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

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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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Department of Chemistry, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada
X-ray Core facility, Faculty of Science, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada

Supporting Information

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 \( \alpha \)-olefins versus polyethylene and distribution of oligomeric products. Ligand PyCH\(_2\)N(Me)P\(_{i}\)Pr\(_2\), in combination with CrCl\(_3\)(THF)\(_3\), afforded selective ethylene tri- 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.\(^1\)–\(^4\) 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,\(^8\)–\(^24\) the Sasol Cr-PNP tetramerization system,\(^9\)–\(^26\) 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) afford 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 C\(_6\)/C\(_8\) product ratio is
mediated by ligand steric, coordination of the pendant methoxy group to chromium, or both.\textsuperscript{8,24,34,35} This finding demonstrates that even subtle ligand modifications can significantly influence the catalytic behavior.

Given the versatility of the Cr-PNP 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 $P$–$Cr$–$N$ 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 1\(_a\) was isolated as a blue powder by removing the solvent in vacuo. Attempts to recrystallize complex 1\(_a\) from dichloromethane/petroleum ether resulted in microcrystalline material, unfortunately not suitable for a single crystal X-ray diffraction analysis. Elemental analysis pointed to the postulated octahedral structure consisting of a chromium atom bonded by one ligand, one THF, and three chlorines: [PyN(Me)PPh\(_2\)]CrCl\(_3\)(THF) (1\(_a\)). The proposed structure of 1\(_a\) is supported by the X-ray crystal structure determination of 2\(_a\) (vide infra).

Ethylene oligomerization reactions were carried out in methylcyclohexane using 500 equiv of methylaluminoxane (MAO) as activator. Since the catalytic behavior of complex 1\(_a\) and a mixture of CrCl\(_3\)(THF)\(_3\) plus ligand 1 in a 1:1 ratio were found to be identical, extensive oligomerization runs were conducted with *in situ* generated catalysts (Table 1). Upon activation, CrCl\(_3\)(THF)\(_3\)//1\(_a\) afforded fairly good activity, which is comparable to the highest activity reported in a similar chromium-catalyzed selective ethylene oligomerization system (1322 g/mmol Cr/h, 80 °C, 40 bar of ethylene).\textsuperscript{17} C\(_6\) and C\(_8\) fractions predominated the liquid oligomeric products with an overall selectivity exceeding 90%. The remaining 10% of liquid products ranged from C\(_{10}\) to higher oligomers, characteristic for a statistical product distribution. Besides oligomers, relatively small quantities (5 wt %) of polyethylene were also obtained. The simultaneous formation of C\(_6\)/C\(_8\) oligomers and minor amounts of a statistical distribution of C\(_{10}\) oligomers and polyethylene suggests the presence of multiple active species possibly bearing chromium in different oxidation states.\textsuperscript{36,37}

The purity of 1-hexene was found to be surprisingly low and over half of the C\(_6\) fraction consisted of methylcyclopentane and methylenecyclopentane in a 1:1 ratio. These cyclic C\(_6\) compounds are inferred to arise from a chromium cyclopentylmethyl hydride species, which is formed upon the rearrangement of the chromacycloheptane intermediate. This postulated mechanism was first proposed for their formation in the Sasol Cr-PNP ethylene tetramerization system, suggesting that the methylcyclopentane and methylenecyclopentane are produced by a reductive elimination and $\beta$-hydrogen transfer from the chromium cyclopentylmethyl hydride species, respectively (mechanism A, Scheme 2); or by disproportionation from two chromium cyclopentylmethyl hydride species (mechanism B, Scheme 2).\textsuperscript{38} A recent DFT study by Budzelaar proved the accessibility of these cyclic C\(_6\) products and proposed an alternative mechanism that the methylcyclopentane and methylenecyclopentane arise from an ethylene insertion into the Cr–H bond of chromium cyclopentylmethyl hydride species followed by hydrogen transfer to or from the

---

**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>
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<tbody>
<tr>
<td>1(_a)</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>60.8 (39)</td>
<td>31.3 (76)</td>
</tr>
<tr>
<td>3(_d)</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>4(_d)</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>5</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>6</td>
<td>DMAO (500)</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>7</td>
<td>DMAO (500)/TIBA (100)</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>
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<td>8(_e)</td>
<td>MAO (500)</td>
<td>0.18</td>
<td>53</td>
<td>0.21</td>
<td>66</td>
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<tr>
<td>9(_e)</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>10(_e)</td>
<td>MAO (500)</td>
<td>0.17</td>
<td>56</td>
<td>0.40</td>
<td>132</td>
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<td></td>
</tr>
<tr>
<td>11(_e)</td>
<td>DMAO (500)/DEAC (50)</td>
<td>3.80</td>
<td>100</td>
<td>0</td>
<td>761</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(\text{**Conditions:** CrCl}_3\)(THF)\(_3\) = 10 \, \mu\text{mol, ligand 1 = 10 \, \mu\text{mol, methylcyclohexane=}100 \, \text{mL, 60 °C, 30 bar of ethylene, 30 min. \textsuperscript{b}Toluene.}\)

\(\text{**CrCl}_3\)(THF)\(_3\) = 10 \, \mu\text{mol, ligand 1 = 20 \, \mu\text{mol. \textsuperscript{d}50 bar of ethylene. \textsuperscript{c}Cr(acac)}_3\textsuperscript{2}\textsuperscript{Cr(EH)}_3\).}
chromium cyclopentylmethyl ethyl species to form the cyclic products (mechanism C, Scheme 2).\textsuperscript{39} Given the rather low 1-hexene purity in our system, we speculate that at the stage of the chromacycloheptane, the rearrangement step according 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-enecycloheptane (these have also been observed in the Sasol Cr-PNP ethylene tetramerization system\textsuperscript{38}) generated in a similar mechanism as for the formation of cyclic C6 products.

Subsequently, the influence of reaction conditions on the catalytic performance of the CrCl\textsubscript{3}(THF)\textsubscript{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 methycyclohexane and a significant increase of PE formation. The retarding effect of toluene is possibly due to the formation of inert Cr(1)–\(\eta^6\)-toluene complexes.\textsuperscript{40} 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.\textsuperscript{41,42} 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 \textit{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.\textsuperscript{43,44}

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)\textsubscript{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)\textsubscript{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)\textsubscript{3}/1/MAO/DEAC system, the \textit{in situ} generated active species is expected to differ from the one resulting from CrCl\textsubscript{3}(THF)\textsubscript{3}/1/MAO, although both combinations contain

**Scheme 2. Postulated Mechanisms A, B, and C for the Formation of Cyclic C\textsubscript{6} Products**

**Scheme 3. Further Reaction Routes from Chromacycloheptane Species**

\textsuperscript{a}Transition states are exhibited in the dotted rectangles.
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)$_3$ 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 α-olefin-P and the o-tolyl groups in the phosphine moiety with Cr−Cr−N bite angles (76°). Chlorides and THF occupy the other four vacant sites in the octahedral coordinating sphere. The THF is located trans to the phosphorus donor. In an analogous octahedral complex [Py(CH$_2$)$_2$N(Me)PPh$_2$]$_2$CrCl$_3$/THF, the THF also resides trans to the phosphine functionality. The o-tolyl substitutions in the two o-tolyl groups are oriented opposite to each other. This might be attributed to steric factors as was revealed by DFT calculations (B3LYP/TZVP level) showing a 2.4 kcal/mol difference in energy between the most and least stable conformations.

A small change in the ligand structure by replacing the phenyl groups in the phosphine moiety with o-tolyl groups led to a remarkable change in catalytic behavior (Table 2, entries 1 and 2). The catalytic activity of 2a in toluene was found to be 5-fold higher than that in methycyclohexane, whereas 1a is almost 3 times more active in methycyclohexane than in toluene. The positive and negative effects of methycyclohexane on the catalytic activity of 1a and 2a are confusing and possibly result from a combined contribution of solvent effects and a shift in the equilibrium of multiple active species. Interestingly, increased steric bulk on the phosphine moiety was found to give rise to improved purity of both 1-hexene and 1-octene.

Another interesting phenomenon observed for 2a is the very long induction period for the reaction conducted in toluene. Unlike other chromium complexes in the present study, which invariably resulted in an instant exotherm after catalyst injection, 2a consumes ethylene very slowly in the first 30 min of the reaction. The acceleration of ethylene uptake only starts when the temperature has reached a certain point (around 80 °C). Further conducted oligomerizations performed in toluene at varying temperatures using 2a have revealed that this catalyst shows a strong dependence of its catalytic behavior on reaction temperature. Selective formation of C$_6$ and C$_8$ oligomers was only observed at elevated temperatures (Table 2, entries 1 and 4). However, when the reaction temperature of an uncontrolled reaction exceeded 105 °C, a rapid decay of the catalyst was indicated by the gradual decline of temperature. Reactions carried out under isothermal conditions (80 °C) led to nonselective oligomerization and higher percentages of PE, although a rather long catalyst lifetime was accomplished, with the rate of ethylene uptake remaining unchanged even after 150 min (Table 2, entry 3). Different catalytic outcomes under varying temperatures suggest that the active species responsible for PE formation is generated at a relatively low (<80 °C) temperature, while the active species responsible for selective ethylene oligomerization is formed only at elevated temperature. A similar correlation between temperature and selectivity has also been reported for the Cr-NNN tetramerization system, in which 1-octene is only produced when the reactor temperature is uncontrolled and allowed to raise above 100 °C.

Upon activation with MAO in toluene, 3a also afforded C$_6$ and C$_8$ with good overall selectivity (Table 2, entries 5 and 6). Using methycyclohexane as solvent led to a drop of activity and lower selectivities, and the selectivity slightly from C$_6$ to C$_8$. In general, the oligomer distribution and reactivities of 2a and 3a show the same trend and differ from the catalytic behavior of 1a. Compounds 2a and 3a both exhibit higher activity in toluene than in methycyclohexane and an improved purity of short chain linear α-olefins, although the purity is still far from being satisfactory. The fact that the catalytic behavior of 2a resembles...
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 CH₂ 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.¹⁻⁹ 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 CrCl₃(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 chloride 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. All bond lengths and bond angles are within the expected range.

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 C₆ and C₈ oligomers alongside significant amounts of PE (Table 2, entry 7). The C₆ and C₈ 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 C₈ selectivity with an 88% purity of 1-octene), the production of C₆ selectivity switched from C₈ toward C₆ while the overall C₆ and C₈ selectivity remained unchanged.¹⁰ 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 9). Although 4a produces a large amount of PE, over 50% of 1-octene selectivity for the liquid fraction indicates the existence of an active species for selective ethylene tetramerization, which is intriguing. To seek a highly selective ethylene tetramerization catalyst, ligand 4 was utilized in combination with more chromium precursors. The first attempt was to complex ligand 4 with methyl chromium dichloride, resulting in the microcrystalline green material 4b. Regrettably, the crystal shape of 4b was not suitable for undertaking a single crystal X-ray diffraction analysis. However, on the ground of elemental analytical and chemical degradation data, we propose a structure with the same octahedral geometry and group distribution as 4a. Complex 4b showed a similar trend as 4a: high activity for nonselective behavior in toluene and an increased selectivity for 1-hexene and 1-octene fractions when tested in methylcyclohexane. The activity of complex 4b was slightly higher than its trichloro analogue 4a, likely due to the

Table 2. Ethylene Oligomerization Tests on 2a−6a⁺

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst</th>
<th>solvent</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⁺</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⁺</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>
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<td>toluene</td>
<td>1.24</td>
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<td>2945</td>
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<td>12.5 (87)</td>
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<td>toluene</td>
<td>0.63</td>
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<td>1394</td>
<td>65.5 (73)</td>
<td>31.9 (90)</td>
</tr>
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<td>toluene</td>
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<td>2177</td>
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<td>31.0 (&gt;99)</td>
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<td>276</td>
<td>50.7 (&gt;99)</td>
<td>29.5 (&gt;99)</td>
</tr>
<tr>
<td>14</td>
<td>6a</td>
<td>MCH</td>
<td>0.31</td>
<td>12</td>
<td>3.18</td>
<td>500</td>
<td>71.5 (98)</td>
<td>26.7 (&gt;99)</td>
</tr>
</tbody>
</table>

*Reaction conditions: catalyst = 10 μmol, 500 equiv of MAO, solvent = 100 mL, 60 °C, ethylene (30 bar), 30 min. *⁺50 min, 60−110 °C. *⁺150 min, 80 °C. *⁺80−110 °C. *⁺50 bar. *⁺500 equiv of DMAO and 50 equiv of TEA. *⁺MCH = methylcyclohexane.

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−Cl1 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).
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 C6 and C8 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)−η6-toluene complexes. The yield of PE was less affected by solvent, implying that PE is generated from chromium species with higher oxidation states.

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 5, 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 C6 and 31% of C8 to 35% of C6 and 58% of C8 with a significant increase in the PE fraction for 4a. By addition of one CH2 spacer between the pyridine and the aminophosphine fragments in 4a, the resultant complex [Py(CH2)2N(Me)PPh2]CrCl3(THF) (Cr-PNPy) has recently been reported to produce C8 with further enhanced selectivity of 75%. Complexes 4a and Cr-PNPy 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 P−Cr−N bite angle and selectivity. In the case of the o-toly-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 alkylphosphine moieties, the increased bite angle results in higher overall selectivity for 1-hexene and 1-octene, better purity of α-olefin, and less PE. Variations of the ligand systems proved that for the phosphine substituents the P−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/oligomer 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 CH2 unit between the pyridine and the aminophosphine moiety increases the flexibility of the ligand scaffold, resulting in a less distorted octahedral geometry with a P−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 PyCH₂N(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 (DMAO) was prepared by pumping off from Sigma-Aldrich and used as received. Dried MAO (DMAO) was prepared by pumping off from Sigma-Aldrich and used as received. Dried MAO (DMAO) was dried 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(N(Me)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 3 h. The solvent was evaporated under reduced pressure until precipitation occurred. The supernatant was washed with cold diethyl ether (2 × 15 mL). The solvent was evaporated in vacuo, yielding a beige solid (2.4 g, 8 ml, 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). ³¹P NMR (400 MHz, CDCl₃): δ: 50.82 (s). ¹³C NMR data were consistent with that reported in the literature.

Py(N(Me)P(o-tolyl)) (2). Ligand 2 was synthesized similarly to ligand 1, using chlorodiisopropylphosphine (1.25 mL, 10 mmol) and chlorodiisopropylphosphine (1.25 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: 8.50 (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). ³¹P NMR (400 MHz, CDCl₃): δ: 89.99 (s). ¹³C NMR (500 MHz, CDCl₃) δ: 160.6, 148.8, 136.3, 121.8, 64.3, 36.9, 26.7, 19.6, 19.2. Complex Synthesis. [Py(N(Me)P(o-tolyl))₃]CrCl₃(THF) (1a). A suspension of CrCl₃(THF)₃ (0.375 g, 1 mmol) in CH₂Cl₂ (15 mL) was treated with ligand 1 (0.292 g, 1 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, 9.91 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. Calc’d (found) for C₁₅H₁₃Cl₃CrN₃O: C 42.26 (42.26), H 6.43 (6.40), N 6.16 (6.15).

[Py(N(Me)P(o-tolyl))₃]CrCl₃(THF) (2a). A suspension of CrCl₃(THF)₃ (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 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. Calc’d (found) for C₁₆H₁₇Cl₃CrN₃O: C 53.99 (53.31), H 5.99 (6.00), N 4.50 (4.97).

[Py(N(Me)P(o-tolyl))₃]CrCl₃(THF) (3a). A suspension of CrCl₃(THF)₃ (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. Calc’d (found) for C₁₆H₁₇Cl₃CrN₃O: C 42.26 (42.63), H 6.43 (6.04), N 6.16 (6.15).

Py(N(Me)PPh₂)CrCl₃(THF) (4a). A suspension of CrCl₃(THF)₃ (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. Calc’d (found) for C₁₅H₁₁Cl₃CrN₃O: C 51.46 (50.86), H 5.07 (5.07), N 5.22 (5.15).

Py(N(Me)PPh₂)₃MeCl₃(THF) (4b). A suspension of MeCl₃(THF)₃ (0.18 g, 0.5 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 then dried in vacuo (0.19 g, 0.37 mmol, 74%). Anal. Calc’d (found) for C₁₅H₁₁Cl₃CrN₃O: C 51.46 (41.44), H 5.95 (5.87), N 9.72 (9.66).

Py(N(Me)P(o-tolyl))₃Cl₃(THF) (5a). A suspension of CrCl₃(THF)₃ (0.375 g, 1 mmol) in THF (15 mL) was treated with ligand 5 (0.334 g, 1 mmol). The suspension was stirred overnight at 50 °C.

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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 $\text{C}_8\text{H}_4\text{Cl}_2\text{Cr}_2\text{N}_2\text{O}_3$: C 53.16 (54.43), H 5.53 (5.83), N 4.96 (5.49).

Ethylene Oligomerization. All of the ethylene oligomerization experiments were performed in a 200 mL steel Büchi autoclave. The autoclave was heated in an oven overnight at 150 °C before each run. After evacuation and rinsing with argon three times, the solvent (volume of solvent = total volume (100 mL) — volume of catalyst solution) was charged in the preheated autoclave. Then catalyst was injected, and the solvent was saturated with ethylene by pressurizing to 30 bar. After 30 min of stirring, the autoclave was temporarily vented to allow the injection of the catalyst solution. The autoclave was repressurized to the desired pressure, and the pressure was maintained throughout the run. The temperature of the autoclave was controlled by a thermostat bath. After 30 min, the reaction was quenched by cooling to 0 °C, depressurizing, and injection of a mixture of ethanol and diluted hydrochloric acid. The polymer was separated by filtration and dried overnight at 60 °C under reduced pressure before mass determination. The oligomers were analyze by GC-FID for oligomer composition by $^1\text{H}$ NMR spectroscopy for activity.

X-ray Crystallography. Data collection results for compounds 2a and 4a represent the best data sets obtained in several trials for each sample. The crystals were mounted on thin glass fibers using paraffin oil. Prior to data collection, crystals were cooled to 200.15 K. Data were collected on a Bruker AXS KAPPA single crystal diffractometer equipped with a sealed Mo tube source (wavelength 0.71073 Å) APEX II CCD detector. Raw data collection and processing were performed with APEX II software package from Bruker AXS. 4a Diffraction data for 2a and 4a samples were collected with a sequence of 0.5°/ω scans at 0, 120°, and 240° in ϕ. Initial unit cell parameters were determined from 60 data frames with 0.3° ω scan each, collected at the different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied. 49 Systematic absences in the diffraction data set and unit-cell parameters were consistent with monoclinic $P_2_1/n$ (No. 14, alternative settings) for compound 2a and orthorhombic $P_2_1_2_1_2_1$ (No. 19) for 4a. Solutions in the centrosymmetric space group for 2a compound yielded chemically reasonable and computationally stable results of refinement. However, data for the complex 4a suggested noncentrosymmetric space group for the structural solution and model refinement. The structures were solved by direct methods, completed with difference Fourier synthesis, and refined with full-matrix least-squares procedures based on $F^2$. Diffraction data for the crystal of the complex 2a were collected to 0.75 Å resolution; however due to small crystal size and weak diffraction it was discovered that both $R$(int) and $R$(sigma) exceed 35% for the data below 1.00 Å resolution. Based on $R$(σ) value, data were truncated to 0.95 Å resolution for refinement. Asymmetric unit for this crystallographic model of 2a consists of one target complex molecule and one THF crystallization solvent molecule. Both molecules are located in the general positions. Occupancy of atomic positions for THF solvent molecules was initially allowed to refine in order to achieve acceptable values for thermal motion parameters. After initial refinement, occupancy of THF molecule was restrained at 50%. All non-hydrogen atoms in the structure were refined anisotropically. Asymmetric unit of 4a contains one chiral compound molecule and one THF solvent molecule. Both parts of the structural model are located in the general positions. Location of strong residual electron density peak next to oxygen atom of the THF molecule suggested oxygen positional disorder. Atomic position was split in two, and occupancies of the both positions were restrained to 50%, providing acceptable values of thermal motion parameters. Initially the attempt was made to refine THF solvent molecule atomic positions with anisotropic displacement coefficients. However, this attempt required introduction of significant amount of displacement and geometry constrains. 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 v.6.12. Crystallographic data and selected data collection parameters are reported in Tables 1.

ASSOCIATED CONTENT

Supporting Information
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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REFERENCES
