Heterogenization of Some PNP Ligands for the Oligomerization of Ethylene

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ABSTRACT

Bis(diphenylphosphino)amine ligands were supported on Merrifield's resin and tested in catalytic ethylene oligomerization reactions with a chromium source. The supported ligands were characterized *via* IR, solid-state NMR, SEM and TGA-DSC. In order to compare activity of the supported and unsupported ligands, homogeneous bis(diphenylphosphino)amine ligands were synthesized and characterized *via* NMR, elemental analysis, IR and GC-MS. Oligomerization reactions were carried out in a Parr pressure reactor using Cr(acac)$_3$ as the precursor and MMAO-3A as the activator. The system with the homogeneous ligands proved active in the tetramerization of ethylene, with the selectivity of 1-octene in the C8 fraction being comparable with that mentioned in literature (>98 wt%). When comparing the homogeneous ligands with their heterogeneous counterparts, the latter showed a four-fold drop in activity compared to their homogeneous counterparts. The selectivity towards the main product, 1-octene, was less than 10 wt%. These supported ligands created a system that favoured the formation of C6 products more than any other product, with C6 cyclics (methylcyclopentane and methylenecyclopentane) being the most dominant, probably due to steric effects caused by the polymer chain.

1. Introduction

Full range linear alpha olefin (LAO) production is based on non-selective oligomerization catalysts and more selective systems are desireable.[1] The oligomerization of ethylene to LAOs is an important process because the products are useful intermediates in the synthesis of polymers, lubricants and detergents. The catalysts for ethylene oligomerization and or polymerization most mentioned in literature are complexes of chromium, titanium, nickel, and zirconium. These have been studied extensively and are very active. There have been reports on copper and palladium catalysts but these are not common. Other metals that have been investigated in olefin oligomerization are iron and cobalt.[2–9] A broad Schultz-Flory distribution of olefins is obtained by non-selective catalytic oligomerization of ethylene.[10–13] Only some of these are commercially useful, 1-hexene and 1-octene being two of the most important required for synthesis of linear low-density polyethylene.[14,15] Over the years, the market demand for 1-hexene and 1-octene has increased rapidly and the selective oligomerization of ethylene to these two products has become highly attractive.[15–19] The most direct routes to 1-hexene and 1-octene are the trimerization and tetramerization of ethylene respectively.

The only commercial process converting ethylene to 1-hexene (Chevron-Philips) is based on a homogeneous Cr catalyst using a pyrrole ligand and TEA as an activator.[15] In addition to this, the only known catalyst system selectively converting ethylene to 1-octene is also based on a homogeneous Cr catalyst system.[14] Tetramerization of ethylene to 1-octene is thought to proceed *via* a similar mechanism to that for trimerization (Scheme 1).[20,21] Tetramerization occurs probably as a result of both the relative stability of the metallacycloheptane intermediate and the

instability of the metallacyclononane intermediate which rapidly eliminates to 1-octene.[22,23]

To date there have been very few examples of heterogeneous selective oligomerization catalysts in the open and patent literature.[24–28] Since the co-catalyst cost, modified methylaluminoxane (MMAO), represents a significant portion of the total cost of a selective oligomerization process, the successful heterogenization of these catalyst systems could present significant savings for the process, since this could result in a recyclable catalyst which can also be easily separated from the product mixture. It would therefore be prudent to pay attention to this, up to now, somewhat neglected area of research. We now report on an attempt to heterogenize existing tetramerization catalysts in order to develop a re-usable catalyst for the oligomerization of ethylene.

2. Experimental

2.1. Materials

All synthetic work was carried out under a nitrogen atmosphere using standard Schlenk techniques. Nitrogen gas (HP) used was obtained from Afrox. The amines, phosphines and reaction solvents (tetrahydrofuran, dichloromethane and diethyl ether) were obtained from Merck and solvents were dried prior to use. Merrifield's resin with 1.0–1.5 mmol g^{-1} Cl-loading, 1 % cross-linked (Sigma-Aldrich) and MMAO-3A (Akzo Nobel) were used without further purification. Ethylene gas was supplied by Air Liquide and used as received.

2.2. Instrumentation

NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer fitted with a 5 mm BBOz probe and equipped with an autosampler; and a Bruker Avance III 600 MHz solid-state
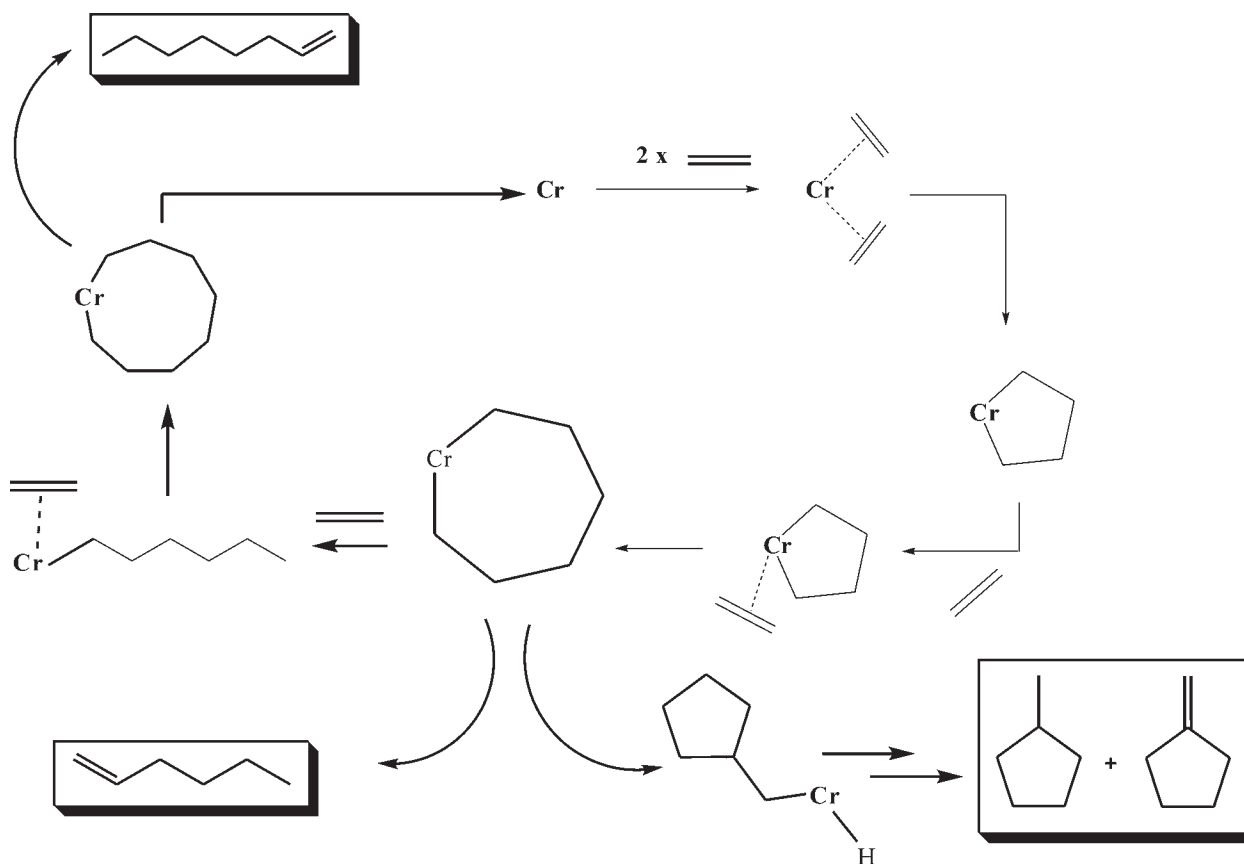
Scheme 1
Postulated mechanism for the tetramerization of ethylene, with the main products in boxes.[22,23]

MAS spectrometer fitted with a 4 mm MAS BB/1H probe. Elemental analyses were performed using a LECO Elemental Analyzer. Infrared spectra were recorded on a Perkin Elmer Attenuated Total Reflectance spectrophotometer (4000–400 cm^{-1}). SEM images were obtained using a Jeol JSM-6100 Scanning Microscope. TGA-DSC was performed from room temperature to 1000 °C at a rate of 10 °C min^{-1} under static air using an SDT Q 600 TGA-DSC instrument. Catalytic testing was carried out using a 450 mL stainless steel Parr 4843 high pressure reactor and the ethylene flow rate was monitored using a Siemens Sitrans Massflo flowmeter. GC-FID analyses were carried out on a Perkin Elmer Clarus 500 chromatograph using a PONA 50 m × 0.32 mm column, carrier gas: nitrogen. GC-MS spectra were recorded on a Perkin Elmer Clarus 500 chromatograph equipped with an autosampler using a PONA SGE 50 m × 0.15 mm column, carrier gas: helium.

2.3. Preparative Work

2.3.1. Synthesis of Bis(diphenylphosphino)amine Ligands

The bis(diphenylphosphino)amine ligands **1–5** were synthesized according to literature procedures.[29,30] Full details are given in the supplementary information.

2.3.2. Synthesis of Functionalized Bis(diphenylphosphino)amine Ligands

2.3.2.1. Synthesis of Diphenylphosphinoamines

The diphenylphosphinoamines RN(H)PPh$_2$ (R = iPr[31], cyclohexyl[32], Ph[32]) were prepared according to the literature procedures or modifications thereof. Full details are given in the supplementary information.

2.3.2.2. Synthesis of (Chlorophenylphosphino)(diphenyl-phosphino)-N-amines

The chlorophenylphosphino)(diphenylphosphino)-*N*-amines **6–8** were synthesized according to a modified literature procedure.[33] Triethylamine (2.8 mL, 10 mmol) was added to a solution of the corresponding diphenylphosphinoamine (10 mmol) in dichloromethane (30 mL). After 30 min this solution was added to a stirred solution of dichlorophenylphosphine (1.4 mL, 10 mmol) in dichloromethane (20 mL) at 0 °C. The reaction mixture was stirred overnight at room temperature. Amine hydrochloride was removed by filtration, and the product was isolated as a yellow oil by column chromatography using silica gel and a hexane:ethyl acetate ratio of 90:10.

(Chlorophenylphosphino)(diphenylphosphino)-*N*-isopropy-amine (6)
^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.46 (d, 1 H, CH), 3.12 (m, 6 H, 2 CH$_3$), 7.31–7.51 (m, 15 H, CH). ^{13}C NMR (400 MHz, CDCl$_3$): δ = 22.0 (2 CH$_3$), 45.9 (t, CH), 129.1 (3 CH), 131.5 (t, 2 CH), 133.8 (t, CH). ^{31}P NMR (400 MHz, CDCl$_3$): δ = 43.0 (br s), 135.1 (br s). IR (ATR) ν_{max} cm^{-1}: 3056, 2969, 1586, 1479, 1434, 1382, 875, 741, 692. MS (EI, 70 eV): m/z (%) = 385 (11, [M + H]$^+$), 384 (100, [M]$^+$), 349 (8, [M – Cl]$^+$), 343 (2, [M – iPr]$^+$), 199 (6, [M – PPh$_2$]$^+$), 185 (17, [PPh$_2$]$^+$). Yield: 56 %.

(Chlorophenylphosphino)(diphenylphosphino)-*N*-cyclo-hexylamine (7)
^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.52 (m, 2 H, CH$_2$), 1.41 (m, 2 H, CH$_2$), 1.82 (m, 3 H, CH$_2$ + CH), 3.12 (q, 4 H, 2 CH$_2$), 7.31–7.43 (m, 15 H, CH). ^{13}C NMR (400 MHz, CDCl$_3$): δ = 25.3 (CH$_2$), 25.9 (2 CH$_2$), 45.9 (2 CH$_2$), 59.9 (t, CH), 128.9 (3 CH), 131.7 (t, 2 CH),

139.8 (t, CH). ^{31}P NMR (400 MHz, CDCl$_3$): δ = 47.4 (br s), 134.9 (br s). IR (ATR) ν_{max} cm^{-1}: 3054, 2930, 2853, 1587, 1478, 1434, 868, 742, 692. MS (EI, 70 eV): *m/z* (%) = 426 (7, [M + H]$^+$), 425 (5, [M]$^+$), 342 (7, [M – C$_6$H$_{11}$]$^+$), 240 (3, [M – PPh$_2$]$^+$), 185 (4, [PPh$_2$]$^+$), 83 (1, [C$_6$H$_{11}$]$^+$). Yield: 64 %.

(Chlorophenylphosphino)(diphenylphosphino)-*N*-phenyl-amine (8)

^{1}H NMR (400 MHz, CDCl$_3$): δ = 6.50 (d, 2 H, 2 CH), 7.00 (unresolved coupling, CH), 7.20 (m, 2 H, 2 CH), 7.36–7.92 (m, 15 H, CH). ^{13}C NMR (400 MHz, CDCl$_3$): δ = 123.8 (CH), 127.7 (CH), 128.6 (CH), 129.7 (CH), 131.2 (t, CH), 140.4 (t, CH), 146.6 (t, CH). ^{31}P NMR (400 MHz, CDCl$_3$): δ = 44.6 (d), 124.7 (d). IR (ATR) ν_{max} cm^{-1}: 3024, 1602, 1494, 1452, 824, 740, 697. MS (EI, 70 eV): *m/z* (%) = 421 (2, [M + H]$^+$), 420 (6, [M]$^+$), 385 (0.5, [M – Cl]$^+$), 271 (3, [M – C$_6$H$_5$]$^+$), 235 (0.5, [M – PPh$_2$]$^+$), 185 (4, [PPh$_2$]$^+$), 149 (15, [C$_6$H$_5$]$^+$). Yield: 51 %.

2.3.3. *Functionalising of Merrifield's Resin*

Merrifield's resin was functionalized according to a literature procedure.[34] Full details are given in the supplementary information.

2.3.4. *Supporting of (Chlorophenylphosphino)(diphenylphosphino)-N-amines on Functionalized Resin*

The (chlorophenylphosphino)(diphenylphosphino)-*N*-amines were supported on functionalized Merrifield's resin to form compounds **9–11** by modification of a reported procedure.[34] A solution of the corresponding (chlorophenylphosphino) (diphenylphosphino)-*N*-amine (0.5 mmol) in tetrahydrofuran (20 mL) was treated slowly with functionalized Merrifield's resin (2.5 mmol g^{-1}, 0.1 mmol) while stirring at room temperature for a period of 30 min before triethylamine (0.4 mmol) was added. The resulting suspension was stirred at room temperature overnight before the resin was filtered off. The resin was washed with dichloromethane (5 × 8 mL), and hexane (5 × 5 mL). The resulting resin was dried overnight under vacuum.

Supported Isopropyl PNP (9)

^{13}C MAS SS-NMR (600 MHz): δ = 28.0, 41.3, 46.9, 62.1, 128.6, 145.9. ^{31}P MAS SS-NMR (600 MHz): δ = 9.02 (s), 16.5 (s). IR (ATR) ν_{max} cm^{-1}: 3044, 2915, 1601, 1493, 1437, 747, 694.

Supported Cyclohexyl PNP (10)

^{13}C MAS SS-NMR (600 MHz): δ = 22.5, 25.2, 32.4, 40.5, 45.9, 62.1, 127.9, 145.0. ^{31}P MAS SS-NMR (600 MHz): δ = 9.00 (s), 21.0 (s). IR (ATR) ν_{max} cm^{-1}: 3059, 2944, 2854, 1636, 1541, 1438, 1434, 924, 739, 697.

Supported Phenyl PNP (11)

^{13}C MAS SS-NMR (600 MHz): δ = 22.4, 29.9, 40.6, 47.9, 62.1,

128.6, 139.6, 146.5. ^{31}P MAS SS-NMR (600 MHz): δ = 8.37 (s), 21.4 (s). IR (ATR) ν_{max} cm^{-1}: 3024, 1601, 1494, 1451, 824, 740, 697.

2.4. Catalytic Testing

2.4.1. *Homogeneous Runs*

These were performed using PNP ligands **1–5**. A solution of ligand (0.005 mmol) in methylcyclohexane (2 mL) was added to a solution of Cr(acac)$_3$ (0.005 mmol) in methylcyclohexane (2 mL). The mixture was stirred for 5 min at room temperature after which MMAO (9.6 mmol, 2.50 mL) was added. The mixture was then transferred to a pressure reactor containing methyl-cyclohexane (93.5 mL) at the required temperature (60 or 80 °C). The pressure reactor was charged with ethylene at 45 bar and the temperature was controlled. The reaction was terminated after 30 min by discontinuing the ethylene feed and quenching with ethanol (10 mL). The liquid phase was analysed by GC-FID using nonane as the internal standard.

2.4.2. *Heterogeneous Runs*

These were done using supported ligands **9–11**. The loading of the ligand on the polymer was determined by ICP-OES and reported as mmol phosphorus g^{-1} of supported ligand. From this information, the appropriate amount of supported ligand could be weighed out using the same mole quantities as those of the homogeneous runs. Full details are given in the supplementary information.

3. Results and Discussion

3.1. Ligand Synthesis and Characterization

The chlorophosphine PNP ligands were synthesized by reacting one equivalent of the respective diphenylphosphinoamine with one equivalent of dichlorophenylphosphine. The target ligands were similar to the bis(diphenylphosphino)amine ligands, except that one phenyl group attached to the one of the phosphorus atoms was replaced by a chlorine atom. The yields were low due to the sensitivity of these ligands to air and moisture, they are easily oxidized and a lot of product was lost during purification. The ligands, **6–8**, that were synthesized, contained the functional groups of the most active and selective ligands **1–5**. The reaction is shown in Scheme 2.

Merrifield's resin was the polymer chosen for the supporting of the chlorophsphine PNP ligands as it is commercially available and relatively inert. It has also been widely used as a support in catalyst immobilization.[35] Merrifield's resin was functionalized by reacting it with excess *tert*-butylamine under reflux for two days (Scheme 3). The functionalized resin was characterized *via* infrared, solid-state NMR, thermogravimetric analysis and scanning electron microscopy. The infrared spectrum of functionalized Merrifield's resin contained similar stretching absorbances to

Scheme 2
Synthesis of the chlorophosphine PNP ligands.
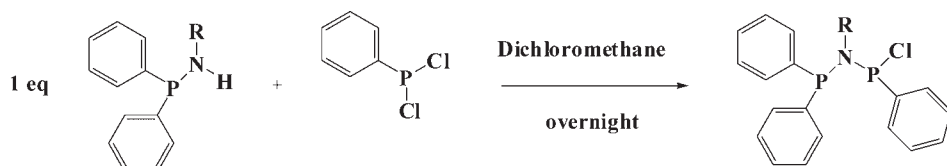
6: R = Isopropyl
7: R = Cyclohexyl
8: R = Phenyl
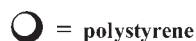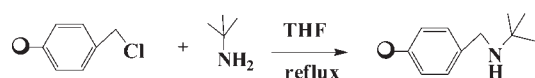
Scheme 3
Functionalization of Merrified's resin with *tert*-butylamine.

those of Merrifield's resin such as at 1602 and 1493 cm^{-1} due to the aromatic rings, at 1452 cm^{-1} due to the methylene carbon atoms on the polymer backbone and at 757 and 697 cm^{-1} owing to C-H stretching on the monosubstituted aromatic rings. The exception was the appearance of secondary amine stretching at 3025 cm^{-1} and a band at 2923 cm^{-1} for the methyl groups on the *tert*-butyl moiety. In the ^{13}C MAS NMR spectrum of Merrifield's resin, peaks were observed at 28.2 ppm due to the carbon atoms on the CH$_3$ groups on *tert*-butyl group, at 41.0 ppm due to the tertiary carbon atom on *tert*-butyl, at 46.7 ppm due to the methylene carbon atoms on the polystyrene backbone and at 128.6 and 145.8 ppm due to the carbon atoms of the aromatic rings.[35,36] The peak at 145.8 ppm was also characteristic of an isotactic polymer, which means all the substituents are situated on the same side on the polymer backbone.[36,37]

The (chlorophenylphosphino)(diphenylphosphino)-*N*-amines were supported on the polymer by reacting the polymer with excess chlorophosphine (Scheme 4). The supported ligands were characterized *via* infrared, ^{13}C and ^{31}P solid-state NMR, thermogravimetric analysis and scanning electron microscopy. Similarly to functionalized Merrifield's resin, the infrared spectra of ligands **9–11** contained stretching absorbances at ~1600 and ~1490 cm^{-1} due to the aromatic rings, at 1430–1450 cm^{-1} due to the methylene carbon atoms on the polymer backbone, at 760 and 700 cm^{-1} due to C-H stretching on the monosubstituted aromatic rings, secondary amine stretching at 3020–3050 cm^{-1} and bands at 2920–2960 cm^{-1} for the methyl groups on the *tert*-butyl group. There P-Cl stretching bands at ~520–540 cm^{-1} observed for the (chlorophenylphosphino)(diphenylphosphino)-*N*-amines were no longer observed and the P-N stretching bands which are found in the range ~780–100 cm^{-1}, as reported in literature[38], were more intense. Characteristic peaks for the ligands were as follows: for ligand **9**, a stretch at 1378 cm^{-1} due to the methyl groups on the isopropyl group; for ligand **10**, at 1051 cm^{-1} due to C-N on the aliphatic amine and at 1438 cm^{-1} due to CH$_2$ on the cyclohexyl ring; for ligand **11**, the stretch for the aromatic ring on nitrogen overlapped with those for the other aromatic rings on the ligand at 1601 and 1494 cm^{-1}. In the MAS ^{13}C NMR spectra of ligands **9–11**, peaks were observed at ~22 ppm due to the carbon atoms on the CH$_3$ groups on the *tert*-butyl group, at ~41 ppm due to the tertiary carbon on the *tert*-butyl group, at ~47 ppm due to the methylene carbon atoms on the polystyrene backbone and at ~128 and ~145 ppm due to
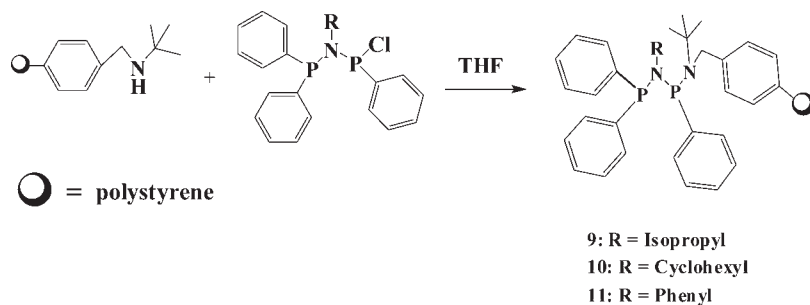
the carbon atoms on the aromatic rings. In the solid state ^{31}P NMR spectra of ligands **9–11** two signals were observed, each due to the two phosphorus atoms present in a different environment.

Mapping the images of the supported ligands for phosphorus (Fig. 1) using scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) by using colour to indicate the presence of phosphorus, showed that the particles on the surface of the polystyrene balls contained phosphorus, which led to the conclusion that the PNP ligands were on the surface of the support.

3.2. Catalytic Testing

3.2.1. *General Comments*

The bis(diphenylphosphino)amine and supported (chlorophenylphosphino)(di-phenylphosphino)-*N*-amine supported ligands were evaluated in the oligomerization of ethylene using a high pressure Parr reactor. The source of chromium was Cr(acac)$_3$ (chromium acetylacetonate) and the activator was modified methylaluminoxane (MMAO-3A). The solvent chosen was methylcyclohexane because it has been reported that reactions in this solvent show improved catalytic activity.[39] Evaluation was done at temperatures of 60 and 80 °C and at an ethylene pressure of 45 bar. Only the main products obtained are discussed.

3.2.2. *Testing of Homogeneous Catalyst Systems*

The use of ligands **1–5** with chromium in the tetramerization of high purity ethylene, which was then still further extensively purified, has been reported. We now report on the activity of these ligands with commercial grade ethylene; work which was done to establish baseline values for comparison with the supported ligands.

Figure 2 shows the selectivities towards the C6 products and these were 1-hexene, internal hexenes and the cyclic C6 products, methylenecyclopentane and methylcyclopentane. An increase in steric bulk of the substituent on the ligand led to a decrease in the formation of these compounds, which corresponds with what is also reported.[40,41]

Figure 3 shows the selectivity of 1-hexene in the C6 products for each catalyst system at different temperatures. 1-Hexene is formed by the reductive elimination of the chromacycloheptane species in the tetramerization catalytic cycle.[40] The figure shows that generally as the temperature increases, so too does the selectivity towards 1-hexene. This also corresponds to what is reported.[42,43] This occurs at the expense of 1-octene and the C6 cyclics. The cyclohexyl and phenyl systems yielded higher selectivities to 1-hexene due to their steric nature. It has been reported that ligands having the bulkiest moieties on the N-atom yield the best alpha olefin selectivity.[40]

Figure 4 shows the selectivity of 1-octene in the C8 products for each catalyst system at different temperatures. The C8 products
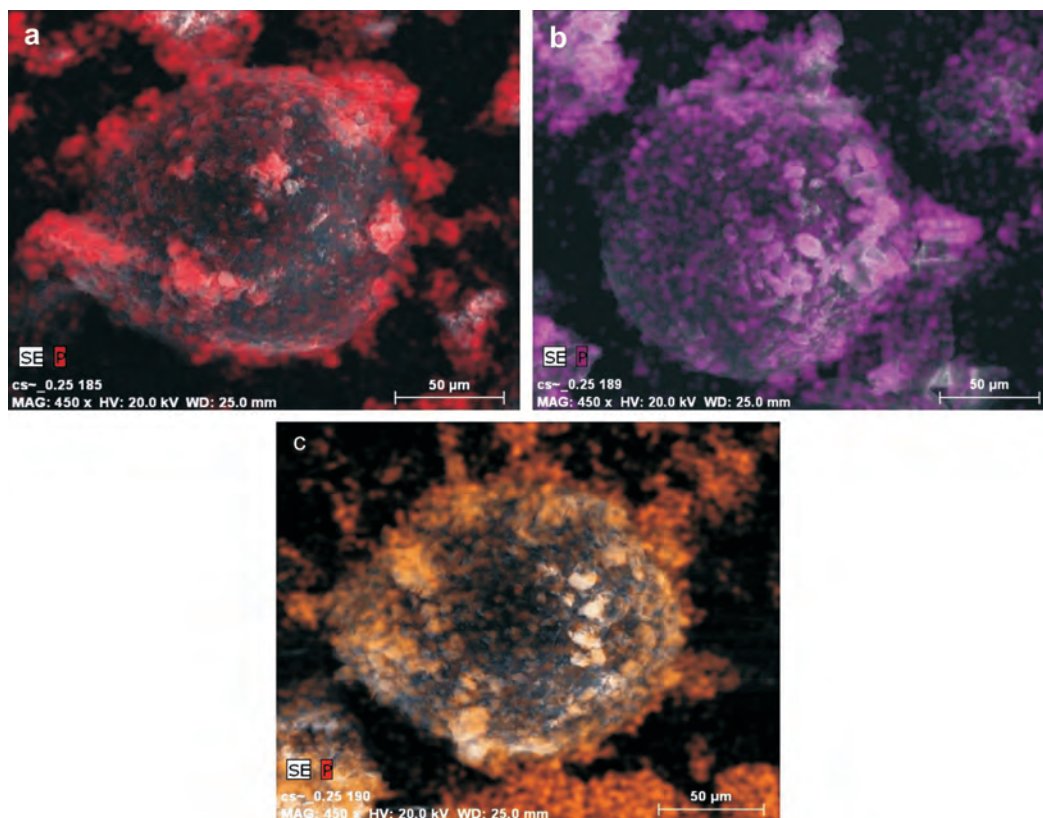

9: R = Isopropyl
10: R = Cyclohexyl
11: R = Phenyl

Scheme 4
Supporting of (chlorophenylphosphino)(diphenylphosphino)-*N*-amines on functionalized Merrifield's resin.

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S. Afr. J. Chem., 2012, **65**, 214–222,
<http://journals.sabinet.co.za/sajchem/>.

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Figure 1 Electron mapping images of the supported (**a**) isopropyl, (**b**) cyclohexyl and (**c**) phenyl PNP ligands.

consist of octane, 1-octene and internal octenes. Selectivities greater than 98 wt% were obtained and these are comparable with those in literature.[22,40,41] The bulky ligands (isopropyl, cyclohexyl and phenyl) yielded the highest selectivity towards 1-octene.

When looking at the activity profile, an increase in temperature yielded a slight increase in the activity of the systems as seen in Fig. 5, with the cyclohexyl and phenyl systems yielding the highest activity. The activity was in the 10^4–10^5 g g^{-1} Cr.h range, whereas in literature it is in the 10^6 g g^{-1} Cr.h range.[43] This is most likely due to the difference in the quality of the ethylene gas used in the experiments.

3.2.3. *Testing of Heterogeneous Catalyst Systems*

Testing of the heterogeneous catalysts was carried out using the supported ligands (isopropyl, cyclohexyl and phenyl) under the same conditions as those used for the homogeneous catalytic testing. These systems proved unfavourable for the tetramerization of ethylene, yielding a high selectivity towards the C6 products (>80 wt%, Fig. 6) with a low selectivity towards 1-hexene in the C6 products (Fig. 7). The systems also gave a low selectivity towards 1-octene in the C8 products (Fig. 8).

In the C6 fraction, the majority of the products were the cyclics, i.e. methylcyclopentane and methylenecyclopentane with a selectivity towards these two products greater than 60 wt% (Fig. 9). This may be rationalized that the catalytic cycle is favoured up until the insertion of three ethylene molecules to form the chromacycloheptane intermediate, after which the disproportionation step to form the cyclic products is favoured over the reductive elimination step to form 1-hexene. Similar
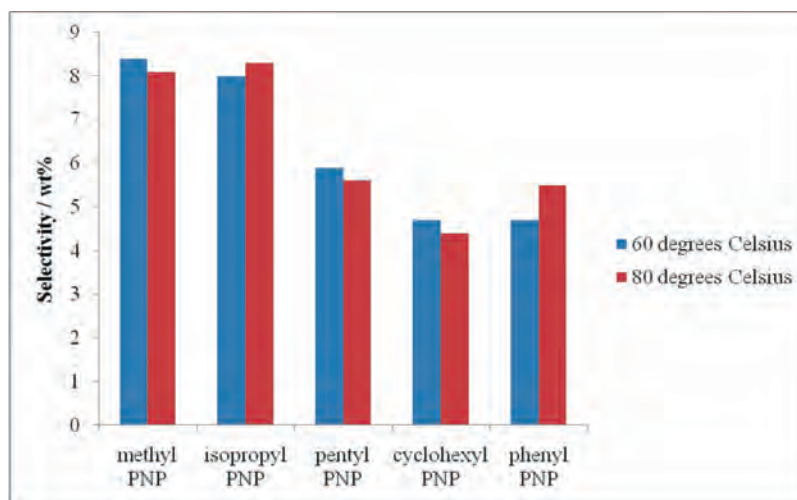

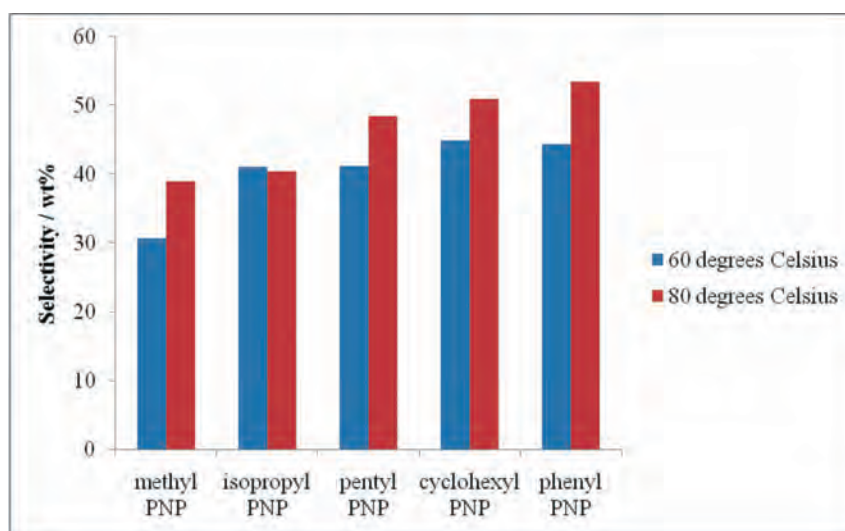**Figure 2** Selectivity for the C6 products by each catalyst system at different temperatures.

Figure 3 Selectivity for 1-hexene in the C6 products by each catalyst system at different temperatures.
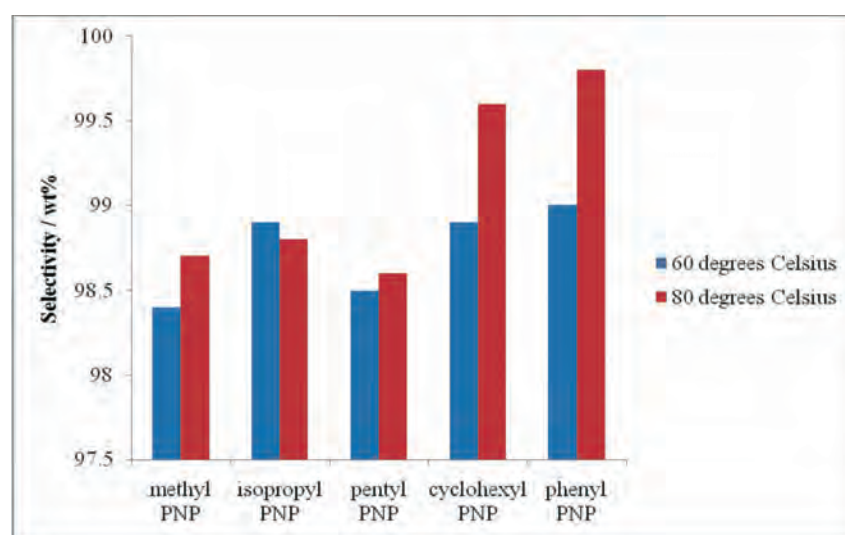
Figure 4 Selectivity for 1-octene in the C8 products by each catalyst system at different temperatures.
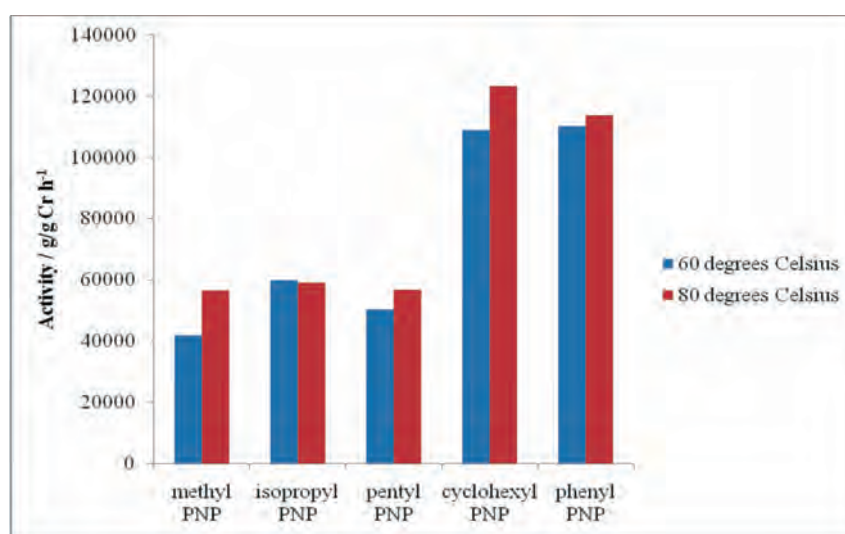
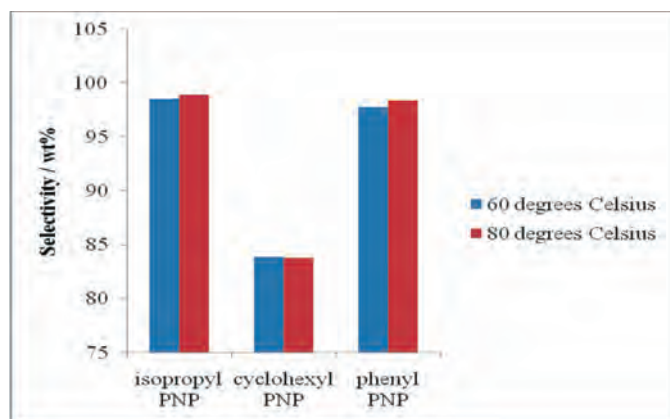**Figure 5** Activity for each homogeneous catalyst system at different temperatures.

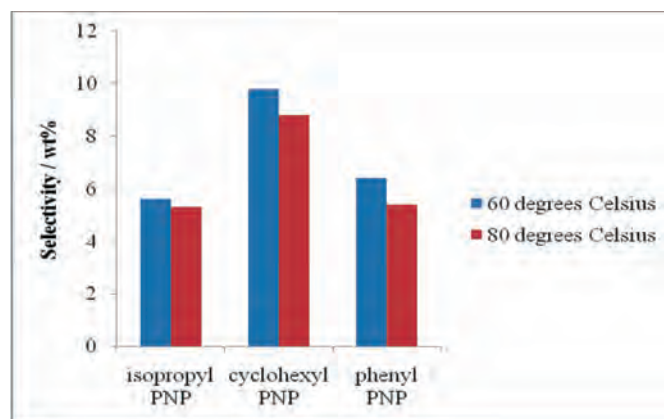**Figure 6** Selectivity for the C6 products by each heterogeneous catalyst system at different temperatures.

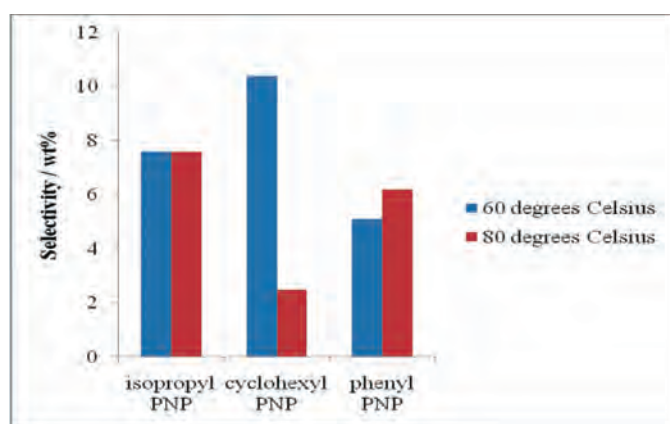**Figure 7** Selectivity for 1-hexene in the C6 products by each heterogeneous catalyst system at different temperatures.

Figure 8 Selectivity for 1-octene in the C8 products by each heterogeneous catalyst system at different temperatures.
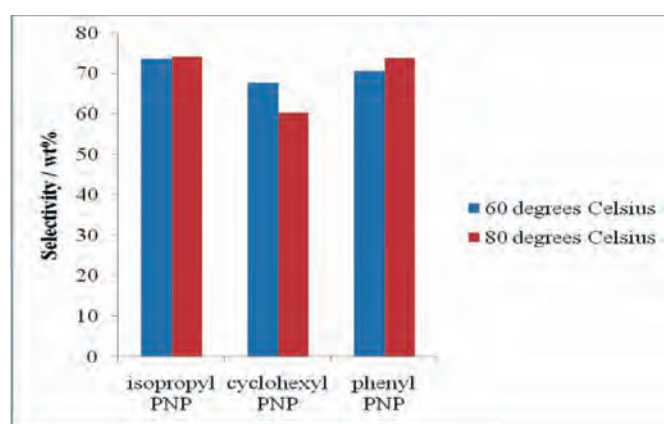

Figure 9 Selectivity of the C6 cyclics in the C6 fraction for each heterogeneous catalyst system at different temperatures.
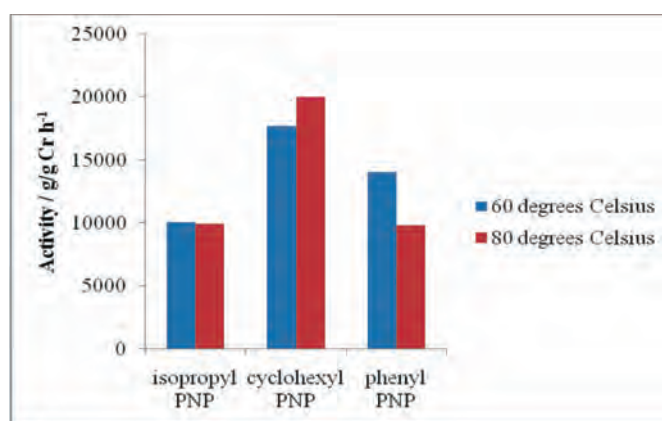

**Figure 10** Activity for each heterogeneous catalyst system at different temperatures.

observations were made by Wang *et al.*[44] who investigated the oligomerization of ethylene using Cp_2ZrCl_2 as the catalyst and obtained predominantly cyclic products. Scheme 5 shows a proposed catalytic cycle for the catalyst system reported in this work and is adapted from that proposed by Wang *et al.*

The low selectivity towards C8 products could be a result of steric hinderance, since as mentioned earlier, it has been shown that the bulkier ligands favour the formation of the C6 products. Also the steric hinderance could result in a partial blocking of the active sites of the intermediate, which would also explain the

decrease in the activity (Figure 10) compared to the homogeneous counterparts.

4. Conclusion

The heterogenization of some selective tetramerization ligands has been achieved. This involved the supporting of these PNP ligands on functionalized polystyrene to give supported isopropyl, cyclohexyl and phenyl bis(diphenylphosphino) amine analogues. With chromium, the homogeneous ligands proved active in the tetramerization of commercial grade
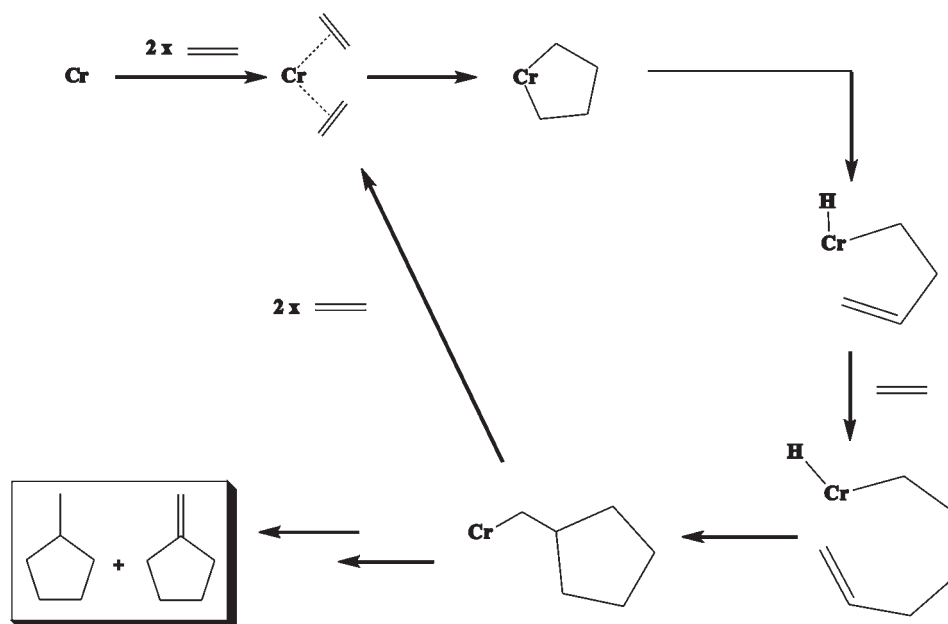
Scheme 5
Proposed catalytic cycle for the oligomerization of ethylene using the polymer-supported PNP ligands. Adapted from Wang *et al.*[44]

ethylene, with the selectivity of 1-octene in the C8 fraction being comparable with that mentioned in literature (>98 wt%) although the activity was an order of magnitude lower.

When comparing the homogeneous and heterogeneous ligand systems, the activity dropped for the latter by more than four times relative to that of the homogeneous ligand systems and the selectivity towards 1-octene, was low (<10 wt%). Instead these heterogeneous ligands created a system that favoured the formation of C6 products with the C6 cyclics being dominant. This is believed to be due to steric effects caused by the polymer chain.

References

1 R. Walsh, D.H. Morgan, A. Bollmann and J.T. Dixon, *Appl. Catal. A: Gen*, 2006, **306**, 184–191.

2 G.J.P. Britovsek, V.C. Gibson and D.F. Wass, *Angew. Chem. Int. Ed.*, 1999, **38**, 428–447.

3 S.D. Ittel, L.K. Johnson and M. Brookhart, *Chem. Rev.*, 2000, **100**, 1169–1204.

4 L.S. Boffa, B.M. and Novak, *Chem. Rev.*, 2000, 100, 1479–1494.

5 J. Zhang, X. Wang and G.X. Jin, *Coord. Chem. Rev.*, 2006, **250**, 95–109.

6 B.L. Small and M. Brookhart, *J. Am. Chem. Soc.*, 1998, **120**, 7143–7144.

7. B.L. Small, M. Brookhart and A.M.A. Bennet, *J. Am. Chem. Soc.*, 1998, **120**, 4049–4050.

8 G.J.P. Britovsek, M. Bruce and V.C. Gibson, *J. Am. Chem. Soc.*, 1999, **121**, 8728–8740.

9 J.X. Chen, Y.B. Huang, Z.S. Li, Z.C. Zhang, C.X. Wei, T.Y. Lan and W.J. Zhang, *J. Mol. Catal. A: Chem.*, 2006, **259**, 133–141.

10 S. Kuhlmann, K. Blann, A. Bollmann, J.T. Dixon, E. Killian, H. Maumela, M.C. Maumela, D.H. Morgan, M. Pretorius, N. Taccardi and P. Wasserscheid, *J. Catal.*, 2007, **245**, 279–284.

11 E. Killian, K. Blann, A. Bollmann, J.T. Dixon, S. Kuhlmann, M.C. Maumela, H. Maumela, D.H. Morgan, P. Nongodlwana, M.J. Overett, M. Pretorius, K. Hofener and P. Wasserscheid, *J. Mol. Catal. A: Chem.*, 2007, **270**, 214–218.

12 A. Dulai, H. De Bod, M.J. Hanton, D.M. Smith, S. Downing, S.M.

13 T. de Bruin, P. Raybaud and H. Toulhoat, *Organometallics*, 2008, **27**, 4864–4872.

14 A. Bollmann, K. Blann, J.T. Dixon, F.M. Hess, E. Killian, H. Maumela, D.S. McGuinness, D.H. Morgan, A. Neveling, S. Otto, M.J. Overett, A.M.Z. Slawin, P. Wasserscheid and S. Kuhlmann, *J. Am. Chem. Soc.*, 2004, **126**, 14712–14713.

15 J.T. Dixon, M.J. Green, F.M. Hess and D.H. Morgan, *J. Organomet. Chem.*, 2004, **689**, 3641–3668.

16 A. Wohl, W. Muller, N. Peulecke, B.H. Muller, S. Peitz, D. Heller and U. Rosenthal, *J. Mol. Catal. A: Chem.*, 2009, **297**, 1–8.

17 D.S. McGuinness, *Chem. Rev.*, 2011, **111**, 2321–2341.

18 T. Agapie, *Coord. Chem. Rev.*, 2011, **255**, 861–880.

19 G.P. Belov, *Pet. Chem.*, 2012, **52**, 139–154.

20 N. Meijboom, C. Schaverien and A.G. Orpen, *Organometallics*, 1990, **9**, 774–782.

21 A.N.J. Blok, P.H.M. Budzelaar and A.W. Gal, *Organometallics*, 2003, **22**, 2564–2570.

22 M. Overett, K. Blann, A. Bollmann, J.T. Dixon, D. Haasbroek, E. Killian, H. Maumela, D.S. McGuinness and D.H. Morgan, *J. Am. Chem. Soc.*, 2005, **127**, 10723–10730.

23 K. Blann, A. Bollmann, J.T. Dixon, F.M. Hess, E. Killian, H. Maumela, D.H. Morgan, A. Neveling, S. Otto and M.J. Overett, *Pat. Appl.*, WO 2004/056477, 2002 (to Sasol Technology (Pty) Ltd).

24 C.N. Nenu and B.M. Weckhuysen, *Chem. Commun.*, 2005, 1865–1867.

25 T. Monoi and Y. Sasaki, *J. Mol. Catal. A: Chem.*, 2002, **187**, 135–141.

26 T. Monoi, H. Torigoe, M. Fushimi and M. Yamamoto, JP 09020692, Showa Denko Chemical Company, January 21, 1997.

27 T. Monoi, H. Torigoe, M. Fushimi and M. Yamamoto, JP 09020693, Showa Denko Chemical Company, January 21, 1997.

28 T. Monoi, H. Torikoshi and M. Yamamoto, JP 10060043, Japan Polyolefin Chemical Company, March 3, 1998.

29 K. Blann, A. Bollmann, J.T. Dixon, F.M. Hess, E. Killian, H. Maumela, D.H. Morgan, A. Neveling, S. Otto and M.J. Overett, *Chem. Commun.*, 2005, **5**, 620–621.

30 M.C. Maumela, K. Blann, H. de Bod, J.T. Dixon, W.F. Gabrielli and D.B.G. Williams, *Synthesis*, 2007, **24**, 3863–3867.

31 M.S. Balakrishna, T.K. Prakasha, S.S. Krishnamurthy, U. Siriwardane and N.S. Hosmane, *J. Organomet. Chem.*, 1990, **390**, 203–216.

32 S. Priya, M.S. Balakrishna, J.T. Mague and S.M. Mobin, *Inorg. Chem.*, 2003, **42**, 1272–1281.

33 W. Wiegrabe and H. Bock, *Chem. Ber.*, 1968, **101**, 1414–1427.

34 G.Y. Li, P.J. Fagan and P.L. Watson, *Angew. Chem. Int. Edn.*, 2001, **40**, 1106–1109.

35 F. Feil and S. Harder, *Macromolecules*, 2003, **36**, 3446–3448.

36 R.V. Law, D.C. Sherrington and C.E. Snape, *Macromolecules*, 1996, **29**, 6284–6293.

37 D. Braun, H. Cherdron and H. Ritter, *Polymer Synthesis: Theory and Practice*, 3rd edn., Springer-Verlag, Berlin, 2001.

38 J. Emsley and D. Hall, *The Chemistry of Phosphorus*, Harper & Row, London, 1976.

39 J.T. Dixon, D.H. Morgan, E. Killian, A. Bollmann, R.N. Walsh, M.J. Overett and K. Blann, *Pat. Appl.*, WO 2005/123633, 2005 (for Sasol Technology).

40 K. Blann, A. Bollmann, H. de Bod, J.T. Dixon, E. Killian, P. Nongodlwana, M.C. Maumela, H. Maumela, A.E. McConnell, D.H. Morgan, M.J. Overett, M. Pretorius, S. Kuhlmann and P. Wasscheid, *J. Catal.*, 2007, **249**, 244–249.

41 E. Killian, K. Blann, A. Bollmann, J.T. Dixon, S. Kuhlmann, M.C. Maumela, H. Maumela, D.H. Morgan, P. Nongodlwana, M.J. Overett, M. Pretorius, K. Hofene and P. Wasscheid, *J. Mol. Catal. A: Chem*, 2007, **270**, 214–218.

42 S. Kuhlmann, J.T. Dixon, M. Haumann, D.H. Morgan, J. Ofili, O. Spuhl, N. Taccardi and P. Wasscheid, *Adv. Synth. Catal.*, 2006, **348**, 1200–1206.

43 S. Kuhlmann, C. Paetz, C. Hagele, K. Blann, R.N. Walsh, J.T. Dixon, J. Scholz, M. Haumann and P. Wasscheid, *J. Catal.*, 2009, **262**, 83–91.

44 M. Wang, Y. Shen, M. Qian, R. Li and R. He, *J. Organomet. Chem.*, 2000, **599**, 143–146.