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The use of bis(diphenylphosphino)amines with *N*-aryl functionalities in selective ethylene tri- and tetramerisation

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Abstract

A systematic study was conducted on the Cr catalysed tri- and tetramerisation of ethylene using bis(diphenylphosphino)amine ligands with *N*-aryl functionality. This study revealed that the oligomerisation reaction product selectivity is primarily dependent on the structure and size of the *N*-aryl groups.

Addition of sufficient steric bulk to the *N*-phenyl group via ortho-alkyl substitution increased the combined 1-hexene and 1-octene selectivity (overall alpha selectivity) to above 82% at an overall 1-octene selectivity of 56%. The introduction of a single carbon spacer between the *N*-atom and the aryl-moiety, as well as the addition of branching on this carbon, resulted in further selectivity improvements, achieving an overall 1-octene selectivity of 64% and an overall alpha selectivity of 84%. This was obtained at catalyst productivities in excess of 1,000,000 g/g Cr/h.

Keywords: Linear alpha olefins; Catalysis; Trimerisation; Tetramerisation; Bis(diphenylphosphino)amine ligands

1. Introduction

There has been an ongoing drive over a number of years towards developing new technologies for the selective oligomerisation of ethylene to linear alpha olefins [1]. This drive has been specifically targeted towards the production of 1-hexene and 1-octene due to their increased application as co-monomers in the production of linear low-density polyethylene. Conventional ethylene oligomerisation processes typically yield a mathematical distribution (Schulz-Flory or Poisson) of linear alpha olefins [2]. Several technologies for the selective trimerisation of ethylene to 1-hexene have been developed over the last couple of decades, [3] and recently an analogous selective tetramerisation of ethylene to 1-octene, achieving 1-octene selectivities up to 70% was reported [4]. The catalyst system comprised a chromium(III) salt, a bis(di-arylphosphino) amine (PNP) ligand of the type $(Ar_2P)_2NR$ (where R = alkyl or phenyl and Ar = phenyl, naphthyl, biphenyl, etc.) and a methylaluminoxane (MAO) based co-catalyst. A number of ligand variation studies on the PNP family of ligands have shown that this tetramerisation catalyst can be converted to a trimerisation catalyst. This was achieved by increasing the steric bulk on the *P*-Ar moiety via substitution on the ortho-position [5] or by the addition of ortho-donor groups on this *P*-Ar moiety [6,7]. Furthermore, it has been shown that changing the *N*-moiety of PNP ligands also influences the overall reaction selectivity [8].

Although there are several published studies on the use of PNP ligands in the chromium-catalysed tri- and tetramerisation of ethylene, there is only one reported example of the catalytic application of these ligands having an aromatic-moiety on the central *N*-atom [4]. We herein report the results of a systematic study on the application of PNP ligands containing *N*-aryl moieties for the selective oligomerisation of ethylene.

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Table 1
Ethylene tetramerisation using different ortho-substitutions on the *N*-phenyl PNP

Entry	Time (min)	Productivity (g/g Cr/h)	PE (wt%)	C_6 (wt%)	1-C_6 (wt%)	C_6-cyclics (wt%)	C_8 (wt%)	1-C_8 (wt%)	1-C_6 + 1-C_8 (wt%)	C_{10}–C_{14} (wt%)	1-C_{15} + (wt%)
1	12	765,900	3.3	16.6	54.2	45.5	61.8	97.1	69.0	9.8	7.4
2	18	526,700	4.8	27.1	56.6	36.2	56.8	97.0	70.3	7.5	2.4
3	18	562,600	3.0	29.4	67.2	27.2	57.0	97.8	75.6	7.0	2.6
4	45	159,600	7.8	33.4	86.2	8.0	52.9	99.2	81.3	5.4	0.6
5	21	498,500	3.8	31.0	85.4	6.7	56.9	99.0	82.8	5.9	1.6

All reactions were carried out in a 300 ml Parr reactor using 100 ml methylcyclohexane at 60 °C, 50 barg, 10 μmol $Cr(acac)_3$, 1 eq. of ligand and 480 eq of MMAO-3A (based on total Al).

Table 2
Ethylene tetramerisation using PNP ligands with a single carbon spacer between the *N*-atom and the phenyl group

Entry	Time (min)	Productivity (g/g Cr/h)	PE (wt%)	C_6 (wt%)	1-C_6 (wt%)	C-$_6$ cyclics (wt%)	C_8 (wt%)	1-C_8 (wt%)	1-C_6 + 1-C_8 (wt%)	C_{10} – C_{14} (wt%)	1-C_{15} + (wt%)
1	12	765,900	3.3	16.6	54.2	45.5	61.8	97.1	69.0	9.8	7.4
6	9	1,065,300	1.3	18.8	46.5	50.4	63.5	97.2	70.5	9.3	5.1
7	8	1,001,600	0.6	27.0	77.0	16.0	64.1	99.1	84.3	6.3	0.8
8	18	579,700	25.8	27.1	85.7	8.1	40.7	99.1	63.6	6.4	1.7
9	17	556,200	1.7	25.5	73.4	20.2	63.5	98.9	81.5	6.8	1.7

All reactions were carried out in a 300 ml Parr reactor using 100 ml methylcyclohexane at 60 °C, 50 barg, 10 μmol $Cr(acac)_3$, 1 eq. of ligand and 480 eq. of MMAO-3A (based on total Al).

2. Experimental and methods

2.1. General comments

All synthetic work was carried out under argon using standard Schlenk techniques. Solvents were purchased from Aldrich and percolated through neutral alumina. Cr(acetylacetonate)$_3$ (97% purity) was obtained from Sigma–Aldrich and used without further purification. MMAO-3A (in heptanes, methylaluminoxane with c.a. 30% replacement of methyl groups by isobutyl groups) was obtained from Akzo-Nobel. Ethylene 3.5 was supplied by Linde and used as received. NMR spectra were recorded on a Bruker DPX-300 FT spectrometer. GC-MS spectra were recorded on a Varian Saturn 2100T. GC/FID analyses were carried out on a Hewlett-Packard 5890 chromatograph using a J&W Scientific 50 m × 0.2 mm PONA column.

2.2. Ligand synthesis—general procedure

The aryl-PNP ligands were synthesised by reacting the arylamine and diphenylphosphine chloride (Ph_2PCl) as described in the literature [9]. The ^{31}P NMR shifts of all ligands are given in the Supporting information.

2.3. Ethylene tri-/tetramerisation—general procedure

All the ethylene tri-/tetramerisation reactions described in this paper were conducted at optimised reaction conditions of 60 °C and 50 barg (barg = 100 kPa). Catalysis was conducted in 100 ml solvent using 10 μmol Cr to ensure reliable catalyst productivity and selectivity data.

Prior to each catalytic run, the respective autoclave was heated under vacuum at elevated temperature (i.e. 120 °C) overnight and placed under an inert gas atmosphere. The reaction vessel was then charged with solvent as indicated in the results and discussion part and heated to 60 °C. Stock solutions of the catalyst components (chromium, ligand and MMAO-3A) were combined in a Schlenk vessel in ratios as indicated in Tables 1–4. After stirring the mixture for 1 min, it was transferred to the autoclave and the reaction was started by pressurising the system with ethylene to 50 barg. Isothermal process conditions were ensured throughout the duration of the run (via the use of an

Table 3
Ethylene tetramerisation using *N*-naphthyl PNP analogues

Entry	Time (min)	Productivity (g/g Cr/h)	PE (wt%)	C_6 (wt%)	1-C_6 (wt%)	C-$_6$ cyclics (wt%)	C_8 (wt%)	1-C_8 (wt%)	1-C_6 + 1-C_8 (wt%)	C_{10} – C_{14} (wt%)	1-C_{15} + (wt%)
10	17	516,900	3.4	25.5	63.9	34.2	57.9	97.3	72.6	8.2	3.7
11	14	707,900	1.0	22.4	61.6	29.1	65.0	98.4	77.8	7.1	3.3
12	9	1,012,900	0.8	27.1	82.1	12.0	62.8	99.2	84.5	7.4	1.5
13	60	145,500	0.8	31.4	90.8	8.4	61.8	98.5	89.4	5.7	2.2

All reactions were carried out in a 300 ml Parr reactor using 100 ml methylcyclohexane at 60 °C, 50 barg, 10 μmol $Cr(acac)_3$, 1 eq. of ligand and 480 eq. of MMAO-3A (based on total Al).

Table 4
Ethylene tetramerisation using different electronic substituents on the *N*-phenyl PNP

Entry	Time (min)	Productivity (g/g Cr/h)	PE (wt%)	C_6 (wt%)	1-C_6 (wt%)	C-$_6$ cyclics (wt%)	C_8 (wt%)	1-C_8 (wt%)	1-C_6 + 1-C_8 (wt%)	C_{10} – C_{14} (wt%)	1-C_{15} + (wt%)
1	12	765,900	3.3	16.6	54.2	45.5	61.8	97.1	69.0	9.8	7.4
14	9	1,147,200	1.9	17.7	53.5	42.9	62.3	96.6	69.7	10.1	6.3
15	13	932,800	16.2	14.8	53.5	43.2	53.3	96.9	59.6	10.3	6.6
16	26	385,900	4.6	22.1	40.2	34.1	58.2	96.7	65.1	9.0	4.8

All reactions were carried out in a 300 ml Parr reactor using 100 ml methylcyclohexane at 60 °C, 50 barg, 10 μmol $Cr(acac)_3$, 1 eq. of ligand and 480 eq. of MMAO-3A (based on total Al).

internal cooling coil) with the ethylene being fed on demand. After the indicated reaction time or when the reactor was full (as in most cases), the reaction was terminated by shutting in the ethylene feed after which the autoclave was cooled rapidly to 0 °C with an ice bath and slowly depressurized. A sample of the liquid reaction mixture was filtered and analysed via GC. Solid by-products (polyethylene/waxes) were collected by filtration, dried in an oven overnight and weighed.

3. Results and discussion

Previously Bollmann et al. [4] showed that changing the alkyl substituent on the *N*-atom of a PNP ligand from a methyl group to a cyclohexyl group had little effect on the 1-octene selectivity, but led to a significant increase in 1-hexene formation, mainly at the expense of the cyclic by-products, methylcyclopentane and methylene cyclopentane. Indeed, the highest overall alpha selectivity was obtained with isopropyl and cyclohexyl substituents on the *N*-atom, indicating that α-branching and thus also steric considerations play an important role in determining the reaction product selectivity. It was further demonstrated that changing the substituent on the *N*-atom from a cyclohexyl group to a phenyl group resulted in a marked decrease in both the C6:C8 ratio and the 1-hexene selectivity, while the selectivity towards 1-octene remained relatively unaffected. The overall alpha selectivity using this ligand was therefore considerably lower (approximately 10%) compared to that obtained with the cyclohexyl-PNP ligand, indicating that electronic properties of the *N*-substituent also affect reaction selectivity.

More recently Kuhlmann et al. [8] reported that increasing the steric demand of cyclohexyl-PNP ligands using alkyl substituents on the 2- and 6-positions of the *N*-cycloalkyl moiety, resulted in significant changes to the C6:C8 ratio of the product slate. Generally it was found that the bulkier the group on the *N*-atom of the ligand, the higher the overall alpha selectivity [as high as 89.5% in the case of Ph_2PN(2,6-dimethylcyclohexyl)PPh_2].

In view of the limited catalytic data on aryl-PNP [Ph_2PN(aryl)PPh_2] ligands and the abovementioned study on the analogous cycloalkyl-PNP family of ligands, we decided to conduct a systematic catalytic study on PNP ligands with aryl and aryl functionalised groups. Throughout the discussion, C_6 is defined as the percentage of all C_6 compounds in the reaction mixture; 1-C_6 is the percentage 1-hexene within this fraction. Similarly this notation applies to the rest of the carbon fractions in the reaction mixture.

3.1. Adding ortho-substituents onto the N-phenyl ring of $Ph_2PN(Ph)PPh_2$

The first phase of this study involved adding progressively larger substituents onto the ortho-position of the *N*-phenyl ring of $Ph_2PN(Ph)PPh_2$ (see Fig. 1).

From Table 1 it is apparent that increasing the size of the moiety on the ortho-position, from an H-atom to an isopropyl group (**1**–**4**), increases both the C_6 and 1-C_6 selectivities. The 1-C_6 selectivity increased by 32% over this range at the expense of the C_6-cyclic products (methylcyclopentane and methylene cyclopentane). Similarly, the C_6 selectivity increased due to a 8.9% decrease in C_8 products. The overall alpha selectivity also increased substantially by more than 12% on going from **1** to **4**. Given the above results, one may conclude that these selectivity changes are primarily due to changes in ligand sterics. It is noteworthy that the bulkiest of these ligands, i.e. ligand **4**, exhibited the lowest catalyst productivity and yielded the most PE (polyethylene/waxes, 7.8%).

Efforts to increase the overall alpha selectivity even further included the introduction of methyl groups on both the 2- and 6-positions of the phenyl ring to give **5**. Catalysis with **5** did indeed lead to a 1.5% increase in the overall alpha selectivity compared to **4** (see Table 1, entries 4 and 5). Comparing the selectivities obtained using **5** with those of the mono-methyl analogue **2**, indicated a small increase in the C_6:C_8 ratio from 0.48:1 to 0.54:1. However, the 1-C_6 selectivity in this case increased significantly by 28.8%, resulting in a 12.5% improvement in the overall alpha selectivity. This result is expected due to the higher steric bulk of ligand **5** compared to **2**.

3.2. The influence of a single carbon spacer between the N-atom and phenyl group

The scope of this study was extended to include a range of ligands containing a single carbon spacer between the *N*-atom and the phenyl group (see Fig. 2). It is apparent from the results of Bollmann et al. [4] that in the presence of a *N*-alkyl group,

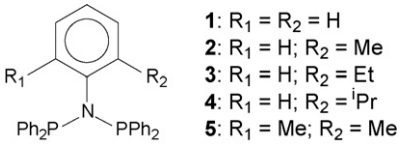

Fig. 1. Ortho-substitutions on the *N*-phenyl PNP.

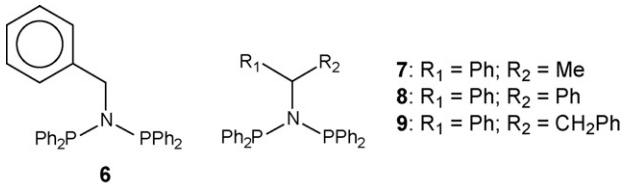

Fig. 2. PNP ligands with a single carbon spacer between the *N*-atom and the phenyl group.

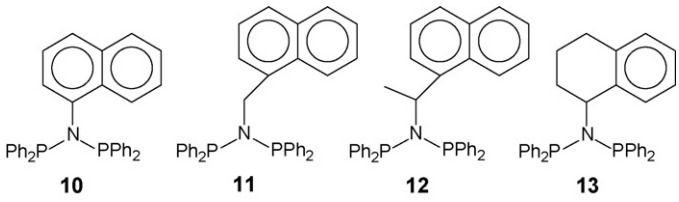

Fig. 3. *N*-naphthyl PNP analogues.

α-branching on this alkyl moiety leads to an increase in overall alpha selectivity. The introduction of a single carbon spacer between the *N*-atom and the aryl group allowed us to investigate ligands having both α-branching as well as an aryl group within the substituent on the *N*-atom.

Releasing some steric strain by the introduction of a methylene spacer between the *N*-atom and the phenyl group of **1** to yield **6**, had remarkably little effect on the product composition, although the catalyst productivity did improve by approximately 30% (see Table 2, entries 1 and 6). The re-introduction of steric strain in the ligand by replacing a H-atom on the methylene spacer with a methyl group to give ligand **7**, led to a 13.8% increase in the overall alpha selectivity when compared to **6** (see Table 2, entry 7). This increase is mainly due to a 33.6% decrease in the formation of C_6 cyclic products. This catalytic run also yielded the highest C_8 selectivity (64.1%), and incidentally, also the highest overall alpha selectivity (84.3%) amongst ligands **1** to **7**. This is probably due to the fact that it is the only ligand in this set having α-branching on the *N*-substituent. As was the case for **6**, ligand **7** also exhibited high catalyst productivity (>1,000,000 g/g Cr/h) and low PE formation (0.6%).

Increasing the steric strain on the ligand even further by introducing another phenyl group onto the carbon spacer to give **8**, did not yield a further increase in the overall alpha selectivity (see Table 2, entry 8). Instead, in repeated catalytic runs, this ligand yielded high quantities of PE (25.8%). The catalyst productivity was also more than 40% lower than that obtained with **7**. This result is difficult to explain in the light of the above trends, but could be due to non-innocence of this ligand through reaction of the activator with the acidic benzylic proton.

The introduction of a benzyl group onto the methylene spacer of **6** yielded ligand **9**, and catalysis with this ligand gave similar selectivities to those obtained with ligand **7** (see Table 2, entries 7 and 9). This is not that surprising given some of the structural similarities between **7** and **9**.

3.3. Catalysis with naphthyl-PNP analogues of ligands 1, 6 and 7

The scope of this study was extended to ligands with larger aromatic groups on the *N*-atom (see Fig. 3). Replacing the *N*-phenyl group of **1** with a 1-naphthyl group to give ligand **10** resulted in a small increase in the overall alpha selectivity to 72.6% (see Tables 1 and 3, entries 1 and 10). This increase in the overall alpha selectivity is probably due to the larger size of the 1-naphthyl group, corroborating the trend observed earlier (see Table 1). Catalysis with ligand **11** led to more distinct selectivity changes (see Table 3, entry 11) compared to those observed upon moving from **1** to **6** (see Table 2, entries 1 and 6); the selectivity trends also appear somewhat different. While both the C_6 and 1-C_6 selectivities remained relatively constant, the C_8 product fraction increased by 7.1%. The catalyst productivity also increased by approximately 40% to more than 700,000 g/g Cr/h.

In line with earlier trends, introduction of α-branching on the *N*-substituent of **11** to give ligand **12**, led to a marked increase in the overall alpha selectivity to 84.5%, mainly due to a 20.5% increase in the 1-C_6 selectivity. The catalyst productivity with this ligand was also comparatively high (>1,000,000 g/g Cr/h).

Catalysis with the 1,2,3,4-tetrahydronaphthyl analogue of **10**, i.e. ligand **13**, [10] gave the best overall alpha selectivity of all ligands evaluated in this study. This very high selectivity of 89.4% was obtained primarily due to a high 1-C_6 selectivity of 90.8%. However, it is noteworthy that this selectivity benefit has to be traded off against the significant drop in catalyst productivity observed.

A comparison of the data obtained for ligands **1–13** shows that, on the whole, PNP ligands with *N*-aryl functionality give ethylene oligomerisation catalysts which are less selective than their *N*-cyclohexyl analogues, both in terms of overall 1-octene formation and overall alpha selectivity [8]. The general selectivity trends observed for both classes of ligands are remarkably similar.

3.4. Changing the electronic nature of the N-phenyl group of $Ph_2PN(Ph)PPh_2$

The ligand variations studied up to now focussed mainly on steric considerations and did not allow for deconvolution of steric and electronic influences. Ligands **14**, **15** and **16** were therefore investigated with the intention of studying these effects (see Fig. 4).

Comparing entries 1 and 14 in Table 4 showed that the introduction of an electron rich tertiary-butyl substituent on the para-position of the *N*-phenyl ring to give ligand **14**, led to higher catalyst productivity and lower PE formation. Minor selectivity

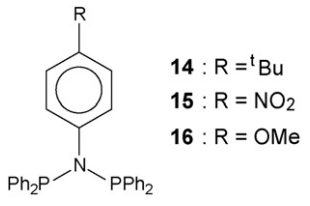

Fig. 4. Different electronic substituents on the *N*-phenyl PNP.

changes were observed in terms of the main liquid products. However, introducing an electron withdrawing nitro substituent to give ligand **15** led to a 9.4% decrease in overall alpha selectivity (see Table 4, entry 15) due to significantly high PE formation (16.2%).

In an attempt to investigate the effects of other electron donating groups on the *N*-phenyl ring, **16** was also evaluated. In this instance, the catalyst productivity decreased by approximately 50% compared to **1** (see Table 4, entries 1 and 16). The overall alpha selectivity decreased by 3.9%, which is due to the low 1-C_6 selectivity of 40.2%. The disparity between the results obtained with **14** and **16** might conceivably be due to reaction of the methoxy moiety of the ligand with the aluminoxane-based co-catalyst (a Lewis acid).

Considering the results obtained with ligands **1**, **14** and **15**, one could conclude that the electronic property of the *N*-phenyl group does indeed affect reaction selectivities, although to a limited extent.

4. Conclusion

In conclusion, this systematic study of the Cr catalysed tri and tetramerisation of ethylene using bis(diphenylphosphino)amine ligands with *N*-aryl functionality revealed that the oligomerisation product selectivity is primarily dependent on the structure and size of this functionality.

Addition of sufficient steric bulk to the *N*-phenyl group via ortho-alkyl substitution increased the overall alpha selectivity to above 82% with an overall 1-octene selectivity of 56%. The introduction of a single carbon spacer between the *N*-atom and the aryl-moiety, as well as the addition of branching on this carbon, resulted in further selectivity improvements, achieving an overall 1-octene selectivity of 64% and an overall alpha selectivity of 84%. This was obtained at catalyst productivities in excess of 1,000,000 g/g Cr/h.

The electronic nature of the *N*-phenyl group does indeed play a role in determining the oligomerisation reaction selectivities. Albeit playing a minor role, PNP ligands containing electron rich *N*-phenyl groups did give higher overall alpha selectivities.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2007.01.046.

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