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Ethylene tetramerisation: Subtle effects exhibited by *N*-substituted diphosphinoamine ligands

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Abstract

Since the first report of ethylene tetramerisation to 1-octene using Cr-bis(diphenylphosphino)amine (PNP) catalysts, numerous studies have investigate the influence of ligand structure on the outcome of the catalysis. Although these studies have highlighted some key "ligand structure–reaction selectivity" relationships, a systematic study of the effect of steric bulk and basicity of various *N*-substituted PNP ligands has not been reported to date. The present study characterises in more detail the subtle effects of varying the *N*-substituent on overall oligomerisation performance and selectivity over a broad range of Cr-PNP based catalyst systems. A clear distinction was made between the basicity and steric bulk effects of each *N*-substituent, with the latter being the dominant parameter influencing the reaction selectivity. The experimental evidence suggests that for alkyl PNP ligands, branching (i.e., further substitution) of the carbon atom directly attached to the N-atom of the PNP ligand was essential for obtaining highly selective tetramerisation catalysts. The best systems achieved total alpha selectivity as high as 88% with exceptional catalyst activities (up to 3,200,000 $g/(g_{Cr}\ h)$).

Keywords: Linear α-olefins; Tetramerisation; Ethylene; 1-Hexene; 1-Octene; Chromium; Catalysis; Bis(diphenylphosphino)amine ligands

1. Introduction

Conventional oligomerisation of ethylene to linear α-olefins by transition metal catalysts generally produces a broad range of olefins characterised by either Schulz–Flory or Poisson distributions. Due to the differing commercial value and market demand of each olefin within the product slate, for decades chemists have attempted to manipulate the relative amounts of olefins produced by these catalysts. One example of this is Shell's famous SHOP process, whereby consecutive isomerisation and metathesis steps are used to alter the oligomerisation product slate to yield a distribution containing predominantly co-monomers (C_6–C_8), lubricant and detergent range olefins (C_{10}–C_{14}), and C_{11}–C_{15} internal olefins [1]. Reports of a number of selective oligomerisation catalysts have appeared in the literature in the last few years; most of these selectively trimerise ethylene to 1-hexene [2]. Interest in these systems increased markedly after the successful commercialisation of the Q-Chem trimerisation plant in Qatar in 2003, using the Phillips Petroleum Cr-pyrrole-triethylaluminum catalyst package [3].

Sasol has been active in the field of selective trimerisation for the past eight years [4] and has recently published the first accounts of Cr-based catalysts with biphosphine ligands that selectively tetramerise ethylene to 1-octene [5]. Subsequent mechanistic studies [5d] on these catalyst systems have demonstrated that the 1-octene is formed by an extension of the classical metallacycle mechanism [6] for 1-hexene production from ethylene, that cationic chromium species are implicated in the

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formation of the active species, and that a Cr(I)Cr(III) redox couple [7] is likely involved.

Since the first report of ethylene tetramerisation, numerous ligand variation studies have been reported. These include investigations into biphosphine systems containing a range of carbon [8] and nitrogen [5a] bridges between the two phosphine atoms and their subsequent effect on the selectivity of the catalysis. In addition, the effect on selectivity of various phosphine substitution patterns within a specific class of ligands, namely the bis(diarylphosphino)amines (PNPs) [4d,5i] have been investigated. Catalysis with cycloalkyl *N*-substituted PNP ligands and the effect of steric hindrance of the *N*-group on determining the reaction selectivity also have been reported [9]. Although the above studies have highlighted some key "ligand structure–reaction selectivity" relationships, a systematic study on the effect of steric bulk and basicity of various *N*-substituted PNP ligands has not been reported to date. Herein we describe in more detail the subtle effect of varying the *N*-substituent on the overall oligomerisation performance and selectivity over a broad range of Cr-PNP-based catalyst systems.

2. Experimental

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. $Cr(acac)_3$ (97% purity) and $CrCl_3(THF)_3$ (99%) were obtained from Sigma Aldrich and used without further purification. $Cr(EH)_3$ (Cr(III) 2-ethylhexanoate) was obtained from Strem Chemicals (8–10% Cr in mineral oil) and used without further purification. MAO (∼7 wt% aluminoxane solution in toluene) was obtained from Crompton Corp. MMAO-3A (in heptanes, methylaluminoxane with ca. 30% replacement of methyl groups by isobutyl groups) was obtained from Akzo-Nobel. Ethylene 3.5 was supplied by Linde Germany 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 PNP ligands (see Figs. 1, 2, 4) were synthesised by reacting the amine and diphenylphosphine chloride (Ph_2PCl) as described previously [10]. A more detailed description of these syntheses, the synthesis of the Cr-PNP complexes (Fig. 3) as well as ^{31}P NMR shifts (ppm) of all the compounds is given in the supporting information.

2.3. Ethylene oligomerisation: general procedure

Before each run, the respective 300-ml Parr autoclave equipped with a gas-entrainment stirrer was heated under vacuum at elevated temperature (i.e., 120 °C) overnight and placed in an inert gas atmosphere. The reaction vessel was then charged with reaction solvent and heated to the desired reaction temperature. Stock solutions of the catalyst components (chromium, ligand, and MMAO-3A) were combined in a Schlenk vessel in the ratios indicated in Tables 1–4. The catalyst mixture was stirred for 1 min and then transferred to the autoclave. The reaction was started by pressurisation with ethylene to the desired pressure. Isothermal process conditions were ensured throughout the duration of the run using an internal cooling coil, and the ethylene was fed on demand. After the specified reaction time or when the reactor was full (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 depressurised. A sample of the liquid reaction mixture was filtered and analysed by gas chromatography using a known amount of nonane as the internal standard. Solid byproducts (polyethylene/waxes) were collected by filtration, dried in an oven overnight, and weighed.

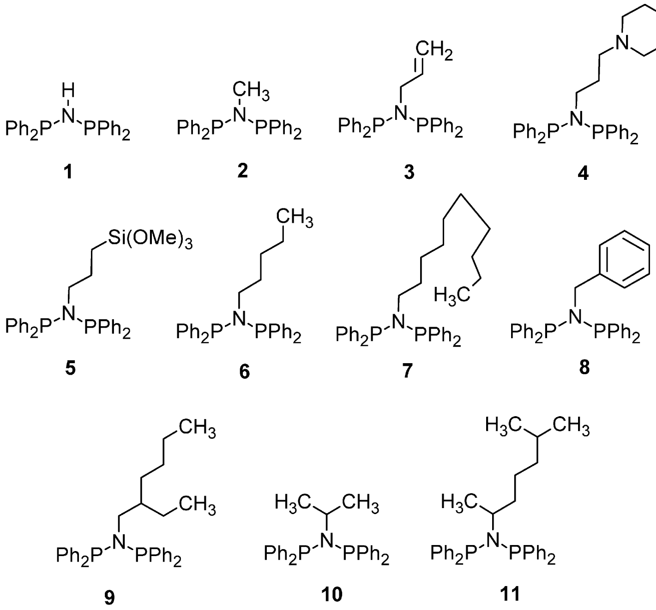


Fig. 1. Biphosphine ligands evaluated with Cr in selective ethylene oligomerisation reactions.

3. Results and discussion

The coordination chemistry of bis(diphenylphosphino)amine (dppa, **1**) has been extensively studied and its unique chemistry demonstrated over a range of different metals [11]. In light of this and our previous experience with substituted PNP ligands, we were interested to see how this ligand without any *N*-substituent would perform in a Cr-mediated ethylene oligomerisation reaction. This ligand, although commercially available from Strem Chemicals, was synthesised from ammonia and diphenylphosphorus chloride and evaluated together with MAO and $Cr(EH)_3$ in toluene at 65 °C and 30 bar gauge ethylene pressure. The results, shown in Table 1 (entry 1), indicate a moderately active catalyst system (13,000 g/(g_{Cr} h)) with no apparent selectivity toward C_6 and C_8 but a rather broad distribution of α-olefins. Throughout the discussion, C_6 is defined as the percentage of all C_6 compounds in the reaction mixture,

Table 1
Ethylene tetramerisation with *N*-substituted PNP ligands[a]

Entry[b]	Ligand	Time (min)	Activity (g/(g_{Cr} h))	S_{C_6} (wt%)	$S_{1\text{-}C_6 \text{ in } C_6}$ (%)	S_{Cyclic} C_6's (%)	S_{C_8} (wt%)	$S_{1\text{-}C_8 \text{ in } C_8}$ (%)	$S_{C_{10}\text{–}C_{14}}$ (wt%)	$S_{C_{16+}}$ (wt%)	**S_α**[f] **(wt%)**	Solids (wt%)
1[c]	**1**	60	13,100	17.7	97.5	0.8	16.4	97.5	32.6	20.2	**33.2**	2.1
2[d]	**2**	60	26,500	24.8	39.4	54.8	59.0	94.1	10.1	2.2	**65.3**	1.4
3[c]	**3**	60	7400	22.2	53.9	43.6	53.6	96.6	6.9	4.9	**63.7**	9.8
4[e]	**4**	30	12,900	19.2	55.7	41.6	45.4	96.4	6.3	2.8	**54.5**	23.9
5[e]	**5**	30	42,500	23.5	54.7	42.8	55.2	96.4	8.8	9.6	**66.1**	0.5
6[d]	**6**	60	43,600	24.9	54.7	43.0	58.1	96.8	10.8	1.8	**69.9**	0.3
7[e]	**7**	30	50,000	25.4	54.9	42.9	59.0	96.5	10.2	2.3	**70.9**	0.7
8[d]	**8**	180	12,800	28.0	61.7	37.1	60.2	98.1	3.5	2.2	**76.3**	3.7
9[e]	**9**	30	49,200	27.3	66.2	32.8	57.3	98	9.2	3.9	**74.1**	0.8
10[d]	**10**	180	35,100	32.7	86.5	13.1	60.6	99.2	5.8	1.8	**88.4**	0.3
11[e]	**11**	30	11,800	36.2	82.1	17.2	57.7	99.2	2.3	1.8	**84.7**	1.8

[a] All reactions were carried out in a 300 ml Parr reactor using 100 ml toluene at 65 °C, 30 barg, 3.3 µmol Cr source, 10 µmol ligand, 300 eq. MAO.

[b] Comparative studies using different Cr precursors (with all other variables constant) have shown that the nature of the Cr precursor employed, does not significantly influence the catalytic behaviour.

[c] $Cr(EH)_3$.

[d] $CrCl_3(THF)_3$.

[e] $Cr(AcAc)_3$.

[f] $S_\alpha = 1\text{-}C_6 + 1\text{-}C_8$.

and 1-C_6 is the percentage of 1-hexene within this fraction. Similar notation applies to the rest of the carbon fractions in the reaction mixture.

Having a single carbon substituent on the N-atom (**2**, see Table 1, entry 2) gave a very different results, however, with 59% selectivity toward C_8 (94% 1-C_8) and 25% selectivity toward C_6 (39% 1-C_6). Considering the significant selectivity differences between the product slates obtained with **1** and **2**, it seems likely that **1** deprotonates under the reaction conditions used in this study and thus acts as a monodentate anionic N-donor for Cr as opposed to a biphosphine.

Noteworthy byproducts of this reaction include methylcyclopentane and methylenecyclopentane (at an almost 1:1 ratio), which together composed more than 50% of the C_6 products. These cyclic byproducts had the adverse effect of decreasing the total alpha selectivity, and the loss of valuable ethylene feedstock led to further efforts aimed at reducing these unwanted products.

The C_{10}–C_{14} fraction of the reaction product is due to secondary co-trimerisation and co-tetramerisation reactions of 1-hexene or 1-octene with ethylene. The selectivity to this fraction is determined largely by the concentration profile of primary olefin products in the reaction mixture and to a lesser extent by ligand selectivity effects [5d].

To study the impact of functionalisation of the *N*-groups on the oligomerisation reaction, we decided to introduce an olefin (**3**), an alkyl-morpholine group (**4**), and an alkoxysilyl moiety (**5**) onto the central N-atom of the PNP ligand structure. Although the formation of solids increased for the first two examples (see Table 1, entries 3 and 4), in general the reaction selectivity was unaffected by various functional groups, with all three examples providing total alpha selectivities exceeding 54% at rates up to 40,000 g/(g_{Cr} h). One possible explanation for the increased solid formation with catalysis using ligand **3** may be that the unsaturated moiety is incorporated into a growing metallacycle, and hence the active oligomerisation catalyst concentration will decrease during the course of the reaction. The tertiary amine group of the morpholine moiety in **4**, on the other hand, also might coordinate to the active Cr centre.

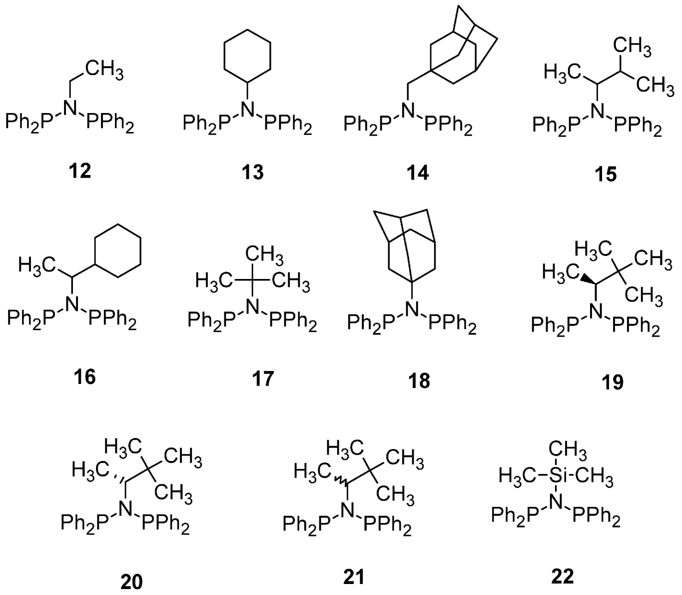


Fig. 2. Biphosphine ligands evaluated with Cr in selective ethylene oligomerisation reactions.

Surprisingly, comparing methyl-, pentyl-, and decyl-PNP (**2**, **6** and **7**, respectively) demonstrates significant improved reaction rate and total alpha selectivity on increasing the chain length by four carbons. Relatively little influence is exerted by the introduction of a further five carbon atoms in the chain (Table 1, compare entries 2, 6, and 7). Interestingly, the C_6 and C_8 fractions remained constant over the series at 25% and 59%, respectively, while C_6-cyclics decreased. Moving from **7** to benzyl-PNP (**8**, Table 1, entry 8) shows a further gain in 1-C_6 selectivity. A similar improvement was observed with 2-ethylhexyl-PNP (**9**, Table 1, entry 9); the 1-C_6 in C_6 cut in-

Table 2
Ethylene tetramerisation with *N*-substituted PNP ligands[a]

Entry	Ligand	Time (min)	Activity (g/(g_{Cr} h))	S_{C_6} (wt%)	$S_{1\text{-}C_6 \text{ in } C_6}$ (%)	S_{Cyclic} C_6's (%)	S_{C_8} (wt%)	$S_{1\text{-}C_8 \text{ in } C_8}$ (%)	$S_{C_{10}\text{–}C_{14}}$ (wt%)	$S_{C_{16+}}$ (wt%)	$\boldsymbol{S_\alpha}$ [b] **(wt%)**	Solids (wt%)
12	**2**	30	964,000	16.4	33.4	66.0	54.0	95.9	12.4	12.4	**57.3**	4.9
13	**12**	30	1,020,000	17.5	40.7	54.6	63.0	97.3	9.2	5.4	**68.4**	2.4
14	**9**	18	1,770,000	20.2	49.7	47.8	65.3	97.7	7.6	3.3	**73.8**	1.50
15	**8**	9	1,070,000	18.8	46.5	50.4	63.5	97.2	9.4	5.1	**70.5**	1.3
16	**10**	17	1,950,000	16.8	75.5	22.0	69.5	99.0	9.5	3.1	**81.5**	0.9
17	**13**	16.5	2,150,000	19.4	75.0	23.8	68.3	99.0	8.2	2.5	**82.2**	0.8
18	**14**	11	2,660,000	20.6	71.6	24.0	67.3	99.1	7.5	2.8	**81.4**	0.1
19	**15**	17	1,920,000	24.3	85.1	14.1	65.7	99.5	7.7	1.1	**86.1**	1.9
20	**16**	11.25	3,200,000	25.1	86.2	13.4	65.5	99.4	7.8	0.6	**86.7**	0.6
21	**17**	22	1,550,000	32.5	94.0	5.7	58.0	99.5	7.3	0.7	**88.3**	1.24
22	**18**	13	2,630,000	30.8	94.5	5.3	*59.3*	99.6	7.9	0.6	**88.1**	1.5
23	**19**	23	1,480,000	44.9	97.4	2.3	44.2	99.4	9.0	0.3	**87.7**	1.5
24	**20**	25	1,360,000	43.5	97.2	2.5	45.6	99.4	9.1	0.4	**87.5**	1.5
25	**21**	24	1,370,000	43.3	97.2	2.5	46.1	99.4	9.0	0.4	**87.9**	1.2
26	**22**	30	20,100	16.9	45.0	49.8	47.3	95.7	8.0	12.9	**52.9**	12.9

[a] All reactions were carried out in a 300 ml Parr reactor using 100 ml methylcyclohexane at 60 °C, 45 barg, 2.5 µmol Cracac$_3$, 3 µmol ligand 300 eq. MMAO-3A.
[b] $S_\alpha = 1\text{-}C_6 + 1\text{-}C_8$.

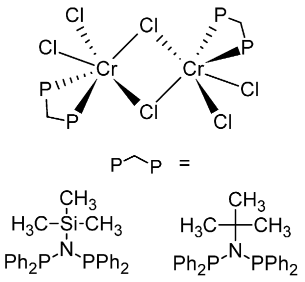
creased to 66.2% relative to that of Me-PNP (39%). Both the benzyl and 2-ethylhexyl moieties contain β-branching (relative to the bridging nitrogen atom), and both provided similar increases in 1-C_6 selectivity. We thus decided to investigate branching at the *N*-bound carbon (α-branching) and synthesised the isopropyl-PNP ligand (**10**). Evaluation of **10** revealed that the 1-C_6 selectivity increased to >86% while the alpha selectivity reached a maximum of 88%. Additional branching, four atoms away from the α-branch as in the case of **11**, gave no further benefit (Table 1, entry 11).

At this point, we turned our attention to the reaction medium and attempted the ethylene oligomerisation reactions in an aliphatic solvent, such as methylcyclohexane. Calculations performed in Aspen Plus 12.1 showed that more ethylene could be dissolved in methylcyclohexane (on both mass and molar bases) than in toluene, which would provide a more ethylene-rich environment for the catalyst (see the supporting information). Consequently, we changed to a modified aluminoxane activator (MMAO-3A), which is soluble in aliphatic medium and well known for its greater temperature stability [12].

The results shown in Table 2 (all runs performed at 60 °C and 45 bar gauge) indicate a dramatic increase in reaction rate in the aliphatic environment (compare, e.g., the values for isopropyl-PNP in Table 1, entry 10 and Table 2, entry 16), with rates as high as 3,200,000 g/(g_{Cr} h) (Table 2, entry 20). This 40-fold increase in rate cannot be attributed to improved catalyst and ethylene solubility effects alone, but rather may be due to the partial inhibition of Cr-PNP catalysts by coordination of the aromatic solvent to the active Cr-centre. Preliminary studies have shown that a methylcyclohexane solution containing 1% toluene led to a >50% reduction in reaction rate. Indeed, there is literature precedence for the formation of cationic Cr(tolyl)$_2$ complexes on the reaction of Cr(acac)$_3$ with trialkylaluminum activators in toluene [13]. Similar to the results given in Table 1, there was a 14% increase in total alpha selectivity (compare entries 12 and 16 in Table 2), together with a twofold improvement in reaction rate, in moving from methyl-PNP (**2**) to ethyl-PNP (**12**) through to isopropyl-PNP (**10**). Significant drops in the formation of C_{16+} products as well as solids were also observed when moving through the series. It is noteworthy that cyclohexyl-PNP (**13**) and isopropyl-PNP (**10**), which are structurally similar compounds, yielded very comparable results (compare entries 16 and 17 in Table 2).

We next focused our attention on the question around steric bulk (i.e., positioning of substituents on the *N*-group) versus basicity (of the *N*-group), and thus prepared a number of sterically encumbered primary (**14**), secondary (**15**, **16**, **19–21**), and tertiary (**17** and **18**) *N*-alkyl amino-biphosphines. Table 2 clearly shows that 1-C_6 selectivity increased predominantly as a function of the steric bulk of the *N*-moiety across this series (Table 2, entries 18–25), not due to the basicity of the *N*-alkyl moiety. For example, the bulkier secondary *N*-alkyl amino-biphosphine **19** furnished 97% 1-C_6 and almost no cyclic C_6 side products, versus 94% for the tertiary *N*-alkyl PNP ligand **17**, which was synthesised from the most basic alkylamine. Furthermore, comparing the steric bulk within a group of ligands containing *N*-alkyl moieties with similar basicity [i.e., ligands **10**, **15**, and **21**, all synthesised from secondary alkylamines, and ligands **12** and **14**, synthesised from primary alkylamines (see Table 2)] provides additional support for the argument that steric considerations outweigh basicity effects.

Another interesting observation is that although the total alpha selectivity increased with increasing steric bulk of the *N*-alkyl group [e.g., 81% vs 88% for entries 18 and 25 (**14** and **21**) in Table 2], there was a concurrent decrease in C_8 formation and an increase in C_6 (C_8:C_6 = 3.3 and 1.1 for entries 18 and 25 in Table 2). A possible explanation for this finding is that as the *N*-substituent increases in size, a steric repulsion occurs between this substituent and the phenyl groups on the phosphines. The positioning of the *P*-aromatic moieties in turn will have an effect on the relative stabilities of the various metallacycle reaction intermediates (in other words, a translated steric effect), similar to that postulated to be in effect



23 **24**

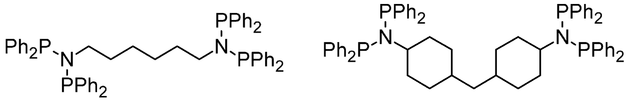
Fig. 3. Biphosphine ligands complexed with $CrCl_3(THF)_3$ and evaluated in selective ethylene oligomerisation reactions.

with the bis[di(*o*-alkylphenyl)phosphino]-methylamine trimerisation catalysts [5i].

Both the pure *R* and *S* enantiomers, as well as the racemic mixture of 3,3-dimethyl-2-butylamine, were used to prepare ligands **19**–**21**. As can be seen from the results given in Table 2 (entries 23–25), there is no stereoisomer effect at play, with all three sets of results being similar.

Having explored a wide range of possible alkyl substituents for the N-atom, we next turned our attention to *N*-heteroatom substitution. We conveniently synthesised trimethylsilyl-PNP (**22**), an interesting target due to its structural similarity to tertiary butyl-PNP **17**, from **1** via deprotonation with butyl lithium and subsequent quenching with trimethylsilyl-chloride. With this ligand in hand, we attempted an in situ oligomerisation reaction as before; although we obtained an alpha selectivity of 53%, the solids were relatively high (13%) and the activity was poor (20,000 $g/(g_{Cr}\,h)$).

Because the ligand seemed unstable in the presence of MMAO-3A (the catalyst preparation solution turned turbid on the addition of the MMAO), we decided to test the precomplexed catalyst **23** (Fig. 3). Remarkably, the rate improved to >2 million $g/(g_{Cr}\,h)$, with the total α-olefin content increasing to 75% (Table 3, entry 27). Although the nitrogen–silicon bond is known to be labile, it seems that it can be preserved by complexing the ligand and the Cr before catalysis. Thus, the high solids and lower selectivity of the in situ catalysis (Table 2, entry 26) can be attributed to the presence of small amounts of **1**, the decomposition product. The analogous *t*-butyl-PNP:Cr complex **24** was also prepared and tested as a benchmark (for alkyl-PNP ligands) for in situ catalysis versus catalysis with a defined complex. As can be seen (compare Table 2, entry 21 and Table 3, entry 28), there was no noticeable difference between the product slates obtained. The higher tendency toward cyclic formation with **23** compared with **24** possibly can be attributed to the slightly longer N–Si bond and hence a lower steric effect from the trimethylsilyl group.



25 **26**

Fig. 4. Multi-site ligands evaluated with Cr in selective ethylene oligomerisation reactions.

Finally, the success with monomeric ligand structures led us to believe that multi-site catalysis indeed could be possible. Toward this end, we synthesised the bifunctional PNP ligands **25** and **26** from their respective amines. As shown in Table 4 (entries 29 and 30), the dual-site ligands (**25** and **26**) indeed gave selective oligomerisation catalysts with reaction rates and selectivities comparable to those of their respective single-site analogues.

4. Conclusion

In this study, we synthesised various PNP ligands with different alkyl/heteroatom substituents attached to the N-atom of the ligand backbone. These displayed good activity and selectivity toward 1-octene and 1-hexene during chromium-catalysed ethylene oligomerisation, with the best ligand systems (in terms of alpha selectivity) having the bulkiest moi-

Table 3
Ethylene tetramerisation with *N*-substituted PNP-$CrCl_3$ complexes[a]

Entry	Complex	Time (min)	Activity ($g/(g_{Cr}\,h)$)	S_{C_6} (wt%)	$S_{1\text{-}C_6\text{ in }C_6}$ (%)	S_{Cyclic} C_6's (%)	S_{C_8} (wt%)	$S_{1\text{-}C_8\text{ in }C_8}$ (%)	$S_{C_{10}\text{–}C_{14}}$ (wt%)	$S_{C_{16+}}$ (wt%)	$\boldsymbol{S_\alpha}$[b] (**wt%**)	Solids (wt%)
27	**23**	13	2,250,000	19.5	56.1	41.6	65.7	97.7	7.4	5.0	**75.1**	0.7
28	**24**	16.5	2,070,000	30.7	93.9	6.1	59.8	99.6	7.7	0.9	**88.4**	0.8

[a] All reactions were carried out in a 300 ml Parr reactor using 100 ml methylcyclohexane at 60 °C, 45 barg, 1.25 µmol of complex (i.e., 2.5 µmol Cr), 300 eq. MMAO-3A.

[b] $S_\alpha = 1\text{-}C_6 + 1\text{-}C_8$.

Table 4
Ethylene tetramerisation with *N*-substituted PNP bifunctional ligands[a]

Entry	Ligand	Time (min)	Activity ($g/(g_{Cr}\,h)$)	S_{C_6} (wt%)	$S_{1\text{-}C_6\text{ in }C_6}$ (%)	S_{Cyclic} C_6's (%)	S_{C_8} (wt%)	$S_{1\text{-}C_8\text{ in }C_8}$ (%)	$S_{C_{10}\text{–}C_{14}}$ (%)	$S_{C_{16+}}$ (%)	$\boldsymbol{S_\alpha}$[b] (**wt%**)	Solids (wt%)
29	**25**	30	662, 000	18.3	39.2	55.7	56.6	99.6	9.6	6.6	**63.5**	6.3
30	**26**	17	1, 760, 000	17.6	75.5	23.6	69.4	99.0	7.2	3.7	**82.0**	1.4

[a] All reactions were carried out in a 300 ml Parr reactor using 100 ml methylcyclohexane at 60 °C, 45 barg, 2.5 µmol $Cracac_3$, 300 eq. MMAO-3A; 2:1 Cr:ligand ratio.

[b] $S_\alpha = 1\text{-}C_6 + 1\text{-}C_8$.

eties on the N-atom. A clear distinction was made between the basicity and steric bulk effects of each N-substituent, with the latter being the dominant parameter influencing the reaction selectivity. A significant rate improvement was observed when the reactions were carried out in an aliphatic medium (methylcyclohexane) relative to those performed in toluene. Two bifunctional PNP ligands were also tested and yielded selective tetramerisation catalysts, providing similar selectivities to their single-site analogues. *N*-heteroatom substitution (trimethylsilyl-PNP) also yielded a highly active tetramerisation catalyst. We conclude that α-branching (i.e., further substitution of the carbon atom attached directly to the N-atom of the PNP ligand) is essential for obtaining highly selective tetramerisation catalysts, with the best systems achieving total alpha selectivities as high as 88% with exceptional catalyst activities (up to 3,200,000 $g/(g_{Cr}\,h)$).

Supporting information

The online version on this article contains additional supplementary information.

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