Highly Efficient Ethylene Tetramerization Using Cr Catalysts Constructed with Trifluoromethyl-Substituted N-Aryl PNP Ligands

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ABSTRACT: Tetramerization of ethylene by chromium catalysts stabilized with functionalized N-aryl phosphineamine ligands C6H4(m-CF3)N(PPh2)2 (1), C6H4(p-CF3)N(PPh2)2 (2), C6H4(o-CF3)N=PPh2-PPh2 (3), and C6H3(3,5-bis(CF3))N(PPh2)2 (4) was evaluated. The parameter optimization includes temperature, co-catalyst, and solvent. Upon activation with MMAO-3A, the new catalyst system especially with m-functional PNP ligand (1) exhibited high 1-octene selectivity and productivity while giving minimum undesirable polyethylene and C10+ olefin by-products. Using PhCl as a solvent at 75 °C led to a remarkable α-olefin (1-C6 + 1-C8) selectivity (>90 wt %) at a reaction rate of 2000 kg-gCr−1·h−1. Under identical conditions, analogous PNP ligands bearing −CH3, −Et, and −Cl functional moieties at the meta position of the N-phenyl ring displayed significantly lower reactivity. The catalyst with p-functional ligand (2) exhibited lower activity and comparable selectivities, while the Cr/PPN (with ligand 3) system gave no noticeable reactivity. The molecular structure of the precatalyst (1-Cr), exhibiting a monomeric structural feature, was elucidated with the aid of single-crystal X-ray diffraction study.

1. INTRODUCTION

Selective ethylene oligomerization to linear α-olefins (LAOs) is an increasingly important route to access valuable comonomers, such as 1-hexene and 1-octene, which are in high demand and are used extensively in the production of linear low-density polyethylene (LLDPE).1−8 The catalytic reaction employing bidentate phosphine ligands,9−19 especially PNP,9−13 with chromium to promote selective tri/tetramerization emerged as a topic of great interest. In addition, the effect of N-substituents of the PNP ligand on productivity and selectivity toward 1-octene has been widely investigated.9 The N-aryl-functionalized ligands encompassing various electron-withdrawing/donating groups at the ortho/para positions of the N-phenyl ring were first systematically studied by Killian et al.12 It was evident that the addition of sufficient steric bulk to the N-phenyl group via ortho-alkyl substitution or through introduction of a suitable spacer unit between the N-atom and the aryl-moiety, as well as the addition of branching on this unit, could significantly enhance the combined α-olefin selectivity up to 84 wt %. Additional studies involving N-aryl-functionalized ligands revealed that the substituents at the meta position, in particular, can have significant incremental effects on the reaction rate as well as 1-octene selectivity.20,21

In an endeavor to this end, we sought to develop a chromium-based catalyst system supported by N-aryl-functionalized PNP ligands (C6H4(m-CF3)N(PPh2)2 (1), C6H4(p-CF3)N(PPh2)2 (2),22 and C6H4(o-CF3)N=PPh2-PPh2 (3)23) bearing an electron-withdrawing trifluoromethyl (−CF3) group at various positions of the aniline moiety (Scheme 1) and investigate the effect of the −CF3 functional moiety, with a particular emphasis on meta-substituted ligand 1, on ethylene tetramerization performance.

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Scheme 1. Brief Outline of the Synthetic Scheme for the Preparation of Ligands 1–3

Table 1. Temperature-Dependent Ethylene Tetramerization Using the Cr(acac)₃/1/MMAO-3A System

| entry | temp (°C) | productivity (kg·g⁻¹·h⁻¹) | 1-C₆ | I-C₆ cycles | I-C₆⁺I-C₄ | C₁₀⁺PE | product selectivity (wt %) |
|-------|-----------|-----------------------------|------|-------------|------------|--------|---------------------------|
| 3    | 75        | 236                         | 11.4 | 8.9         | 73.2       | 84.4   | 4.3                        |
| 4    | 75        | 315                         | 18.1 | 7.7         | 69.4       | 87.5   | 2.3                        |
| 5    | 75        | 551                         | 18.2 | 8.2         | 69.1       | 87.3   | 1.1                        |
| 6    | 75        | 789                         | 19.1 | 7.4         | 69.6       | 88.3   | 1.1                        |
| 8    | 75        | 700                         | 20.2 | 6.7         | 67.8       | 88.0   | 1.5                        |
| 9    | 90        | 208                         | 22.0 | 12.4        | 59.0       | 81.0   | 2.2                        |

Conditions: Cr(acac)₃ (2 μmol), 1/Cr (1), MMAO-3A (2 mmol; Al/Cr 1000), cyclohexane (total reaction volume, 100 mL), 45 bar, 30 min (productivity in kg·mol⁻¹·h⁻¹), see Table S3; a 1/Cr (1.2); b Cr(acac)₃ (1 μmol), Al/Cr 2000; c Cr(acac)₃ (1 μmol), Al/Cr 2000, 10 min; d Al/Cr 2000, total solution volume of 150 mL, 10 min.
The reaction temperature was maintained constant during the reaction by circulating hot oil in the jacket and by allowing the cool liquid to flow from the chiller through the cooling coil present inside the reactor vessel. The SCADA software controlled the reaction temperature and pressure of the reactor precisely using an electronic controller. Ethylene was fed on demand to keep the reactor pressure constant, and the uptake was monitored using a mass flow controller (MFC).

After the desired reaction time, 2 mL methanol was injected to quench the reaction which was then cooled and depressurized slowly to atmospheric pressure. The small portion of the crude products was filtered and analyzed by GC-FID using nonane as an internal standard. The remaining mixture was added to 50 mL of acidic methanol (5% HCl), and the polymeric products were recovered by filtration and washed with distilled water (3 × 50 mL) followed by drying at 60 °C under vacuum.

| entry | solvent | productivity (kg g⁻¹ h⁻¹) | 1-C₆ | C₆ cyclics | 1-C₈ | 1-C₆ + 1-C₈ | C₁₀+ | PE |
|-------|---------|--------------------------|------|------------|------|-------------|------|----|
| 1     | CyH     | 789                      | 19.1 | 7.4        | 69.3 | 88.3        | 1.1  | 1.0|
| 2     | MeCy   | 447                      | 20.8 | 9.0        | 69.4 | 79.6        | 4.7  | 2.0|
| 3     | TMP     | 281                      | 22.5 | 7.5        | 69.3 | 81.0        | 5.1  | 2.8|
| 4     | PhCl    | 2000                     | 31.0 | 6.2        | 59.5 | 90.5        | 0.6  | 0.9|

**Table 3.** Solvent Effect on Ethylene Tetramerization Using the Cr(acac)₃/1/MMAO-3A System at 75 °C

| entry | R       | productivity (kg g⁻¹ h⁻¹) | 1-C₆ | C₆ cyclics | 1-C₈ | 1-C₆ + 1-C₈ | C₁₀+ | PE |
|-------|---------|--------------------------|------|------------|------|-------------|------|----|
| 1     | m-CF₃  | 2000                     | 31.0 | 6.2        | 59.5 | 90.5        | 0.6  | 0.9|
| 2     | m-CH₃  | 999                      | 29.5 | 5.8        | 60.2 | 89.7        | 0.2  | 1.7|
| 3     | m-C₆H₅ | 1377                     | 29.6 | 6.1        | 61.2 | 90.8        | 0.6  | 0.7|
| 4     | bis m-CH₃ | 1127                   | 29.8 | 5.9        | 60.5 | 90.3        | 0.4  | 2.1|
| 5     | m-Cl   | 661                      | 29.4 | 5.8        | 53.9 | 83.3        | 0.2  | 8.7|
| 6     | bis m-CF₃ | 329                     | 30.9 | 6.7        | 52.5 | 83.4        | 0.1  | 5.2|

**Table 4.** Temperature-Dependent Ethylene Tetramerization Using Cr Catalysts Supported with 1 and Sasol’s Benchmark Ligand

| entry | temp (°C) | productivity (kg g⁻¹ h⁻¹) | 1-C₆ | C₆ cyclics | 1-C₈ | 1-C₆ + 1-C₈ | C₁₀+ | PE |
|-------|-----------|--------------------------|------|------------|------|-------------|------|----|
| 1⁺    | 75        | 2000                     | 31.0 | 6.2        | 59.5 | 90.5        | 0.6  | 0.9|
| 2⁺    | 60        | 1852                     | 20.6 | 7.9        | 67.7 | 88.3        | 1.4  | 0.7|
| 3⁺    | 45        | 1492                     | 13.5 | 10.6       | 69.1 | 82.5        | 2.6  | 0.8|
| 4⁺    | 45        | 1184                     | 18.6 | 4.2        | 69.9 | 88.5        | 1.6  | 3.5|
| 5⁺    | 60        | 680                      | 28.7 | 3.5        | 59.7 | 88.4        | 1.7  | 3.1|
| 6⁺    | 75        | 502                      | 40.2 | 3.1        | 49.4 | 89.6        | 2.0  | 2.9|

**Table 2.** Solvent Effect on Ethylene Tetramerization Using the Cr(acac)₃/1/MMAO-3A System at 75 °C

| entry | solvent | productivity (kg g⁻¹ h⁻¹) | 1-C₆ | C₆ cyclics | 1-C₈ | 1-C₆ + 1-C₈ | C₁₀+ | PE |
|-------|---------|--------------------------|------|------------|------|-------------|------|----|
| 1     | CyH     | 789                      | 19.1 | 7.4        | 69.3 | 88.3        | 1.1  | 1.0|
| 2     | MeCy   | 447                      | 20.8 | 9.0        | 69.4 | 79.6        | 4.7  | 2.0|
| 3     | TMP     | 281                      | 22.5 | 7.5        | 69.3 | 81.0        | 5.1  | 2.8|
| 4     | PhCl    | 2000                     | 31.0 | 6.2        | 59.5 | 90.5        | 0.6  | 0.9|

**Table 3.** Effects of meta-Substituents (−R) of the N-Aryl PNP Ligands on Catalytic Activity and Product Selectivity at 75 °C

The reaction temperature was maintained constant during the reaction by circulating hot oil in the jacket and by allowing the cool liquid to flow from the chiller through the cooling coil present inside the reactor vessel. The SCADA software controlled the reaction temperature and pressure of the reactor precisely using an electronic controller. Ethylene was fed on demand to keep the reactor pressure constant, and the uptake was monitored using a mass flow controller (MFC). After the desired reaction time, 2 mL methanol was injected to quench the reaction which was then cooled and depressurized slowly to atmospheric pressure. The small portion of the crude products was filtered and analyzed by GC-FID using nonane as an internal standard. The remaining mixture was added to 50 mL of acidic methanol (5% HCl), and the polymeric products were recovered by filtration and washed with distilled water (3 × 50 mL) followed by drying at 60 °C under vacuum.

**Figure 1.** Effect of temperature (a) and co-catalysts at 75 °C (b) on C₆ and C₈ olefin selectivity and productivity using the Cr(acac)₃/1/ aluminoxane catalytic system in CyH. Reaction conditions: (for a) Cr(acac)₃ (2 μmol), 1/Cr (1), MMAO-3A (2 mmol; Al/Cr 2000), 45 bar, 30 min; (for b) Cr(acac)₃ (1 μmol), Al/Cr 2000, 45 bar, 30 min.
3. RESULTS AND DISCUSSION

The treatment of C₆H₄(m-CF₃)NH₂ with 2 equiv of chlorodiphenylphosphine in the presence of triethylamine resulted in the white powder material 1 in good yield (see Section 2.1 for details). Employing C₆H₄(o-CF₃)NH₂ in place of m-CF₃-substituted aniline under an identical reaction condition yielded isomeric compound 3. The 31P NMR spectrum of 1 (Figure S1a, Supporting Information) shows an intense single peak at 67.63 ppm, a chemical shift value which could typically be attributed to the P-atom of the PNP-type ligands. The 1H and 13C NMR spectra (Figure S2) of 1 also support the formation of the expected PNP ligand. On the other hand, the 31P NMR spectrum of 3 (Figure S1b, Supporting Information) shows a doublet peak at 67.63 ppm with a J value of 33 Hz, indicating the presence of a PNP-type ligand.

Table 5. Chromium-Catalyzed Ethylene Tetramerization Using CrCl₃·3THF/2/MMAO-3A

| entry | solvent | temp (°C) | productivity (kg C₆·g⁻¹·h⁻¹) | product selectivity (wt %) |
|-------|---------|-----------|-------------------------------|-----------------------------|
| 1     | PhCl    | 75        | 89                            | 1-C₆ 2.5 1-C₈ 5.5 C₁₀⁺ 0.1 PE 94.0 |
| 2     | PhCl    | 75        | 522                           | 1-C₆ 5.5 1-C₈ 88.5 C₁₀⁺ 0.1 PE 29.0 |
| 3     | PhCl    | 75        | 1329                          | 1-C₆ 5.9 1-C₈ 59.8 C₁₀⁺ 0.4 PE 2.9 |
| 4     | PhCl    | 75        | 1168                          | 1-C₆ 5.9 1-C₈ 59.8 C₁₀⁺ 0.4 PE 1.9 |
| 5     | PhCl    | 75        | 1168                          | 1-C₆ 5.9 1-C₈ 59.8 C₁₀⁺ 0.4 PE 1.9 |
| 6     | PhCl    | 75        | 1168                          | 1-C₆ 5.9 1-C₈ 59.8 C₁₀⁺ 0.4 PE 1.9 |
| 7     | PhCl    | 75        | 1168                          | 1-C₆ 5.9 1-C₈ 59.8 C₁₀⁺ 0.4 PE 1.9 |

Conditions: CrCl₃·3THF (1 μmol), MMAO-3A (2 mmol; Al/Cr 2000), ligand/Cr = 1, total solution volume of 100 mL, 45 bar, 10 min (productivity in kg mol⁻¹ Cr⁻¹ h⁻¹, see Table S6); Cr(acac)₃, ligand 3; Cr(acac)₃.
other hand, the $^{31}$P NMR spectrum of 3 in $\text{C}_{6}\text{D}_{6}$ (Figure S1c) displayed two sets of doublets centered at 2.34 and $-1.89$ ppm with a $J_{P-P}$ value of 259.2 Hz, which suggests the formation of iminobiphosphine (PPN), consistent with a literature report.$^{23}$ The $^{31}$P NMR spectrum of 2 in CCl$_4$ (Figure S1b) shows only one intense peak at 66.78 ppm, which is in accordance with the literature data.$^{22}$ Ligand 2 was further characterized by single-crystal X-ray diffraction study, which reveals the molecular structure of the expected compound (Figure S6 and Table S2).

With the $-\text{CF}_3$-substituted ligands in hand, we first investigated ethylene oligomerization using an in situ-formed precataylsis system (in which ligand 1 was combined with Cr(acac)$_3$ in desired solvents) at 45 bar pressure. To achieve optimal productivity and 1-ocetene selectivity, the reaction parameters such as temperature (30–90 °C),$^{24}$ co-catalyst (MAO, MMAO-12, and MMAO-3A), L/Cr ratio, Al/Cr ratio, and solvent type such as nonpolar methyclohexane (MeCy), cyclohexane (Cy), decalynaphthalene (DHN), 2,2,4-trimethylpentane (TMP), and polar chlorobenzene (PhCl) were systematically examined (Tables 1–4 and Figures 1–3). Based on the data presented in Table 1, it is apparent that at mild temperature (30 °C), the Cr(acac)$_3$/1/MMAO-3A system is able to catalyze ethylene oligomerization in cyclohexane (CyH) solvent, which results in an activity of 12 kg g$_{\text{Cr}}$$^{-1}$ h$^{-1}$ with a moderate 1-C$_6$ olefin selectivity of 58.6 wt % (entry 1). Reaction at 45 °C yielded a higher productivity (116 kg g$_{\text{Cr}}$$^{-1}$ h$^{-1}$) in conjunction with a high 1-C$_6$ olefin selectivity (69.4 wt %, entry 2). Note that the PE formation was suppressed by many folds as compared to that observed at 30 °C (12.7 wt % vs 2 wt % at 45 °C). When the 1/Cr ratio of 1.2 was applied, nearly identical results in terms of productivity and 1-C$_6$ olefin selectivity were observed (entry 3). Interestingly, a further increase in reaction temperature led to even improved catalytic performance (entries 4–8) with the highest productivity of 789 kg g$_{\text{Cr}}$$^{-1}$ h$^{-1}$ (1-C$_6$ olefin selectivity of 69.3 wt %) being achieved at 75 °C (entry 7) for a reaction time of 10 min, although the 1-C$_6$ olefin selectivity was slightly better at 60 °C (73.2 wt %) at a productivity of 236 kg g$_{\text{Cr}}$$^{-1}$ h$^{-1}$ (obtained after 30 min of reaction time, entry 4). It is also important to note that the PE formations at these reaction temperatures were significantly reduced (<1 wt %). At higher temperature (90 °C), the Cr(acac)$_3$/1/MMAO-3A system was active; however, it yielded relatively lower productivity with reduced selectivity toward 1-C$_6$ olefins (entry 9). Overall, the above studies illustrate that the temperature range of 45–75 °C (Figure 1a) could be optimum for achieving better 1-C$_6$ olefin selectivity (69–73 wt %), which tends to drop either at higher or lower temperatures. Moreover, the 1-C$_6$ olefin selectivity remains modestly stable up to 60 °C (entries 1–4) but increases at higher reaction temperatures (entries 5–9). The 1-C$_6$ + 1-C$_8$ selectivity on the other hand increases gradually from 70.5 to 87.5 wt % as the temperature of the reaction is increased from 30 to 75 °C (Table 1, entries 1–5).

After determining the temperature-dependent tetramerization performance, the impact of different co-catalysts in the CyH solvent was studied. The obtained results, summarized in Table S1, reveal that both methylalumin oxide (MAO) and modified methylaluminoxanes (MMAO-3A and MMAO-12) can serve as activators; however, the rate of the reaction and 1-ocetene selectivity achievable using MMAO-3A are significantly higher (Figure 1b). Moreover, 1-hexene formation is relatively higher in the MMAO-12-based system. It is worth mentioning at this point that the superiority of the MMAO-3A activator over other aluminoxanes in the ethylene tetramerization process was recently studied with the aid of multitechnique in situ spectroscopic studies, where the bidentate coordination of the ligand to form an active (PNP)Cr$_{(3)}$(CH$_3$)$_2$ chelate complex was suggested.$^{25}$

Next, we studied the effect of selected solvents such as CyH, MeCy, TMP, and PhCl on the tetramerization performance using the Cr(acac)$_3$/1/MMAO-3A system at 75 °C. The results presented in Table 2 evidence that PhCl clearly outperforms others in terms of productivity, which reached 2000 kg g$_{\text{Cr}}$$^{-1}$ h$^{-1}$ (entry 4 and Figure 2a),$^{26}$ although the 1-C$_8$ olefin selectivities in CyH, MeCy, and TMP (entries 1–3) were relatively higher (∼69.3 wt % vs 59.5 wt % in PhCl). In addition, the reaction in PhCl yielded the highest total α-olefin (1-C$_6$ + 1-C$_8$) selectivity of 90.5 wt % followed by 88.3 wt % in CyH. Moreover, the formation of cyclic by-products such as methylcyclopentane and methylecyclopentane was minimum in PhCl, which in turn resulted in the best 1-C$_6$ selectivity of ∼31 wt % (83% of 1-C$_6$ in C$_6$ fraction) (entry 4). Under identical reaction conditions, analogous N-aryl-functionalized PNP ligands, reported elsewhere,$^{20,21}$ bearing $-\text{CH}_3$, $-\text{Et}$, and $-\text{Cl}$ functional moieties at the meta position of the N-phenyl ring exhibited notably lower reaction rates (Table 3, entries 2–5, and Figure 2b). One possible reason for the weaker tetramerization performance at 75 °C could be due to the partial catalyst decomposition (a similar phenomenon was also observed for the benchmark Sasol’s system, vide infra), which however could be overcome by the ligand 1-based Cr system. The bis meta-$\text{CF}_3$-substituted PNP [C$_6$H$_4$(3,5-bis(CF$_3$))N(PPh$_2$)$_2$]N(PPh$_3$)$_2$ (4)-based system on the other hand yielded a much inferior productivity of 329 kg g$_{\text{Cr}}$$^{-1}$ h$^{-1}$ (Table 3, entry 6) and higher PE (5.2 wt %) fraction. These anomalies in the reaction profile with respect to the 1/Cr system led us to believe a partial isomerization of ligand 4 during the catalysis process, as already indicated by the appearance of weak $^{31}$P NMR signals (in addition to the peak for PNP at 68.63 ppm) ascribable to the PPN-type moiety (Figure S1d). Such an isomerization process might originate from the presence of two electron-withdrawing CF$_3$ groups in

### Table 6. Ethylene Tetramerization Performance Comparison Using In Situ and Preformed Cr Complexes in PhCl at 60 °C$^{4}$

| entry | catalyst | productivity (kg g$_{\text{Cr}}^{-1}$ h$^{-1}$) | product selectivity (wt %) |
|-------|----------|---------------------------------------------|----------------------------|
|       |          | C$_6$ + 1-C$_8$ | 1-C$_6$ | 1-C$_8$ | C$_{10+}$ | PE |
| 1     | Cr(acac)$_3$/1/MMAO-3A | 1852 | 20.6 | 20.4 | 21.0 | 19.8 | 7.9 | 67.7 | 67.8 | 7.2 | 67.6 | 7.0 | 69.2 | 89.0 |
| 2     | 1-Cr     | 2315 | 8.0 | 8.0 | 7.2 | 7.0 | 68.8 | 68.8 | 86.6 | 86.6 | 0.9 | 0.9 | 0.9 | 0.9 |
| 3     | Cr(acac)$_3$/2/MMAO-3A | 1168 | 1.4 | 1.4 | 0.9 | 0.9 | 0.9 | 0.9 | 0.9 | 0.9 | 0.9 | 0.9 | 0.9 | 0.9 |
| 4     | 2-Cr     | 1247 | 7.0 | 7.0 | 7.0 | 7.0 | 68.8 | 68.8 | 86.6 | 86.6 | 0.9 | 0.9 | 0.9 | 0.9 |

$^{4}$Conditions: catalyst (1 μmol), MMAO-3A (2 mmol; Al/Cr 2000), ligand/Cr = 1, total solution volume of 100 mL, 45 bar, 10 min (productivity in kg mol$_{\text{Cr}}^{-1}$ h$^{-1}$), see Table S7.)
the N-phenyl ring and could be assisted by the presence of Lewis acidic Al sites of the MMAO-3A activator.\textsuperscript{23,27}

To improve the 1-octene selectivity in PhCl solvent, the role of temperature was investigated. From the data summarized in Table 4 and Figure 3, it is apparent that as the temperature of the reaction decreases from 75 to 45 °C, the 1-C\textsubscript{8} olefin selectivity gradually increases from 59.5 to 69.1 wt %, although a reverse trend was observed in terms of productivity. Thus, reaction rates of 1852 and 1492 kg g\textsubscript{Cr}\textsuperscript{-1} h\textsuperscript{-1} at 60 and 45 °C were decreased, respectively (entries 2 and 3). Slightly higher C\textsubscript{10} \textsuperscript{-1} fractions especially at 45 °C were also noted. Nevertheless, the PE formation was below 1 wt % under all different temperatures investigated. The oligomerization reaction using Sasol’s benchmark Cr system with (Pr)\textsubscript{N}(PPh\textsubscript{2})\textsubscript{3}, PNP ligand\textsuperscript{1} in PhCl was also conducted under our experimental condition for comparison purposes. As apparent from the data in entry 4, Sasol’s system yielded a slightly lower productivity of 1184 kg g\textsubscript{Cr}\textsuperscript{-1} h\textsuperscript{-1} (entry 4) at 45 °C but gave a similar 1-octene selectivity. Additionally, the PE formation was relatively higher (3.5 wt % vs 0.8 wt %, entry 3). Furthermore, it was observed that at higher temperature, the benchmark catalyst system in PhCl tends to deactivate significantly, resulting in a weaker tetramerization performance (entries 5 and 6 and Figure S4) especially at 75 °C. These results are consistent with those observed for other meta-functionalized N-aryl PNP ligands mentioned above (vide supra).

The higher catalytic activity in PhCl by the Cr(acac)\textsubscript{3}/1/MMAO-3A system can be envisaged by a correlation depicted in Figure S5, where the reaction rates in various solvents are plotted against their polarity as measured by log(S\textsubscript{p}) (where S\textsubscript{p} is the predicted solubility of the solvent molecule in water mol/L).\textsuperscript{25} This correlation may result from higher solvent polarity, allowing a greater charge separation between a cationic catalyst and a bulky methylaluminoxane-derived anion.

After evaluating the Cr(acac)\textsubscript{3}/1/MMAO-3A system in detail, we turned our attention to the in situ-formed catalyst system where a suitable chromium precursor was combined with para (2) or ortho (3) -CF\textsubscript{3}-substituted ligands. As expected, considering the PPN structural motifs,\textsuperscript{27} no selective oligomerization could be observed with iminobiphosphine ligand 3 under the catalysis condition optimized for 1 (Table 5, entry 1). This suggests that the PPN binding motifs of 3 could not be converted to PNP, an isomerization earlier achieved with Pd and Pt metals,\textsuperscript{29} which is required to form a favorable coordination complex during tetramerization reaction. The catalyst system incorporating -CF\textsubscript{3}-substituted ligand 2 on the other hand promoted tetramerization with a 1-C\textsubscript{8} olefin selectivity of 57.6 wt % at a reaction rate of 522 kg g\textsubscript{Cr}\textsuperscript{-1} h\textsuperscript{-1} (entry 2), which however is significantly lower compared to that achieved with 1 (Table 2, entry 4). While exploring other reaction parameters to enhance catalytic performance using 2, we inferred that the productivity could be improved considerably (1168–1329 kg g\textsubscript{Cr}\textsuperscript{-1} h\textsuperscript{-1}) when CrCl\textsubscript{3}/3THF was employed as the chromium precursor (entries 3–4). Furthermore, it was also noted that the reaction at 60 °C yields a higher 1-C\textsubscript{8} selectivity (67.6 wt %) while maintaining PE formation at 0.5 wt % of the total product selectivity (entry 4). The total \alpha-olefin selectivity however was quite similar (∼89 wt %) at the two different temperatures studied. At this point of time, we are unable to provide any direct evidence that could explain the improved activity in the later reaction conditions; we believe however that the formation of a relatively stable Cr(II)/2 complex might be favorable when CrCl\textsubscript{3}/3THF is used as a metal source. We next studied the effect of solvents on tetramerization performance using the CrCl\textsubscript{3}/3THF/2/MMAO-3A system at 60 °C. In line with that observed with 1 (Table 2), the later precatalyst system also exhibited similar solvent-dependent catalytic behavior (entries 5–7). Much lower reaction rates were observed when PhCl was replaced with aliphatic hydrocarbon solvents such as CyH, MeCy, and DHN, although the 1-octene selectivities were better. The \alpha selectivities in aliphatic solvents were also lower mainly due to the reduced 1-C\textsubscript{6} selectivity in C\textsubscript{6} fraction.

Overall, the aforementioned catalytic studies suggest that apart from the reaction parameters, the position of the N-phenyl substituent of the PNP ligand can significantly alter the tetramerization performance. The catalytic results obtained employing the m-CF\textsubscript{3}-substituted N-aryl PNP ligand (1) are in particular encouraging. This further prompted us to strive for establishing a well-defined precatalyst structure and investigate its tetramerization activity. To achieve this, high-quality single crystals were prepared and subjected to X-ray diffraction analysis (see the Supporting Information for details), which reveals a monomeric PNP-CrCl\textsubscript{3}/3THF complex with distorted octahedral geometry around the Cr atom (Figure 4 and Table S2). The P1–Cr–P2 bite angle of 67.6° was observed, which is marginally wider than that found in the (Pr)N(PPh\textsubscript{2})\textsubscript{3}/Cr (65.5°).\textsuperscript{19} Similarly, the Cr–P bond distances in the 2.434–2.513 Å range for 1-Cr are also quite similar to those found in the Pr-PNP-Cr complex (2.424–2.553 Å). A catalytic run using preformed 1-Cr system in PhCl at 60 °C (optimum condition for the best catalytic performance in terms of selectivity) gave selectivity for \alpha-olefin products comparable to that derived from the in situ-generated Cr(acac)\textsubscript{3}/1/MMAO-3A, but with a considerably higher productivity of 2315 kg g\textsubscript{Cr}\textsuperscript{-1} h\textsuperscript{-1} (Table 6). This is in contrast to the trend observed for other preformed L-Cr(III) complexes (L = phosphineamine ligands)\textsuperscript{9,15,30} where a typical dimeric structural formation is reported, but in line with those observed for the preformed Cr(III) complexes supported by PNP- and phospholane-based ligands.\textsuperscript{19} A similar trend in productivity was also observed when the preformed metal complex of 2 was employed.

4. CONCLUSIONS

In summary, systematic catalytic studies were pursued to develop a new highly efficient Cr-based catalyst system supported by -CF\textsubscript{3}-substituted N-aryl-functionalized PNP ligands for ethylene tetramerization. While the activator (MMAO-3A), reaction medium (PhCl), and temperature were important reaction parameters, the positional effect of the -CF\textsubscript{3} group of the N-phenyl ring played the key role in accomplishing an outstanding reaction rate. The new catalyst system was also able to efficiently control the formation of PE and higher olein (C\textsubscript{10}+) by-products under optimized conditions, which in turn resulted in excellent 1-C\textsubscript{8} olefin selectivities (>70 wt %) and exhibited high \alpha selectivity (>90 wt %). A temperature-dependent study further evidences that the m-CF\textsubscript{3}-substituted ligand-based catalyst system is relatively more stable at higher temperatures than Sasol’s benchmark and other meta-functionalized PNP ligands. A detailed molecular structure of the precatalyst 1-Cr was established based on single-crystal X-ray diffraction studies and evaluated for tetramerization reaction.
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