Selective ethylene oligomerization with chromium complexes bearing pyridine-phosphine ligands: influence of ligand structure on catalytic behavior

Citation for published version (APA):

DOI:
10.1021/om5003683

Document status and date:
Published: 01/01/2014

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
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Selective Ethylene Oligomerization with Chromium Complexes Bearing Pyridine–Phosphine Ligands: Influence of Ligand Structure on Catalytic Behavior

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ABSTRACT: Chromium complexes bearing a series of pyridine–phosphine ligands have been synthesized and examined for their catalytic behavior in ethylene oligomerization. The choice of solvent, toluene versus methylcyclohexane, shows a pronounced influence on the catalytic activity for all these complexes. Variations of the ligand system have been introduced by modifying the phosphine substituents affecting ligand bite angles and flexibility. It has been demonstrated that minor differences in the ligand structure can result in remarkable changes not only in catalytic activity but also in selectivity toward α-olefins versus polyethylene and distribution of oligomeric products. Ligand PyCH₂N(Me)P(i)Pr₂, in combination with CrCl₃(THF)₃ afforded selective ethylene trimerization and tetramerization, giving 1-hexene and 1-octene with good overall selectivity and high purity, albeit with the presence of small amounts of PE.

INTRODUCTION

1-Hexene and 1-octene are utilized as comonomers for the production of linear low density polyethylene (LLDPE). Their rapidly growing market demand in recent years has stimulated research for finding new selective ethylene trimerization and tetramerization catalysts.1−6

The majority of the currently existing ethylene trimerization and tetramerization systems are based on chromium complexes bearing a wide variety of ancillary ligands.1,3,4 As a result of ready interconversion between mono-, di-, and trivalent oxidation states of chromium, the same precursor might promote state-dependent selective or nonselective ethylene oligomerization as well as ethylene polymerization as a function of the reaction conditions (i.e., cocatalyst, solvent, temperature). This versatility in catalytic performance makes chromium catalysts excellent candidates for investigating factors that influence catalytic behavior.

The nature of the ancillary ligand also plays a fundamental role in determining the performance of the catalysts. In general, multidentate ligands containing P and N donors have a strong potential to facilitate the selective ethylene oligomerization affording 1-hexene with high selectivity but also the highly desired 1-octene.7−23 Typical examples are the BP Cr-PNPOMe trimerization system,8,24,25 the Sasol Cr-PNP tetramerization system,9,26−28 and the Cr-PNPN trimerization system developed by Rosenthal and co-workers.10,29−32 The Cr-PNPN system recently reported by Gambarotta and co-workers was found to be capable of producing 91% 1-octene with 9% 1-hexene as the only side product, which reiterates the viability of P, N-based ligands to drive the reaction toward selective oligomerization.17 Albeit in the absence of a P donor, chromium complexes bearing aminodipyridine ligands (Cr-NNN) afforded pure 1-octene or 1-hexene, depending on the steric bulk of the ancillary ligand, alongside significant amounts of PE wax.33 Similarly, removing the ortho-methoxy substituents from the phenyl group of Cr-PNP complexes shifted the catalytic selectivity from ethylene trimerization (ca. 90% 1-hexene) into tetramerization (up to 70% 1-octene).8,9 Although it is not clear whether the switch in the C₆/C₈ product ratio is...
mediated by ligand steric effects, coordination of the pendant methoxy group to chromium, or both.\textsuperscript{24,34,35} This finding demonstrates that even subtle ligand modifications can significantly influence the catalytic behavior.

Given the versatility of the Cr-PNNP and Cr-NNN systems as catalysts for 1-octene production, in the present study, we have attempted to synthesize ligand 1, which is assembled from fragments of both the PNNP and the aminodipyridine ligand (Scheme 1), hoping that it would provide high 1-octene selectivity. To investigate the correlation between the catalytic performance and the ligand structure, the skeleton of ligand 1 was modified, giving a series of ligands with different phosphine moieties or \( \text{P} = \text{Cr} = \text{N} \) bite angles. The corresponding chromium adducts of the various ligands were activated with different cocatalysts and subsequently examined for their ethylene oligomerization behavior.

**RESULTS AND DISCUSSION**

Ligand PyN(Me)PPh\(_2\) (1) was readily prepared by the reaction of 2-(methylamino)pyridine and chlorodiphenylphosphine. Complexation of 1 with CrCl\(_3\)(THF)\(_3\) was conducted in dichloromethane, and the ligation was indicated by an instant color change from purple to blue upon mixing in dichloromethane. The resulting complex 1a was isolated as a blue powder by removing the solvent in vacuo.

**Table 1. Ethylene Oligomerization Tests on Cr/Ligand 1**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cocatalyst (equiv)</th>
<th>PE (g)</th>
<th>PE (wt %)</th>
<th>LAO (mL)</th>
<th>Activity (g/(mmol Cr-h))</th>
<th>C(_6) (1-C(_6)) (%)</th>
<th>C(_8) (1-C(_8)) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>MAO (500)</td>
<td>1.04</td>
<td>49</td>
<td>1.49</td>
<td>422</td>
<td>52.0 (62)</td>
<td>27.5 (77)</td>
</tr>
<tr>
<td>2</td>
<td>MAO (500)</td>
<td>0.26</td>
<td>5</td>
<td>7.18</td>
<td>1158</td>
<td>68.0 (39)</td>
<td>31.3 (76)</td>
</tr>
<tr>
<td>3a</td>
<td>MAO (500)</td>
<td>0.56</td>
<td>10</td>
<td>7.04</td>
<td>1105</td>
<td>57.2 (40)</td>
<td>30.1 (73)</td>
</tr>
<tr>
<td>4d</td>
<td>MAO (500)</td>
<td>1.18</td>
<td>14</td>
<td>12.43</td>
<td>2023</td>
<td>58.5 (44)</td>
<td>31.3 (73)</td>
</tr>
<tr>
<td>6</td>
<td>MMAO (500)</td>
<td>0.18</td>
<td>2</td>
<td>11.18</td>
<td>1612</td>
<td>60.4 (41)</td>
<td>30.3 (72)</td>
</tr>
<tr>
<td>7</td>
<td>DMAO (500)/TIBA (100)</td>
<td>0.47</td>
<td>14</td>
<td>4.23</td>
<td>685</td>
<td>63.3 (37)</td>
<td>29.0 (72)</td>
</tr>
<tr>
<td>8e</td>
<td>DMAO (500)</td>
<td>0.18</td>
<td>3</td>
<td>8.32</td>
<td>1207</td>
<td>59.3 (39)</td>
<td>30.5 (70)</td>
</tr>
<tr>
<td>9f</td>
<td>DMAO (500)/DEAC (50)</td>
<td>15.64</td>
<td>100</td>
<td>0</td>
<td>3127</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10f</td>
<td>DMAO (500)</td>
<td>0.37</td>
<td>56</td>
<td>0.40</td>
<td>132</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11f</td>
<td>DMAO (500)/DEAC (50)</td>
<td>3.87</td>
<td>100</td>
<td>0</td>
<td>761</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}Conditions: CrCl\(_3\)(THF)\(_3\) = 10 \mu mol, ligand 1 = 10 \mu mol, methylocyclohexane = 100 mL, 60 °C, 30 bar of ethylene, 30 min. \textsuperscript{b}Toluene. \textsuperscript{c}CrCl\(_3\)(THF)\(_3\) = 10 \mu mol, ligand 1 = 20 \mu mol. \textsuperscript{d}50 bar of ethylene. \textsuperscript{e}Cr(acac)\(_3\). \textsuperscript{f}Cr(EH).
chromium cyclopentylmethyl ethyl species to form the cyclic products (mechanism C, Scheme 2). Given the rather low 1-hexene purity in our system, we speculate that at the stage of the chromacycloheptane, the rearrangement step affording the chromium cyclopentylmethyl hydride species should be very competitive to the formation of 1-hexene (either concerted or stepwise routes) and further ring growth (Scheme 3). Moreover, the main side products (around 30%) in the C8 fraction detected in our system are two C8 compounds in a 1:1 ratio, which are probably methylcycloheptane and methyl-enecyclcloheptane (these have also been observed in the Sasol Cr-PNP ethylene tetramerization system). Subsequently, the influence of reaction conditions on the catalytic performance of the CrCl3(THF)3/1 system was investigated (Table 1). Toluene as solvent negatively affected the catalytic performance, leading to an activity that corresponds to approximately 40% of the original activity obtained in methylcyclohexane and a significant increase of PE formation. The retarding effect of toluene is possibly due to the formation of inert Cr(1−η^6)-toluene complexes. Although 1-hexene purity is enhanced in toluene, the actual 1-hexene selectivity does not improve much, due to a reduced overall C6 selectivity. Increasing the ethylene pressure from 30 to 50 bar doubled the catalytic activity. The production of both polyethylene and oligomers increased under higher ethylene pressure, albeit that PE formation was influenced more strongly. On the other hand, the C6/C8 ratio was unaffected. Increasing the ligand/Cr ratio did not affect the catalytic behavior with respect to ethylene oligomerization; however, it doubled the amount of PE. Hence, the in situ generated catalytic active species for ethylene oligomerization is inferred to comprise chromium and ligand 1 in a 1:1 ratio.

Changing the cocatalyst did not significantly influence the distribution of oligomers, implying the generation of identical active species for selective oligomerization. Varied weight percentages of PE indicate that the activation procedure affects the generation of the active species for oligomerization and polymerization to different extents. Modified MAO (MMAO) efficiently retards PE formation and drives the reaction toward oligomerization with improved activity, probably as a result of the better reducing capacity of MMAO compared with MAO. Using dried MAO (DMAO) as cocatalyst led to a drop in oligomer yield, which might be a result of insufficient reduction of the trivalent chromium precursor. Addition of triisobutylaluminum (TIBA) in DMAO gave results similar to MMAO in terms of inhibiting ethylene polymerization.

Attempts to improve the catalytic activity for ethylene oligomerization by using more soluble chromium sources appeared to be unsuccessful. Upon activation with MAO, Cr(acac)3/1 only produced small amounts of oligomers and PE, which might imply that chlorine is needed to produce an active catalyst for selective ethylene oligomerization. Introduction of chlorine by using a combination of DMAO and diethylaluminum chloride (DEAC) as an alternative cocatalyst for Cr(acac)3/1, did restore the catalytic activity but unexpectedly shifted ethylene oligomerization toward ethylene polymerization. Given the absence of oligomeric products in the Cr(acac)3/1/MAO/DEAC system, the in situ generated active species is expected to differ from the one resulting from CrCl3(THF)3/1/MAO, although both combinations contain
chlorine. Using another chlorine-free compound, Cr(EH)$_3$ (chromium 2-ethylhexanoate), as the chromium precursor resulted in similar selectivity as that obtained for the Cr(acac)$_3$/1/MAO/DEAC system but with a much lower ethylene polymerization activity.

In an attempt to improve the catalytic selectivity as well as to obtain insight into the factors affecting the catalytic behavior, ligand 1 was modified. Thus, a series of P,N-based ligands with varying substitutions on the phosphine moiety and different P−Cr=N bite angles has been synthesized (Scheme 4). Subsequently, the catalytic behavior of their corresponding in situ-prepared chromium complexes has been examined.

Scheme 4. Synthesis of Ligands 4–6

To investigate the steric and electronic effect determined by the phosphine moiety, the phenyl substituents on P in 1 were replaced by o-tolyl and isopropyl groups, affording ligands 2 and 3, respectively. Their corresponding chromium complexes ([Py(N(Me)PPh$_2$)$_2$]CrCl$_3$/THF; R = o-tolyl (2a), isopropyl (3a)) were obtained from the reaction of 2 and 3 with CrCl$_3$/THF, in THF. In the case of 2a, crystals suitable for single crystal X-ray structure determination were grown by slow vapor diffusion of petroleum ether into a THF solution. The crystal structure of 2a (Figure 1) is in agreement with the earlier proposed structure of 1a featuring a distorted octahedral geometry, in which the trivalent chromium is chelated by the bidentate ligand 2 via the phosphine-P and the pyridine-N atoms. The distortion mainly arises from the acute P−Cr=N bite angles that has been synthesized (Scheme 4). Subsequently, the catalytic behavior of their corresponding in situ-prepared chromium complexes has been examined.

Figure 1. Partial thermal ellipsoid drawing of 2a at 50% probability. Selected bond lengths (Å) and angles (deg): Cr1−P1 2.4298(6), Cr1−N1 2.0977(9), Cr1−Cl1 2.3019(8), Cr1−Cl2 2.3022(3), Cr1−Cl3 2.3086(2), Cr1−O1 2.0547(1), P1−Cr1−N1 75.84(35), O1−Cr1−N1 91.93(26), P1−Cr1−Cl2 99.42(5), P1−Cr1−O1 167.47(14), Cl2−Cr1−N1 175.03(29), Cl3−Cr1−Cl1 174.65(1).
more that of 3a, containing aliphatic isopropyl substitution on phosphorus, than that of 1a, containing aromatic phenyl groups, is puzzling and indicates that electronic effects can be ruled out.

For the PNP type of ligands, introduction of a CH$_2$ unit in one of the P–N bonds shifted the dominant oligomer fraction from 1-octene to 1-hexene, which shows that varying the ligand bite angle and flexibility might dramatically impact the product distribution. Encouraged by this finding, introduction of a carbon linkage between the pyridine and the aminophosphine fragments was endeavored for 1–3, affording the analogous ligands 4–6 (Scheme 4). These ligands were then reacted with CrCl$_3$(THF)$_3$ to afford corresponding chromium complexes. The crystals of 4a were suitable for X-ray diffraction analysis, and the results confirmed the anticipated ligand coordination (Figure 2). The crystal structure of 4a displays the typical octahedral geometry of Cr(III). A six-membered chelate is formed with the bidentate ligand 4, which occupies two coordination sites around chromium, binding through the nitrogen of the pyridine moiety and the phosphorus atom. Three chlorine atoms occupy three meridional coordination sites, while the last coordination site is occupied by one molecule of THF trans with respect to the phosphorus atom.

As expected, variations in the bite angle and flexibility of the ancillary ligand do indeed affect the catalytic performance significantly (Table 2). Upon activation with MAO in toluene, 4a afforded a statistical distribution of oligomers with enrichment in C$_6$ and C$_8$ oligomers alongside significant amounts of PE (Table 2, entry 7). The C$_6$ and C$_8$ fraction existed of nearly pure 1-hexene and 1-octene (>99%). Methylcyclohexane as solvent led to a dramatic drop in activity as well as in purity of 1-hexene and 1-octene. Although 51% of the liquid products consisted of 1-octene (58% overall C$_8$ selectivity with an 88% purity of 1-octene), the production of PE selectivity switched from C$_8$ toward C$_6$ while the overall C$_6$ and C$_8$ selectivity remained unchanged. Similar to 1a, a higher ethylene pressure increased the catalytic activity of 4a, with only a slight influence on the product distribution (Table 2, entry 10). However, a simultaneous decline in the selectivity for C$_6$ and C$_8$ was also observed. In a related Cr-aminophosphine system, a similar reduction of the PE formation has been reported, albeit that in this case the selectivity switched from C$_6$ toward C$_8$ while the overall C$_6$ and C$_8$ selectivity remained unchanged.

![Figure 2. Drawing of 4a with thermal ellipsoids drawn at 50% probability. Select bond lengths (Å) and angles (deg) of 4a: Cr1–P1 2.432(2), Cr1–N1 2.164(6), Cr–C11 2.317(2), Cr1–Cl3 2.301(2), Cr1–O1 2.121(5); P1–Cr1–N1 92.15(16), P1–Cr1–Cl3 89.78(8), N1–Cr1–Cl3 87.09(15), N1–Cr1–Cl1 83.37(15), P1–Cr1–Cl2 88.80(8), O1–Cr1–Cl3 91.72(14).](image)

Table 2. Ethylene Oligomerization Tests on 2a–6a$^a$

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst</th>
<th>solvent$^b$</th>
<th>PE (g)</th>
<th>PE (wt %)</th>
<th>LAO (mL)</th>
<th>activity (g/(mmol Cr·h))</th>
<th>C6 (1-C6) (%)</th>
<th>C8 (1-C8) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1$^e$</td>
<td>2a</td>
<td>toluene</td>
<td>1.68</td>
<td>9</td>
<td>23.47</td>
<td>2180</td>
<td>68.1 (92)</td>
<td>21.2 (85)</td>
</tr>
<tr>
<td>2</td>
<td>2a</td>
<td>MCH</td>
<td>0.26</td>
<td>12</td>
<td>2.62</td>
<td>415</td>
<td>68.1 (85)</td>
<td>27.6 (93)</td>
</tr>
<tr>
<td>3$^e$</td>
<td>2a</td>
<td>toluene</td>
<td>2.24</td>
<td>18</td>
<td>13.87</td>
<td>1660</td>
<td>38.7 (70)</td>
<td>16.3 (62)</td>
</tr>
<tr>
<td>4$^e$</td>
<td>2a</td>
<td>toluene</td>
<td>1.24</td>
<td>8</td>
<td>18.95</td>
<td>2945</td>
<td>77.8 (90)</td>
<td>12.5 (87)</td>
</tr>
<tr>
<td>5</td>
<td>3a</td>
<td>toluene</td>
<td>0.63</td>
<td>9</td>
<td>9.15</td>
<td>1394</td>
<td>65.5 (73)</td>
<td>31.9 (90)</td>
</tr>
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<td>3a</td>
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<td>39.2 (90)</td>
</tr>
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<td>toluene</td>
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<td>2177</td>
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<td>31.0 (+99)</td>
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<tr>
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<td>4a</td>
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<td>35.5 (63)</td>
<td>57.9 (88)</td>
</tr>
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<td>MCH</td>
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<td>82</td>
<td>0.72</td>
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<td>32.4 (59)</td>
<td>60.9 (93)</td>
</tr>
<tr>
<td>10$^f$</td>
<td>4a</td>
<td>MCH</td>
<td>0.40</td>
<td>53</td>
<td>0.48</td>
<td>150</td>
<td>23.2 (84)</td>
<td>52.7 (72)</td>
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<td>11</td>
<td>5a</td>
<td>toluene</td>
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<tr>
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<td>70</td>
<td>0.58</td>
<td>276</td>
<td>50.7 (+99)</td>
<td>29.5 (+99)</td>
</tr>
<tr>
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<td>6a</td>
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<td>0.31</td>
<td>12</td>
<td>3.18</td>
<td>500</td>
<td>71.5 (98)</td>
<td>26.7 (+99)</td>
</tr>
</tbody>
</table>

$^a$Reaction conditions: catalyst = 10 μmol, 500 equiv of MAO, solvent = 100 mL, 60 °C, ethylene (30 bar), 30 min. $^b$50 min, 60–110 °C. $^c$150 min, 80 °C, 80–110 °C. $^d$50 bar. $^e$500 equiv of DMAO and 50 equiv of TEA. $^f$MCH = methylcyclohexane.
increased solubility in aliphatic solvents as introduced to the Cr-alkyl function.

The catalytic behavior of \( 5a \) is different from that of its closely related complexes \( 4a \) and \( 2a \). When activated with MAO in toluene, complex \( 5a \) produced polyethylene as the only product with moderate activity (Table 2, entry 11). In methylcyclohexane, PE was still the major product, but oligomers were formed as well (Table 2, entry 12). Complex \( 6a \) showed promising catalytic behavior upon activation with MAO in methylcyclohexane (Table 2, entry 14). Despite the presence of PE, 1-hexene and 1-octene were obtained in very good purity and dominate the liquid fractions with an overall selectivity exceeding 98%. Toluene negatively affected the catalytic activity and selectivity (Table 2, entry 13). Besides a partial loss of C\(_6\) and C\(_8\) selectivity in the liquid phase, the productivity of oligomers in toluene also exhibits a significant drop compared with that in methylcyclohexane, which possibly arises from the formation of Cr(I)-\( \eta^6 \)-toluene complexes. The yield of PE was less affected by solvent, implying that PE is generated from chromium species with higher oxidation states.\(^{11,45–47}\)

To avoid complications resulting from possible interaction between toluene and the Cr(I) species, the catalytic outcomes of complexes \( 1a–6a \) in methylcyclohexane were selected and summarized for further discussion. As it can be seen in Scheme S, even a minor difference in the ligand structure can give rise to a noticeably different catalytic behavior. Introduction of a methylene bridge in the ligand backbone switches the selectivity of \( 1a \) from 61% of C\(_6\) and 31% of C\(_8\) to 35% of C\(_6\) and 58% of C\(_8\) with a significant increase in the PE fraction for \( 4a \). By addition of one CH\(_2\) spacer between the pyridine and the aminophosphine fragments in \( 4a \), the resultant complex [Py(CH\(_2\))\(_2\)N(Me)PPh\(_2\)]CrCl\(_3\)THF (Cr-PNP\(_y\)) has recently been reported to produce C\(_8\) with further enhanced selectivity of 75%.\(^{18}\) Complexes \( 4a \) and Cr-PNP\(_y\) behave similarly in terms of activity. Furthermore, \( 1a \) shows a much higher overall productivity as well as an improved oligomer/PE ratio than \( 4a \).

This observation indicates a possible correlation between the \( \eta^5 \)-Cr–N bite angle and selectivity. In the case of the \( \sigma \)-tolyl-substituted \( 2a \) and \( 5a \), a similar trend in PE formation is observed with a larger bite angle and flexibility of the ligand resulting in an increased PE production. For \( 3a \) and \( 6a \), containing more basic alkyphosphine moieties, the increased bite angle results in higher overall selectivity for 1-hexene and 1-octene, better purity of \( \alpha \)-olefin, and less PE. Variations of the ligand systems proved that for the phosphate substituents the \( \eta^5 \)-Cr–N bite angle and ligand flexibility play a crucial role in controlling the catalytic performance of the catalysts.

## CONCLUSIONS

In the present study, chromium complexes bearing a series of pyridine–phosphine ligands have been synthesized and have shown varying catalytic behavior under typical reaction conditions for ethylene oligomerization.

The solvent choice has a pronounced influence on the catalytic activity as well as on the PE/oligomers ratio. The preference for aliphatic or aromatic surroundings is dependent on the ligand system. A possible reason could be that the interactions between solvent and active site are affected by the differences in steric bulk of the ancillary ligands, thereby leading to a shift in the equilibrium of active species responsible for ethylene oligomerization and polymerization. On the other hand, the selectivity of oligomer products is less affected by solvents.

Variations of the ligand structure have demonstrated that a dramatic change in catalytic behavior can be obtained upon a subtle modification in the ligand skeleton. For chromium complexes chelated by ligands \( 1–3 \), steric bulk in the phosphine moiety plays a more pronounced role than the electronic effect in controlling catalytic activity, PE/oligomer ratio, and the purity of 1-hexene and 1-octene. Introduction of one CH\(_2\) unit between the pyridine and the aminophosphine moiety increases the flexibility of the ligand scaffold, resulting in a less distorted octahedral geometry with a \( \eta^5 \)-Cr–N bite angle...
close to 90°. According to the reaction conditions adopted, 4a–6a enable nonselective oligomerization, selective tri- and tetramerization, and polymerization of ethylene. The diversity in catalytic outcomes of 4a–6a might be attributed to the formation of various active species facilitated by chromium complexes bearing more flexible ligands 4–6. Nevertheless, 6a bearing the PyCH₃N(Me)PPr₂ ligand shows potential for being a promising selective ethylene oligomerization catalyst, producing 1-hexene and 1-octene with high overall selectivity and very good purity, although thus far the formation of small amounts of PE is very persistent.

### EXPERIMENTAL SECTION

**General Procedures.** All manipulations for air or moisture sensitive materials were carried out under inert atmosphere in a glovebox or using Schlenk techniques. Dry solvents were obtained by passing them through a column purification system. Starting materials for ligand synthesis were purchased from Sigma-Aldrich and used as received. MAO (10 wt % in toluene solution) was purchased from Sigma-Aldrich and used as prepared. Dried MAO (DMAO) was prepared by pumping off all the volatile compounds of MAO at 40 °C for 6 h in vacuo, leaving a free-flowing white powder. All NMR spectra were recorded on Varian Mercury 400 or 500 MHz spectrometers at 25 °C.

**Ligand Synthesis.** *Py(NiMe)PPh₂ (1).* A 2.5 M hexane solution of n-Buli (10 mmol, 4 mL) was added dropwise to a stirred diethyl ether/petroleum ether (35 mL/20 mL) solution of 2-(methylamino)-pyridine (10 mmol, 1.0 mL) at −78 °C. After 30 min of stirring, the reaction mixture was allowed to warm to room temperature and was stirred for additional 3 h. PCIPb₂ (10 mmol, 1.8 mL) was then added dropwise at 0 °C, and the reaction mixture was stirred overnight at room temperature. The resulting suspension was filtered and washed twice with diethyl ether (2 × 15 mL). The solvent was evaporated under reduced pressure until precipitation occurred. The supernatant was kept in the freezer (−30 °C), and the product was filtered and dried in vacuo, yielding a beige solid (2.4 g, 8 mmol, 80%). ¹H NMR (400 MHz, CDCl₃) δ: 8.22 (d, 1H), 7.55 (t, 1H), 7.45–7.38 (m, 11H), 6.76 (t, 1H), 2.92 (d, 3H). ¹³C NMR (400 MHz, CDCl₃) δ: 50.82 (s). ¹³C NMR data were consistent with that reported in the literature.

*Py(NiMe)(p-toly)₂ (2).* Ligand 2 was synthesized similarly to ligand 1, using chlorodiisopropylphosphine (1.25 mL, 10 mmol). Recrystallization from diethyl ether/petroleum ether (10 mL/2 mL) gave colorless crystals (1.8 g, 5.6 mmol, 56%). ¹H NMR (400 MHz, CDCl₃) δ: 8.27 (d, 1H), 7.51 (t, 1H), 7.38–7.11 (m, 9H), 6.74 (t, 1H), 2.88 (d, 3H), 2.29 (s, 6H). ¹³C NMR (400 MHz, CDCl₃) δ: 40.38 (s). ¹³C NMR (500 MHz, CDCl₃) δ: 161.3, 147.7, 141.8, 137.0, 134.4, 130.7, 128.6, 128.3, 121.9, 62.5, 37.4.

*Py(NiMe)P(p-toly)₂ (3).* Ligand 3 was synthesized similarly to ligand 1, using chlorodipropylphosphine (1.6 mL, 10 mmol). After removal of the solvent in vacuo, the product was collected as a brown oil (2.1 g, 8.8 mmol, 88%). ¹H NMR (400 MHz, CDCl₃) δ: 8.50 (d, 1H), 7.64 (t, 1H), 7.43 (d, 1H), 7.12 (t, 1H), 4.28 (d, 2H), 2.52 (d, 3H), 1.92 (m, 2H), 1.13–1.05 (m, 12 H). ¹³C NMR (400 MHz, CDCl₃) δ: 89.99 (s). ¹³C NMR (500 MHz, CDCl₃) δ: 160.6, 148.8, 136.3, 121.4, 64.1, 36.9, 26.7, 19.6, 19.2.

### Complex Synthesis.  

*Py(NiMe)P(p-toly)₂Cl₃(THF) (1a).* A suspension of CrCl₃(THF) (0.375 g, 1 mmol) and chlorodiisopropylphosphine (1.6 mL, 10 mmol). By evaporation of the solvent in vacuo, the product was collected as a brown oil (2.1 g, 8.8 mmol, 88%). ¹H NMR (400 MHz, CDCl₃) δ: 8.22 (d, 1H), 7.55 (t, 1H), 7.45–7.38 (m, 11H), 6.76 (t, 1H), 2.92 (d, 3H). ¹³C NMR (400 MHz, CDCl₃) δ: 50.82 (s). ¹³C NMR data were consistent with that reported in the literature.

*Py(NiMe)P(p-toly)₂Cl₃(THF) (2a).* A suspension of CrCl₃(THF) (0.188 g, 0.50 mmol) in THF (10 mL) was treated with ligand 2 (0.160 g, 0.50 mmol). The suspension was stirred overnight at room temperature. A small amount of insoluble material was removed by filtration, and the filtrate was evaporated in vacuo, affording 1a as a pale blue powder (0.484 g, 0.93 mmol, 93%). Attempts to recrystallize 1a from dichloromethane/petroleum ether resulted in microcrystalline material, unfortunately not suitable for a single X-ray diffraction analysis. Anal. Calcd (found) for C₆H₄Cl₂CrN₂O₆P: C 57.83 (57.84), H 4.86 (4.87), N 5.23 (5.24).

*Py(NiMe)P(p-toly)₂Cl₃(THF) (2b).* A suspension of CrCl₃(THF) (0.375 g, 1 mmol) in THF (15 mL) was treated with ligand 4 (0.306 g, 1 mmol). The suspension was stirred overnight at room temperature. A small amount of insoluble material was removed by filtration, and the resulting solution was concentrated. Green crystals of 2a (0.198 g, 0.36 mmol, 72%) were grown by vapor diffusion of petroleum ether into the THF solution at room temperature. Anal. Calcd (found) for C₁₀H₈Cl₂CrN₂O₆P: C 53.99 (53.91), H 5.99 (6.00), N 4.50 (4.97).

*Py(NiMe)P(p-toly)₂Cl₃(THF) (3a).* A suspension of CrCl₃(THF) (0.375 g, 1 mmol) in THF (15 mL) was treated with ligand 3 (0.224 g, 1 mmol). The suspension was stirred overnight at 50 °C. A small amount of insoluble material was removed by filtration, and the resulting solution was concentrated. Dark green crystals of 3a (0.356 g, 0.78 mmol, 78%) were grown by vapor diffusion of petroleum ether into the THF solution at room temperature. Anal. Calcd (found) for C₁₀H₈Cl₂CrN₂O₆P: C 54.16 (54.06), H 6.43 (6.40), N 6.16 (6.15).

*Py(NiMe)P(p-toly)₂Cl₃(THF) (4a).* A suspension of CrCl₃(THF) (0.375 g, 1 mmol) in THF (15 mL) was treated with ligand 4 (0.306 g, 1 mmol). The suspension was stirred overnight at room temperature. A small amount of insoluble material was removed by filtration, and the resulting solution was concentrated and layered with petroleum ether affording 4a at room temperature as dark green crystals (0.342 g, 0.64 mmol, 64%). Anal. Calcd (found) for Ca₂H₄Cl₂CrN₂O₆P: C 51.46 (50.86), H 5.07 (5.07), N 4.50 (4.51).

*Py(NiMe)P(p-toly)₂Cl₃(THF) (4b).* A suspension of CrCl₃(THF) (0.188 g, 0.50 mmol) in toluene (5 mL) was treated with ligand 4 (0.15 g, 0.5 mmol). The suspension turned dark green immediately, and stirring was continued for additional 12 h. The insoluble complex was collected by centrifugation and redissolved in THF (5 mL). The olive green solution was layered with heptane (2 mL). The formed crystalline mass was washed with cold hexane (2 × 2 mL), and the product was dried in vacuo. A 0.19 g, 0.37 mmol, 74%). Anal. Calcd (found) for C₁₀H₄Cl₂CrN₂O₆P: C 54.16 (54.06), H 5.07 (5.07), N 4.50 (4.51).
A small amount of insoluble material was removed by filtration, and the filtrate was dried in vacuo, affording 5a as a green powder (0.318 g, 0.56 mmol, 56%). Anal. calcld (found) for C₉H₇Cl₂CrN₂OP: C 43.56 (43.16), H 5.53 (5.53), N 4.96 (4.95).

**Determination of thermal motion parameters.**

Initially the attempt to achieve acceptable values for thermal motion parameters. After initial refinement, occupancy of THF solvent molecule atomic positions with anisotropic displacement coefficients. However, this attempt required introduction of significant amount of displacement and geometry constraints. For that reason THF molecule was refined with isotropic thermal displacement parameters set. All non-hydrogen atoms of the target compound were refined anisotropically. Final Flack parameter value due to chiral space group was refined to ~0.015(18).

For all the compounds, all hydrogen atoms positions were calculated based on the geometry of bearing non-hydrogen atoms. All hydrogen atoms were treated as idealized contributions during the refinement. All scattering factors are contained in several versions of the SHELXTL program library, with the latest version used being 6.12. Crystallographic data and selected data collection parameters are reported in Table 1.

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**ASSOCIATED CONTENT**

Crystallographic data for 2a and 4a in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

We’d like to thank the Chinese Scholarship Council, the Natural Science Foundation of China (No. 21004020 and No. 21174037), and the Eindhoven University of Technology for financial support.

**REFERENCES**
