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# A rational approach towards selective ethylene oligomerization *via* PNP-ligand design with an *N*-triptycene functionality†

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**Novel PNP ligands bearing an *N*-triptycene backbone were developed and evaluated for selective ethylene oligomerization. Upon activation with MMAO-3A, the pre-catalyst mixture containing $Cr(acac)_3$/ligand efficiently promotes ethylene tetramerization with remarkably high productivities (up to 1733 kg $g_{Cr}^{-1}$ $h^{-1}$) and $C_8$ olefin selectivities (up to 74.1 wt%). More importantly, ligands with a PNP moiety connecting at the 1- or 1,4-position of the triptycene molecule could achieve exceptionally high alpha (1-$C_6$ + 1-$C_8$) selectivities, exceeding 90 wt%, as a result of high 1-$C_6$ purity (>90 wt%) in the $C_6$ fraction. Based on comparative catalytic studies employing various PNP ligands with or without an *N*-triptycene backbone, we illustrate the fact that a rational design of PNP ligands with an optimum degree of steric profile around the N-center could provide $C_6$ cyclics controlled highly α-selective ethylene oligomerization.**

Owing to the superior material properties of the copolymers derived from 1-hexene/1-octene over other alpha olefins, the search for a catalytic system to selectively produce $C_6$/$C_8$ α-olefins *via* ethylene tri-/tetramerization has witnessed a steady upsurge in recent years.[1–7] Most notably, following the emergence of Sasol's initial reports on tetramerization, the chromium-based pre-catalysts where the metal center is stabilized by bidentate phosphine ligands,[8–18] in particular bisphosphineamines (PNPs),[8–12] have received considerable attention. Since the *N*-substituents of the PNP ligands are believed to play a critical role in oligomerization performance, numerous *N*-functionalized PNP ligands have been developed and investigated for this purpose.[6,19] Indeed, based on systematic studies utilizing various *N*-alkyl/-aryl substituted PNP ligands, it was established that the steric profile of the *N*-substituent could play a pivotal role in achieving selective catalysis.[10,11,20,21] In a rational approach to this end, we sought to introduce a triptycene backbone as the N-substituent with an anticipation that its unique paddle-wheel configuration with $D_{3h}$ symmetry coupled with an inherent β-branching with respect to the PNP moiety at the 1- or 1,4-position of the triptycene backbone, may provide favorable steric bulkiness (supported by the computational study, *vide infra*) required for a selective oligomerization reaction.[22,23] Specifically, we report here the preparation of *N*-triptycene substituted PNP ligands **1** and **2** (Fig. 1) possessing a unique steric environment around the N-center and evaluate its impact on selective ethylene tetramerization reaction. Furthermore, additional *N*-triptycene substituted PNP ligands, **3** and **4**, with an alternative steric profile, where the effect of β-branching was on purpose precluded by sifting the PNP moiety at the 2,6- or 2-position of the triptycene backbone (Fig. 1), was developed and studied for comparison purposes.

The steric influence of N-substituents of PNP ligands on the 1-$C_8$/1-$C_6$ ratio has been previously explored *via* effective

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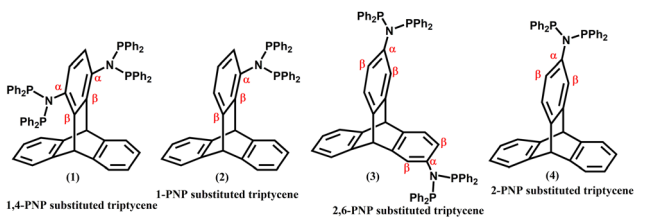


Fig. 1 The targeted *N*-triptycene functionalized PNP ligands **1** and **2** featuring inherent β-branching site(s) and their corresponding isomeric ligands **3** and **4**, respectively, without β-branching site(s).

Tolman-based cone angles, which are only comparable for *N*-alkyl derivatives.[24] In seeking to computationally identify promising *N*-aryl substituents especially bearing a triptycene moiety (*vide supra*), we first developed a metric that would allow steric comparisons between different PNP compounds: percent buried volume about the nitrogen center, $\%V_{Bur}(N)$, as calculated by SambVca.[25] Across a representative sample of ligands and data from the literature, better catalytic performance is achieved with $\%V_{Bur}(N)$ between 88–92 (see Fig. S1, ESI†). For **1**, $\%V_{Bur}(N)$ was estimated to be 91.1, which is well within the desirable range. In comparison, the $\%V_{Bur}(N)$ values of isopropyl-N$(PPh_2)_2$ (**5**, often used as a benchmark ligand in ethylene tetramerization studies)[8] and $C_6H_4$(*m*-$CF_3$)N$(PPh_2)_2$ (**6**, a ligand recently investigated by us to catalyze highly active and octene selective ethylene tetramerization)[26] are 88.9 and 88.5, respectively. Additionally, by using a computational method recently reported by us,[21] the stability energy of the bis-PNP species (**1**) over its hypothetical PNP-PPN isomer was predicted. The results suggest that the former should be stable by about 0.5 kcal $mol^{-1}$. While not exceptionally high, this stability against PNP-to-PPN isomerization is comparable to that of **6** (0.6 kcal $mol^{-1}$), which yielded low amounts of PE,[26] and further encouraged us to develop **1**.

To access the ditopic PNP ligand, the precursor 1,4-triptycenediamine (synthesized by a multistep reaction procedure reported in the literature),[22,27] was treated with four equivalents of chlorodiphenylphosphine in the presence of a triethylamine base. Which resulted in off-white powder compound **1** in moderate yield (see Section S3, ESI† for details).‡ The solution $^{31}P$ NMR spectrum of **1** shows an intense peak at 59.34 ppm, which is consistent with the phosphorus chemical shift value typically observed for the PNP-type ligands.[8] The $^{1}H$ and $^{13}C$ NMR signals are also in accordance with the expected PNP ligand (Fig. S2, ESI†). The elemental composition of **1** was confirmed by microanalysis studies. For synthesizing ligands **2**, possessing a PNP moiety at the 1-position of the triptycene molecule, we first prepared the amine precursor (1-triptyceneamine) *via* selective deamination of 1,4-triptycenediamine followed by reaction with chlorodiphenylphosphine (Scheme S2, ESI†). Both the amine precursor and the ligand **2** were thoroughly characterized by NMR spectroscopy as well as microanalysis studies (see ESI† for detail). The appearance of the $^{31}P$ signal at 60.09 ppm for **2** (Fig. S4, ESI†) confirms the presence of the PNP moiety.

With the two targeted PNP ligands in hand, we first studied chromium-catalyzed ethylene oligomerization at 45 bar pressure using **1** in detail. The data presented in Table 1 (entries 1–3) and Fig. 2 reveal that in aliphatic solvents such as cyclohexane, methylcyclohexane, and decahydronaphthalene, the Cr(acac)$_3$/**1**/MMAO-3A system can promote highly efficient ethylene tetramerization with outstanding $C_8$ olefin selectivities (up to 72.3 wt%) at rates over 1000 kg $g_{Cr}^{-1}$ $h^{-1}$. A slightly inferior catalytic result was obtained in isooctane (entry 4), although the formation of unwanted solid and $C_{10}$+ byproducts (combined selectivity $<0.2$ wt% *vs.* 0.5–1.4 wt% in other aliphatic solvents) was minimum. The reaction in chlorobenzene on the other hand gave significantly higher reactivity (1717 kg $g_{Cr}^{-1}$ $h^{-1}$) but the $C_8$ olefin selectivity was relatively low at 57.5 wt% (entry 5). Conversely, an increased selectivity towards $C_6$ olefins ($\sim$41 wt%) was observed. The total alpha selectivities (1-$C_6$ + 1-$C_8$), however, in all solvents were exceptionally high ($>$92 wt%) primarily due to high 1-$C_6$ purity in the $C_6$ fraction (typically exceeding 90 wt%). A similar alpha selective (94.9 wt%) ethylene oligomerization was also observed when a ligand **2**-based system, *i.e.* Cr(acac)$_3$/**2**/MMAO-3A, was employed as a pre-catalyst (entry 6). The 1-$C_6$ purity of 93.3 wt% in the $C_6$ fraction at a reaction rate of 1544 kg $g_{Cr}^{-1}$ $h^{-1}$ was achieved. The later system also yielded slightly improved $C_8$ fraction (63.2 wt% *vs.* 57.5 wt% for **1**) at 45 °C. In a direct comparison to **1**, ligand **7**[6] ([[$(PPh_2)N]_2$-(*p*-$C_6H_4$)) having similar basic structural features but devoid of the bulky bridgehead functional moiety connecting at the β-position, as illustrated in red color (Fig. 3), resulted in only 64.6% (*vs.* 95.3% for **1**) 1-$C_6$ purity in the $C_6$ fraction (Table 1, entry 7). Consequently, the total alpha selectivity (81.8 wt%) achieved was significantly low. Similarly, catalytic reaction using ligand **8** (see Section S3, ESI† for synthesis detail), resembling an identical 2,3-disubstituted *N*-aryl substructure to **2** but without having the dihydroanthracenyl moiety (illustrated in dark blue) also gave much inferior 1-$C_6$ purity (58 wt% in $C_6$) and total alpha selectivity

Table 1 Ethylene tetramerization using the Cr(acac)$_3$/L/MMAO-3A system

| | | | | Product selectivity (wt%) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Entry | L | Solvent | Productivity (kg $g_{Cr}^{-1}$ $h^{-1}$) | $C_6$ | 1-$C_6$ (in $C_6$) | $C_8$ | 1-$C_8$(in $C_8$) | 1-$C_6$ + 1-$C_8$ | $C_{10}$+ | PE |
| 1 | **1** | CyH | 1098 | 27.6 | 90.1 | 71.9 | 96.2 | 94.1 | 0.3 | 0.2 |
| 2 | **1** | MeCy | 1186 | 27.2 | 90.6 | 72.3 | 96.8 | 94.6 | 0.3 | 0.2 |
| 3 | **1** | DHN | 1009 | 28.5 | 91.1 | 70.1 | 95.4 | 92.8 | 0.2 | 1.2 |
| 4 | **1** | Isooctane | 755 | 30.6 | 92.4 | 69.3 | 94.8 | 93.9 | 0.1 | $<0.1$ |
| 5 | **1** | PhCl | 1717 | 40.9 | 95.3 | 57.5 | 98.2 | 95.4 | 0.1 | 1.5 |
| 6[a] | **2** | PhCl | 1544 | 35.4 | 93.3 | 63.2 | 98.0 | 94.9 | 0.3 | 1.0 |
| 7 | **7** | PhCl | 403 | 26.9 | 64.6 | 69.4 | 92.8 | 81.8 | 1.8 | 2.0 |
| 8[a] | **8** | PhCl | 1661 | 30.3 | 58.0 | 66.8 | 97.1 | 82.4 | 2.1 | 0.8 |
| 9[a] | **5** | PhCl | 1184 | 22.8 | 81.6 | 72.0 | 97.1 | 88.5 | 1.6 | 3.5 |
| 10[a] | **6** | PhCl | 1492 | 24.1 | 56.1 | 72.5 | 95.2 | 82.5 | 2.6 | 0.8 |
| 11 | **3** | PhCl | 1733 | 23.1 | 58.2 | 73.9 | 95.4 | 83.9 | 2.8 | 0.2 |
| 12[a] | **4** | PhCl | 1649 | 22.6 | 63.5 | 74.1 | 96.7 | 86.0 | 2.1 | 1.2 |

Conditions: Cr(acac)$_3$ 1 μmol, L/Cr = 0.5, MMAO-3A 2 mmol (Al/Cr 2000), Total solution volume 100 mL, 45 °C, 45 bar, 10 min. [a] L/Cr = 1. CyH (cyclohexane), MeCy (methylcyclohexane), DHN (decahydronaphthalene), isooctane (2,2,4-Trimethylpentane), and PhCl (chlorobenzene).

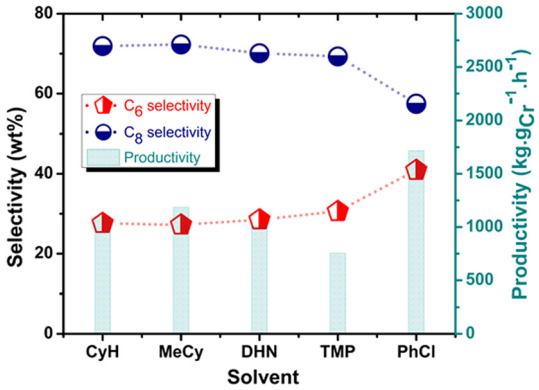


Fig. 2 The effect of solvent at 45 °C on $C_6$ and $C_8$ olefin selectivity and productivity using the Cr(acac)$_3$/**1**/MMAO-3A catalytic system. Reaction conditions: Cr(acac)$_3$ 1 μmol, L/Cr (0.5), MMAO-3A 2 mmol (Al/Cr 2000), 45 bar, 10 min.

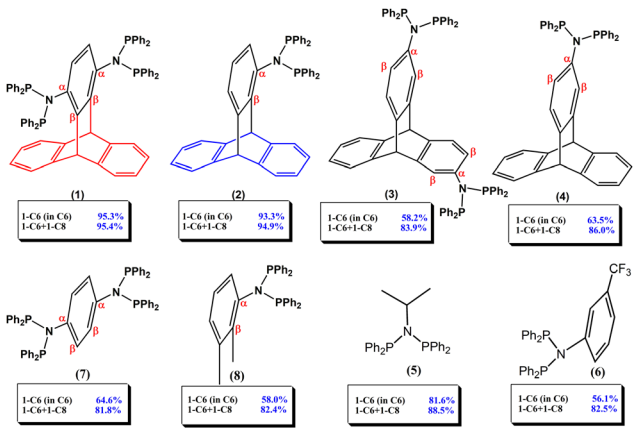


Fig. 3 Illustration of the ligands **1-8** and their exhibited selectivity towards 1-$C_6$ in the $C_6$ fraction and total alpha selectivity.

(82.4 wt%) (entry 8). Moreover, under the identical condition the Sasol's benchmark ligand **5** bearing α-branching and **6** (with *N*-aryl substitution) are also shown to exhibit significantly lower 1-$C_6$ purity and alpha selectivities (entries 9, 10 and Fig. 3).[8,26] To the best of our knowledge, alpha selectivity >92% coupled with productivities in excess of 1000 kg $g_{Cr}^{-1}$ $h^{-1}$, as achieved using **1** and **2**, has never been reported for any Cr-based catalyst supported by $[(Ph_2P)_2N]_nAr$ (Ar = aryl, $n$ = 1–3)-type PNP ligands.[6,11,20] These results clearly substantiate the impact of an appropriately decorated steric environment around the N-center, achieved through incorporating the *N*-triptycene backbone in **1** and **2**, to mitigate the formation of unwanted $C_6$ cyclic byproducts and to elevate alpha selectivities. This was further corroborated by the catalytic results, exhibiting 1-$C_6$ and total alpha selectivities only in the range of 58–63 wt% and 84–86 wt%, respectively (Table 1, entries 11 and 12), obtained using PNP ligands **3** and **4** (see Section S3, ESI† for details of preparation and characterization) where the effect of β-branching was on purpose ruled out by shifting the PNP moiety at the 2,6- or 2-position of the triptycene molecule. Nevertheless, the later ligand-based pre-catalysts were able to achieve considerably higher $C_8$ olefin selectivities (up to 74.1 wt%), thus indicating a relatively facile formation of the metallacyclononane intermediate around the Cr-center as compared to the ligand **1** or **2** based pre-catalyst system.

Higher catalytic activity of Cr(acac)$_3$/**1**/MMAO-3A in chlorobenzene over other aliphatic solvents is consistent with our recent study using ligand **6**,[26] where a correlation between the solvent polarity and catalyst productivity was envisaged. Therefore, solvents with higher polarity were expected to impart greater charge separation between a cationic chromium and a bulky MAO-derived anion.

To increase $C_8$ olefin selectivity coupled with high total alpha selectivity in chlorobenzene, the effect of temperature was studied using the Cr(acac)$_3$/**1**/MMAO-3A system. The data summarized in Table 2 and Fig. 4 reveals that lower reaction temperatures, *i.e.* 38 and 30 °C, can indeed improve the $C_8$ olefin selectivities to 62.3 and 68.3 wt%, respectively, at the expense of $C_6$ olefin selectivity (entries 2 and 3), although a notable drop in reactivity was observed. The Cr(acac)$_3$/**2**/MMAO-3A system on the other hand at 38 °C achieved slightly better $C_8$ selectivity (67.9 wt%, entry 4), a trend previously observed at 45 °C. The 1-$C_6$ and total alpha selectivities however, as expected, were maintained above 91 wt% under the different reaction temperatures studied for both the pre-catalyst systems.

In summary, targeted PNP ligands **1** and **2** possessing an *N*-triptycene functionality were developed in a systematic approach. Upon activation with MMAO-3A, the novel catalyst system exhibited exceptionally high alpha selective (up to 96 wt%) ethylene tetramerization with activities exceeding 1000 kg $g_{Cr}^{-1}$ $h^{-1}$ and C8 olefin selectivities in excess of 70 wt%. Based on a detailed comparative study, we illustrate the fact that the designing of *N*-aryl functionalized PNP ligands with β-branching coupled with a well-defined steric bulk around the N-center could pave the way to accomplishing optimum α-selective catalysis.

Table 2 Temperature-dependent ethylene tetramerization using the Cr(acac)$_3$/**1**/MMAO-3A system in chlorobenzene

| | | | Product selectivity (wt%) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Entry | Temp. (°C) | Productivity (kg $g_{Cr}^{-1}$ $h^{-1}$) | $C_6$ | 1-$C_6$ (in $C_6$) | $C_8$ | 1-$C_8$ (in $C_8$) | 1-$C_6$ + 1-$C_8$ | $C_{10}$+ | PE |
| 1 | 45 | 1717 | 40.9 | 95.3 | 57.5 | 98.2 | 95.4 | 0.1 | 1.5 |
| 2 | 38 | 1394 | 37.1 | 94.7 | 62.3 | 98 | 96.2 | 0.2 | 0.4 |
| 3 | 30 | 928 | 29.7 | 92.6 | 68.3 | 97 | 93.8 | 0.2 | 1.8 |
| 4[a] | 38 | 1361 | 31.3 | 91.6 | 67.9 | 99.6 | 96.2 | 0.2 | 0.6 |

Conditions: Cr(acac)$_3$ 1 μmol, L/Cr (0.5), MMAO-3A 2 mmol (Al/Cr 2000), total solution volume 100 mL, 45 bar, 10 min. [a] Using ligand **2**, L/Cr 1

 

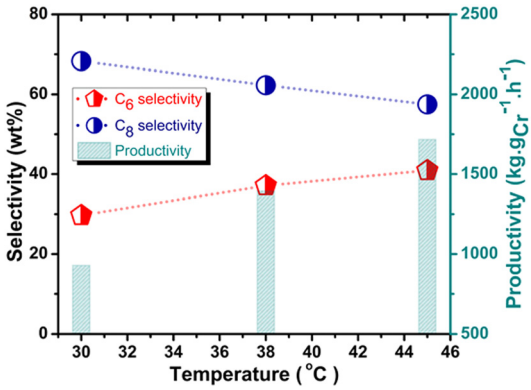


Fig. 4 The effect of temperature in chlorobenzene on $C_6$ and $C_8$ olefin selectivity and productivity using the $Cr(acac)_3$/**1**/MMAO-3A catalytic system. Reaction conditions: $Cr(acac)_3$ 1 μmol, L/Cr 0.5, MMAO-3A 2 mmol (Al/Cr 2000), 45 bar, 10 min.

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## Conflicts of interest

There are no conflicts to declare.

## References

‡ To a solution of 1,4-triptycenediamine (0.161 g, 0.567 mmol) and triethylamine (0.34 g, 3.4 mmol) in 8 mL dichloromethane, $Ph_2PCl$ (0.5 g, 2.26 mmol) dissolved in 2 mL dichloromethane was slowly added at 0 °C. The reaction mixture was stirred at this temperature for 1 h and then allowed to warm up to rt followed by additional stirring for 12 h. After this time, the solvent was removed under reduced pressure and the residue was extracted with anhydrous THF (3 × 5 mL). After removal of the THF solvent the remaining solid residue was triturated with dry $CH_3CN$ (3 × 4 mL) followed by vacuum drying at 40 °C for 6 h to yield ligand **1**. Yield: 0.27 g, 47%. $^1$H NMR ($CDCl_3$): $\delta$ 7.44–6.80 (m, aromatic H), 5.81 (s, 2H, aromatic), 5.55 (s, 2 tertiary H) ppm; $^{13}$C NMR ($CDCl_3$): 49.31, 123.81, 124.64, 125.88, 128.02, 128.43, 129.50, 132.51, 132.71, 133.77, 134.01, 139.52, 142.15, 143.76, 144.98 ppm; $^{31}$P NMR ($CDCl_3$): $\delta$ 59.34 (s) ppm. Anal. calc. for $C_{68}H_{52}N_2P_4$: H 5.13, C 79.99, N 2.74%. Found H 4.6, C 79.14, N 3.52%.

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