized silica surfaces

The patterning agent that was used in this work for tethering on the silica surface was ([3-(triethoxysilanyl) propyl]-(3,3,3-triphenylpropylidene) amine) and was synthesized as shown in Scheme 2. This patterning agent was chosen because of its bulkiness. The bulkiness aids in the synthesis of isolated amine-functionalization, in that the size of the agent strategically blocks the attachment of other groups in close proximity and thereby avoids the possible interactions between the surface and the amine groups.

The patterning agent was grafted onto the SBA-15 as shown in Scheme 3 (i). After contact, the silica surface is left with silanol groups that were determined by IR to have not reacted with the patterning agent. To prevent further reactions of these unreacted silanol groups, the surface was capped using hexamethyldisilizane (HDMS) (Scheme 3 (ii)). The bulky trityl groups on the capped surface were then hydrolyzed, under acidic conditions. The hydrolysis removes the bulky groups (Scheme 3 (iii)). As a result of this treatment, the silica surface forms surface silanols, which were capped by a second aliquot of HDMS (Scheme 3 (iv)).
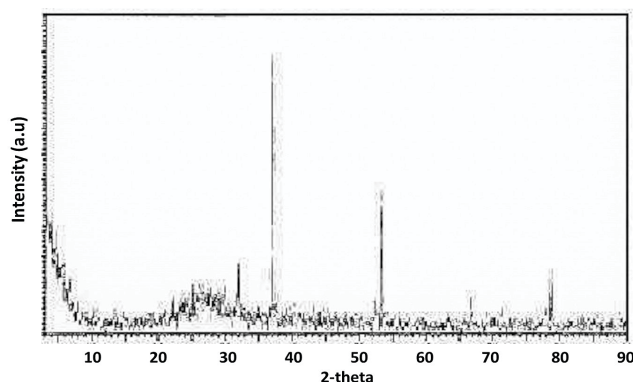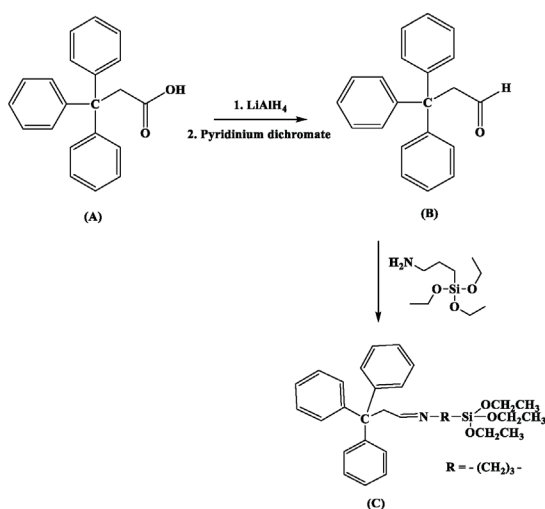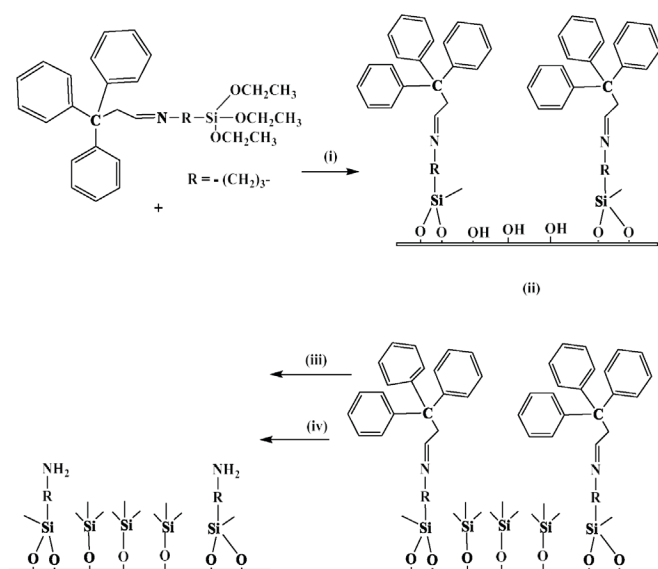

Figure 2: X-ray powder diffractogram of the synthesized SBA-15

Scheme 2: Synthetic route to the patterning agent ([3-(triethoxysilanyl) propyl]-(3, 3, 3- triphenylpropylidene amine)

Scheme 3: The grafting approach to aminopropyl silica for the support of ethylene tetramerization catalysts. (i) patterning, (ii) silanol capping, (iii) hydrolysis and (iv) second silanol capping

After incorporation of the patterning agent onto the SBA-15, the surface decreased to 590 g m^{-2}. The grafting approach was also followed by FT-IR. Upon hydrolysis there were major changes observed in the surface of the material. The characteristic FT-IR band of the imine at 1546 cm^{-1}, which was previously observed, disappeared. The peaks assigned to the aromatic C-H were still present, though greatly reduced. The diagnostic N-H peak at 3500-3200 cm^{-1} was observed as a very weak band. This is probably due to the relatively low amine loading on the material. The only peaks that can be considered strong are the ones that are due to the aliphatic C-H bands of the propyl linker in the material.

Solid-state ^{29}Si CP-MAS NMR was also used to analyse amine-functionalized silica surfaces (Figure 3). After hydrolysis, the resonances for the singly bonded SiOH groups are not observed. Instead, a well-resolved resonance for the geminal and hydrogen bonded SiOH are observed. It can be concluded that the bonding in the material is through both the double and single surface to silane linkages, with very few single linkages.[21, 22]
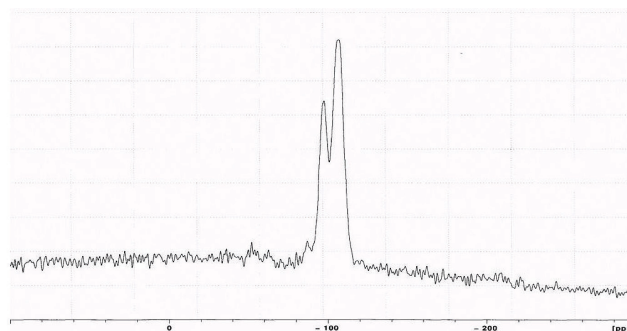

Figure 3: ^{29}Si CP-MAS spectrum of amino-silica after hydrolysis

Coupling of functionalized PNP ligands to aminosilica

The functionalized PNP ligands were reacted with amine functionalized silica in appropriate ratios to give the desired ligand:metal ratios for application in ethylene tetramerization. The successful linkage of these ligands on the amine functionalized silicas was confirmed by FT- IR. The C-N stretching band was observed at 1156 cm^{-1} and simultaneously the disappearance of NH$_2$ (1551 and 3301 cm^{-1}) stretching bands in amino-silica was observed, which confirmed the substitution reaction between the surface linkers and the functionalized ligands.

Catalyst testing

Bollmann et al.[23] reported that oligomerization catalysts performed much better in aliphatic solvents due to higher ethylene solubility, hence the choice of methylcyclohexane as a solvent in this work. The catalyst's activity in this solvent is, however, enhanced at the expense of a slightly lower selectivity to 1-C$_8$ in the C8 fraction. Table 2 shows the activity of the homogeneous isopropyl system **1** together with its supported equivalent **S1** at various temperatures. The change in temperature did not have a pronounced effect on the catalyst activity. The highest activity of **1** was at 60 °C, while that of **S1** was at 80 °C. The selectivities to 1-C$_6$ and 1-C$_8$ were notably different for both **1** and **S1**. The increase in temperature was accompanied by an increase in the selectivity to C6 cyclics at the expense of C8 fraction. The selectivity to 1-C$_8$ in the C8 fraction for S1 was, however, comparable to that obtained for its homogeneous counterpart..

To compare the effect of a branched alkyl substituent (isopropyl) to one that is unbranched, the n-butyl PNP ligand **2** and its heterogeneous counterpart **S2** were tested (Table 3). The catalyst activities with increasing temperature were comparable to those obtained for the

Table 2: Ethylene oligomerization by isopropyl PNP catalysts at various temperatures

Ligand	Temp. (°C)	Activity (g/g Cr.h^{-1})	C6	C6 cyclics	1-C$_6$ in C6	C8	1-C$_8$ in C8	PE
1	45	223 362	27.6	16.9	31.1	66.1	98.4	7.4
1	60	224 193	42.6	15.7	59.2	52.2	97.3	8.0
1	80	221 338	35.9	5.7	39.4	60.6	96.9	4.3
1	90	220 957	38.4	38.2	40.2	62.3	96.5	3.6
1	100	222 489	39.0	49.2	41.9	58.8	97.4	1.1
S1	45	230 500	15.4	28.6	64.6	68.3	94.0	0.9
S1	60	228 406	29.8	13.5	47.1	61.7	95.9	1.0
S1	80	231 398	16.0	34.7	65.4	64.0	96.4	1.3
S1	90	230 909	19.5	29.2	42.5	60.9	94.9	2.9
S1	100	229 498	22.1	33.9	66.7	57.4	95.2	4.2

100 mL methylcyclohexane solvent, 45 bar ethylene, 33 µmol Cr(acac)$_3$, 2 equiv of ligand, 526 equiv of MMAO-3A. Other products: C10, C12, C14 and C16 compounds. Activity = mass of ethylene converted per gram of Cr per hour.

isopropyl catalysts (Table 2). Catalyst **2** achieved its highest activity at 80 °C, which decreased with further increase in temperature to 100 °C. On the other hand, **S2** showed increasing activity up to the maximum temperature. These results suggest catalyst deactivation at elevated temperatures, which seems to be remedied by the presence of the support.

Catalysts which contain ligands that have a single carbon spacer between the N-atom and a phenyl group were shown by Killian et al.[24] to lead to an increase in overall alpha olefin selectivity. The combination of a N-alkyl group and alpha branching on this moiety results in these improved results. Catalysts **3** and **S3** allowed for the investigation of this class of ligands that have both the α-branching as well as an aryl group within the substituent and the results are shown in Table 4. The authors cited above found that releasing the steric strain as a result of the presence of the methylene spacer between the N-atom and the phenyl group had little effect on the product composition, although the catalyst productivity did improve by approximately 30%. In the system reported in this work, the most active catalyst of this set was **3** at 45 °C. This activity decreased with an increase in temperature.

The results shown by these catalysts were particularly interesting because there was an observed interchange between these two catalysts in terms of activity and selectivity to C8 (1- C_8). For example, from 45 to 80 °C the catalytic activity of **3**, although it decreases with the increase in temperature, was superior to that of **S3**. However, from 80 °C, the activity of **3** is surpassed by that of **S3**. In terms of selectivity to C8 (1-C_8), from 45 to 80 °C, an increase is seen over **3** while a decrease in selectivity over **S3** is observed. From 80 to 100 °C both these catalysts show a similar selectivity trend and an increase in C8 (1-C_8) selectivity is observed.

In terms of C6 products, it can be seen that at the lower temperatures, **3** is more active and its selectivity to 1-C_6 is higher than that for **S3**. The support influence in **S3** is noticeable for the C6 products, where the selectivity to C6 cyclics is higher than those of **3**. Similar observations were made previously, where an increase in C6 cyclics was seen when a supported PNP ligand with a phenyl functional group was used.[1]

Kuhlmann et al.[25] had highlighted that exchanging of the relatively small methyl group on the N-atom of the PNP ligand to a cycloalkyl group led to a significant increase in the 1-C6 selectivity within the C6 fraction. This was achieved through the suppression of the formation of C6 cyclic products. The basicity and the size of the cyclohexyl group on the N-atom has been shown by Blann et al.[26] to enhance and increase catalytic activity. The increased bulk around the nitrogen led to an increase in total alpha olefin selectivity. In an attempt to achieve a similar result, the cyclohexyl PNP ligand **4** and its heterogeneous counterpart **S4** were tested in ethylene oligomerization and the results are shown in Table 5. The highest activity by **4** was achieved at 80 °C, which, as with **1**, **2** and **3** decreases with further increase in temperature. Contrary to this, the activity of **S4** increased with increasing temperature up to 100 °C. With increasing temperature, there was also an increase in 1-C_6 in the C6 fraction, while the selectivity to the C6 cyclics decreased over both catalysts.

CONCLUSION

The supported phosphine catalysts that were synthesized were tested for ethylene tetramerization and showed good activity and selectivity to 1-C_8. The role of the support has been found to be mainly in enhancing the catalyst stability at higher temperatures. There is evidence that the steric influence of the support competes with the electronic influence of the substituent on the central donor N-atom. The supported catalysts showed improved selectivity to 1-C_8 at increased temperatures when the selectivity to 1-octene of the homogeneous counterparts was shown to be affected negatively. In most cases in the set of catalysts that were studied, it was observed that the heterogenized catalysts are comparable in activity and selectivity to their homogeneous counterparts, and in a few cases, they surpass the homogeneous catalyst. Another advantage of the supported catalysts is that they

Table 3: Ethylene oligomerization by n-butyl PNP catalysts at various temperatures

Ligand	Temp. (°C)	Activity (g/g Cr.h^{-1})	C6	C6 cyclics	1-C_6 in C6	C8	1-C_8 in C8	PE
2	45	225 071	12.0	1.4	12.2	74.1	90.0	6.8
2	60	228 990	17.9	2.0	25.9	81.2	92.4	4.2
2	80	229 000	20.1	1.7	39.0	88.0	89.0	1.8
2	90	224 745	14.0	0.1	29.1	97.2	62.1	3.1
2	100	221 091	8.0	1.0	12.2	82.8	57.6	9.7
S2	45	227 499	34.9	1.2	96.0	57.9	90.0	2.5
S2	60	232 485	38.8	-	99.9	61.2	99.6	0.2
S2	80	231 521	35.4	3-	88.0	38.9	99.8	4.9
S2	90	231 722	37.3	0.6	81.7	49.2	79.5	3.7
S2	100	234 510	35.4	0.8	84.0	36.9	81.9	3.5

100 mL methylcyclohexane solvent, 45 bar ethylene, 33 µmol Cr(acac)$_3$, 2 equiv of ligand, 526 equiv of MMAO-3A. Other products: C10, C12, C14 and C16 compounds. Activity = mass of ethylene converted per gram of Cr per hour.

Table 4: Ethylene oligomerization by ethylbenzene PNP catalysts at various temperatures

Ligand	Temp. (°C)	Activity (g/g Cr.h^{-1})	C6	C6 cyclics	1-C_6 in C6	C8	1-C_8 in C8	PE
3	45	504 471	27.9	1.1	74.2	34.4	93.3	0.8
3	60	376 700	33.2	8.2	22.3	38.0	94.0	0.2
3	80	200 442	28.9	13.2	44.3	37.5	96.6	1.6
3	90	248 794	24.9	14.4	47.8	36.0	96.4	0.7
3	100	252 749	26.6	15.0	48.5	39.9	97.1	1.8
S3	45	420 601	25.1	11.5	42.4	42.0	98.5	1.3
S3	60	314 824	27.3	39.8	34.1	57.9	97.2	0.9
S3	80	282 632	14.3	9.4	38.6	32.4	96.7	1.1
S3	90	204 430	44.3	22.7	35.4	34.2	98.0	1.1
S3	100	270 260	38.6	22.9	40.9	45.1	99.0	0.6

100 mL methylcyclohexane solvent, 45 bar ethylene, 33 µmol Cr(acac)$_3$, 2 equiv of ligand, 526 equiv of MMAO-3A. Other products: C10, C12, C14 and C16 compounds. Activity = mass of ethylene converted per gram of Cr per hour.

Table 5: Ethylene oligomerization by n-butyl PNP catalysts at various temperature

Ligand	Temp. (°C)	Activity (g/g Cr.h^{-1})	C6	C6 cyclics	1-C_6 in C6	C8	1-C_8 in C8	PE
4	45	231 258	34.5	-	57.9	48.5	96.8	0.4
4	60	232 592	6.9	3.3	50.6	89.8	99.7	8.2
4	80	234 741	44.5	8.4	47.2	50.1	96.1	1.7
4	90	228 184	27.4	13.2	50.8	59.4	94.0	6.3
4	100	229 696	40.2	2.8	60.9	42.4	95.7	9.9
S4	45	229 025	25.4	20.1	40.5	41.7	94.4	0.3
S4	60	229 093	43.3	7.1	33.2	48.4	99.2	0.1
S4	80	233 104	42.1	9.4	47.9	50.6	96.0	1.4
S4	90	231 826	45.8	11.2	61.9	41.2	94.0	2.4
S4	100	234 791	10.0	0.6	61.7	48.6	93.7	1.6

100 mL methylcyclohexane solvent, 45 bar ethylene, 33 µmol Cr(acac)$_3$, 2 equiv of ligand, 526 equiv of MMAO-3A. Other products: C10, C12, C14 and C16 compounds. Activity = mass of ethylene converted per gram of Cr per hour.

suppress the formation of cyclic products, which leads to a desirable increase in the C8 fraction and ultimately 1-C_8. The steric effect of the support has been shown to override the electronic and steric effect of the substituents on the central donor atom and thus enhance catalyst integrity at higher temperatures. From the results, the interactions of the supports, which are steric in nature, can be represented in terms of the strength of influence on catalyst productivity as **S3 > S4 > S2 > S1**. In terms of catalyst stability at elevated temperatures, the influence of the support can be represented as **S4 > S2 > S3 > S1**. Thus, a possible trend, less electron donating substituents give a more stable catalyst.

SUPPLEMENTARY MATERIAL

Supplementary information for this article is provided in the online supplement.

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SUPPLEMENTARY MATERIAL TO:

Synthesis and characterisation of amine-functionalised supported phosphine catalysts and their application in ethylene oligomerisation
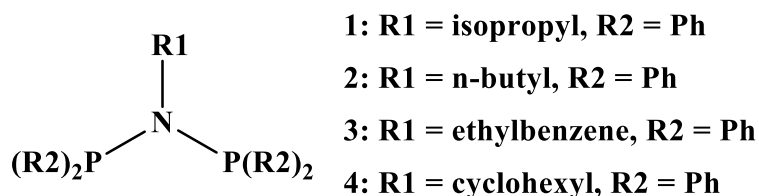
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Synthesis of homogeneous PNP ligands (1 – 4)

To a solution of the corresponding amine (11.2 mmol) in CH_2Cl_2 and Et_3N at room temperature, was added diphenylphosphorus chloride (2.00 mL, 11.2 mmol). The reaction mixture was stirred for 30 min at the same temperature. Another aliquot of diphenyl phosphorus chloride (2.00 mL, 11.2 mmol) was added to the reaction mixture. The reaction mixture was left stirring overnight. The reaction mixture was then cannula filtered to remove the triethylammonium chloride salt formed. The crude product was filtered through neutral alumina. The solvent was subsequently removed in vacuo.

$$R1$$
$$|$$
$$N$$
$$(R2)_2P \diagup \quad \diagdown P(R2)_2$$

1: R1 = isopropyl, R2 = Ph

2: R1 = n-butyl, R2 = Ph

3: R1 = ethylbenzene, R2 = Ph

4: R1 = cyclohexyl, R2 = Ph

Synthesis of functionalised PNP ligands and subsequent supporting on the silica (S1 – S4)

1. Synthesis of the silica support (SBA-15)

Pluronic F-68, diblock co-polymer (1.0 g) was dissolved in de-ionised water (20 mL) and sodium metasilicate (3.0 g) was added at room temperature, which gave a clear solution. To this reaction mixture, 5 mL concentrated HCl (37% v/v) was added quickly with vigorous stirring using a magnetic follower. The resulting foamy, light yellow solution was stirred for 1 day at RT. To swell the pores and increase the degree of silanol group condensation, stirring was stopped and the gel mixture was oven dried at 110 °C. The resulting solid was slurried in a HCl-ethanol mixture. This was filtered off, washed with ethanol, and dried in an oven at 110 °C. Yield = 90% (based on silica recovery). The silica material was calcined in air at 550 °C for 6 hours.

2. Synthesis of the protected amino-functionalised silica surfaces

2.1. Synthesis of tritylimine patterning agent

Firstly, 3,3,3-triphenylpropanal was synthesised by the reduction of 3,3,3-triphenylpropionic acid under argon using standard Schlenk techniques. Triphenylpropionic acid (0.5 g, 1.65 mmol) was added to a flask containing THF. The flask was then cooled in an ice-water bath

and ~2.5 mL pre-cooled 1.0 M LiAlH$_4$ in THF was added dropwise. The mixture was then stirred at RT for 30 - 45 minutes after the apparent evolution of a gas. The solution was then added to a suspension of pyridinium dichromate (0.70 g, 1.86 mmol) in CH$_2$Cl$_2$ and the resulting solution was allowed to stir for 6 hrs. The reaction mixture was diluted with diethyl ether and filtered through a silica column, and subsequently washed with several portions of diethyl ether. The filtrate was collected, concentrated through rotary evaporation and the aldehyde was isolated as a yellow paste-like material. Yield = 0.41g, 87%. ^{1}H NMR (CD$_3$OD): δ 3.59 (d, 2H), 7.10 -7.39 (m, 15H), 9.50 (t, 1H, J$_{(HH)}$ 7.5Hz). ^{13}C NMR (CD$_3$OD): δ 41.2 (C-Ph$_3$), 56.6 (CH$_2$C=O), 126.2-143.7 (Aromatic C's), 200.3 (C=O).

The synthesized 3,3,3-triphenylpropanal (0.30 g, 1.05 mmol) was heated under reflux with 3-aminopropyltriethoxysilane (0.25 mL, 1.07 mmol) in dry methanol equipped with a Dean Stark trap for 24 hrs. The methanol was removed under vacuum. The excess 3-aminopropyltriethoxysilane was removed by heating under vacuum. The imine product was then recrystallised from methanol. Yield = 0.28 g, 53.4%. ^{1}H NMR (CD$_3$OD): δ 0.50 SiCH$_2$ (t, 2H), 1.10 OCH$_2$CH$_3$ (t, 12H), 1.50 SiCH$_2$CH$_2$CH$_2$ (m, 2H), 1.52 NCH$_2$ (t, 2H), 3.80 OCH$_2$CH$_3$ (q, 6H), 7.25 -7.34 (Aromatic protons, 7.25-7.34 (m, 15H), 7.50 CH=N (s, 1H). ^{13}C NMR (CD$_3$OD): δ 8.5 (SiCH$_2$), 18.1 SiCH$_2$CH$_2$ CH$_2$), 19.1 OCH$_2$CH$_3$, 41.5 C-Ph$_3$, 58.5 OCH$_2$CH$_3$, 126.1-139.5(Aromatic C's), 150.0 C=N.

2.2. Synthesis of SBA-15 functionalised with trityl-protected aminoalkoxysilanes

The synthesis of the amino functionalised SBA-15 was achieved in four distinct steps:

(i) Patterning - The tritylimine spacer (0.25 g, 0.56 mmol) was added to 1.0 g SBA-15 with anhydrous toluene and stirred at RT under a N$_2$ atmosphere. The resulting solid was filtered off and washed with toluene and dried under vacuum at 50 °C overnight.

(ii) Silanol Capping- To cap excess silanols on the surface, the material in (i), the protected aminosilica, was contacted with an excess of 1,1,1,3,3,3-hexamethyldisilizane (HMDS) in anhydrous hexane at RT under a N$_2$ atmosphere. The solid was washed with toluene, then hexane and filtered. It was then stored under vacuum at 50 °C overnight.

(iii) Hydrolysis- The capped material in (ii) (0.25 g) was hydrolysed with 25 g of a 2:2:1 solution (by mass) of H$_2$O/MeOH/HCl (aq) and this mixture was stirred in air for 6 hrs. The resulting deprotected solid was collected via filtration, washed with de-ionised water, anhydrous methanol and anhydrous THF. It was then dried under vacuum at 50 °C overnight.

(iv) Second Silanol Capping- The deprotected material in (iii) was reacted with excess HMDS in anhydrous hexane by stirring at RT under N_2 for 24 hrs. The resulting solid was filtered and washed with toluene and then with hexane. It was then dried under vacuum at 50 °C.

2.3. Synthesis of functionalised PNP ligands for supporting on amine-functionalised silica

2.3.1. Synthesis of *tert*-butyl 3-iodobenzoate

To a suspension of 3-iodobenzoic acid (1.24 g, 5 mmol) in dry deoxygenated CH_2Cl_2 (10 mL) at room temperature under N_2 and stirring was added a solution of 4-methylamino pyridine (0.153 g, 1.42 mmol) in CH_2Cl_2. To this mixture a solution of di-tert-butyldicarbonate (*t-Boc*) (1.11 g, 6.25 mmol) was added. The reaction mixture was stirred at room temperature overnight. The mixture was then diluted with CH_2Cl_2 and extracted with water (8 mL) and 1 M HCl (2 mL). The organic layer was separated and dried over anhydrous $MgSO_4$. The resulting solution was filtered and concentrated under reduced pressure. The residue was further purified by chromatography on silica gel, petroleum ether:ethyl acetate (90:10). Yield = 1.22 g, 66%. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.51 (9H, s, (CH_3)$_3$); 7.18 (1H, t, J=7.9 Hz, CH-5); 7.86 (1H, d ,J = 7.9 Hz, CH-4); 7.96 (1H, d, J=7.9 Hz, CH-6); 8.37 (1H, s, CH-2). ^{13}C-NMR: δ = 28.1 (C(CH$_3$)$_3$); 81.7 (C(CH$_3$)$_3$); 93.7 (Ar-CH-3); 128.6 (Ar-CH-5); 129.8 (Ar-CH-6); 133.9 (Ar-C-1); 138.3 (Ar-CH-2); 141.2 (Ar-CH-4); 164.2 (CO$_2$C(CH$_3$)$_3$.

2.3.2. Synthesis of *tert*-butyl 3, 3'-(bromophosphinediyl) dibenzoate

A solution of tert-butyl-3-iodo benzoate (0.99 g, 3.26 mmol) in dry THF under N_2 was cooled to -25 ˚C. Methylmagnesium chloride 3.0 M in THF (0.27 mL, 3.42 mmol) was slowly added thereto with rapid stirring. The reaction mixture was then stirred at -25 ˚C for 30 minutes. A solution of phosphorus tribromide (0.153 mL, 0.44 g, 1.63 mmol) in dry THF was added dropwise to the solution and the mixture was stirred for a further 30 minutes at -25 ˚C. The solution was then stirred at RT overnight. The solvent was then evaporated *in vacuo* and the residual material was subjected to column chromatography on silica gel, petroleum ether:ethyl acetate (90:10 to 60:40) . A residual yellow oily material was obtained after evaporating the solvents *in vacuo*. Yield = 0.48 g, 63%. ^{1}H-NMR (400 MHz, $CDCl_3$): δ ppm = 1. 35 (18H, s, 2x CH_3)$_3$); Aromatic protons: 7.45-8.03 (m). ^{13}C-NMR: δ ppm = 28.2 (CH$_3$); 81.1 (-C- (CH$_3$)$_3$); 164.9(C=O); 128.6 –131.1, 135.9 C-*ortho*P.

2.3.3. Synthesis of 3,3'-(chlorophosphinediyl)dibenzoic acid

Di-*tert*-butyl-3,3'-(hydroxyphosphinediyl)dibenzoate (0.48 g, 1.36 mmol) was treated with a HCl/EtOAc (15% (v/v), 25 mL) solution at room temperature. The solution was left stirring at RT overnight. The solution had turned a light brown. The solvent was then evaporated under reduced pressure to give a brownish precipitate. Yield = (0.35 g, 76%). ^{1}H-NMR (400 MHz, CDCl$_3$): δ = carboxy OH = 12.74 (2H), 7.49 -7.56 (4H, m, *H*-orthoP, *H*-*meta*P) 8.15 (1H, s, *H*-paraP) ^{13}C-NMR: δ = 169.3 (*C*=OOH), (C-P) 130.9, (C-Para) 130.3, (C-ortho) 136.5, (C-meta) 128.5, (C2) 130.5, 130.1 (C-3).

2.3.4. Synthesis of bis [3-(chlorocarbonyl)phenyl] phosphine

The 3,3'-(chlorophosphinediyl)dibenzoic acid (0.35 g, 0.99 mmol) was stirred in refluxing SOCl$_2$ (2 mL) under N$_2$ for 3 hrs. The solution was left to stand overnight. The resulting clear solution was evaporated to dryness *in vacuo*. Yield = (0.21 g, 54%). ^{1}H-NMR (400 MHz, CDCl$_3$): δ= 7.51 (4H, J$_{HH}$ =7.8 Hz, H-*ortho*P), 7.12 (2H, J$_{HH}$=7.85 Hz, H-*meta*P), 7.28-7.33 (2H, m, H-*para*P/P-C2) ; ^{13}C-NMR: δ = 167.9 (*C*=*O*Cl), 131.4 (P-para), 129.0 (P-meta), 137.6 (P-ortho), 137.2 (P-C), 131.0 (P-C2), 130.4 (P-C3).

The bis[3-(chlorocarbonyl)phenyl] phosphine (4.23 mmol) was reduced to the corresponding alcohol (chlorophosphanediyl)bis(3,1-phenylene)dimethanol by slow addition of 3.45 mL of 1.0 M LiAlH$_4$ over an hour. The reaction was left stirring overnight. The solvent was then removed under reduced pressure. Yield= (0.79 g, 67%).

2.3.5. Synthesis of chlorobis(3-(chloromethyl)phenyl)phosphane

The (chlorophosphanediyl)bis(3,1-phenylene)dimethanol (6.28 mmol) was treated with N-chlorosuccinimide (9.43 mmol) in a basic medium, using triphenylphosphine (9.43 mmol). These were heated under reflux in THF overnight. It was then cooled, filtered and the resultant filtrate was evaporated under reduced pressure. Yield= (3.77 g, 96%). ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 4.54 (2H, t, J=7.9 Hz, *CH$_2$*Cl), 7.12 (1H, d, J=7.8 Hz H-*ortho*P), 7.26-7.38 (3H, m, H-*meta*P/H-*para*P/P-C2); ^{13}C-NMR: δ = 46.5 (*CH$_2$*Cl), 128.6 (P-para), 128.9 (P-meta), 131.0 (P-ortho), 131.4 (P-C), 129.9 (P-C2), 137.6.

2.3.6. Supporting functionalised PNP ligands on the silica

To a solution of the corresponding amine (7.5 mmol) in DCM (50 mL) and Et$_3$N at room temperature under N$_2$, diphenylphosphorus chloride (1.39 mL, 7.5 mmol) was added to the reaction mixture. The reaction mixture was then stirred for 30 minutes at room temperature. The functionalised PNP (7.5 mmol) was added as a powder. The reaction mixture was left to stir overnight at room temperature. After stirring overnight, the reaction mixture was filtered and dried under vacuum for 24 hrs. The supported PNP ligands are labeled as follows:

N substituent	Code
isopropyl	S1
n-butyl	S2
ethylbenzene	S3
cyclohexyl	S4