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Ethylene Oligomerization Promoted By Chromium Complexes Bearing Pyrrolide-Imine-Amine/Ether Tridentate Ligands

A. C. Pinheiro,⁴ T. Roisnel,⁵ E. Kirillov,⁶ J.-F Carpenterier,⁶ Osvaldo L. Casagrande Jr.⁶,*

Chromium(III) complexes [CrCl₂(L)(THF)] based on monoanionic tridentate ligands [2a, L = 2-(C₆H₄N₂-2′-CH=NH)C₆H₅NHP]; 2b, L = (5-tert-butyl-2-(C₆H₄N₂-2′-CH=N)C₆H₅OHP) have been prepared. Complexes 2a,b were converted into the monomeric acetonitrile adducts [CrCl₂(L)(NCMe)] by reaction with acetonitrile at room temperature. All Cr complexes were characterized by IR spectroscopy, elemental analysis, magnetochemistry for 2a-c, and by X-ray crystallography for 3a-c. Upon activation with methylaluminoxane (MAO), chromium precatalysts 2a and 2c showed good activity in ethylene oligomerization (TOF = 47.0–57.0 × 10⁴ mol ethylene/(mol Cr)⁻¹·h⁻¹ at 80 °C), producing mostly oligomers (93.0–95.6 wt% of total products). The other hand, under identical oligomerization conditions, 2b/MAO behaved as a polymerization catalyst generating predominantly polyethylene (73.0 wt%). However, the catalytic behavior of precatalyst 2b can be adjusted by varying the MAO-to-Cr ratio. Thus, the use of 500 equiv causes a dramatic shift from polymerization to ethylene oligomerization, eventually producing mainly lighter α-olefins fractions [α-C₄ (68.7 wt%) and α-C₆ (19.2 wt%)]. A further increase of the amount of MAO (1000 equiv) leads to a more balanced distribution of oligomers, with a drastic decrease in the α-C₄ and increase in the α-C₆ fractions.

Introduction

A considerable amount of research effort has been dedicated both recently and in the past to nonselective ethylene oligomerization with the aim of improving the understanding of this industrially relevant catalytic process.¹ The mixtures of linear alpha olefins (LAO) produced by this process are in fact valuable commodity chemicals for a range of industrial and household applications depending on their molar mass distribution (detergents, surfactants, cosmetics, synthetic lubricants, etc.).² A nonselective oligomerization is closely reminiscent of a polymerization randomly truncated at the early stages of the chain growth (Coessae-Arlman mechanism).³

Among all the transition-metal-based catalysts, chromium catalysts occupy a unique position, since they provide both selective (commercially viable tri-, and tetramerization catalytic systems) and nonselective ethylene oligomerization.⁴ Typical examples are the Chevron Phillips trimerization catalyst,⁵ the first and sole trimerization system to be successfully commercialized, and the few existing tetramerization systems towards 1-octene with selectivities close to 70 wt%.⁶

In the past years, several well-defined ethylene oligomerization chromium catalysts bearing N’N’N, P’P’P, S’S’S, P’N,⁷ and N’N’P¹¹ ligands have been reported. Such bi- and tridentate ligands play a central role in stabilizing a particular oxidation state and consequently in determining the catalytic behavior (selective vs. nonselective). While, the vast majority of these ligands are used in the neutral form, just a few examples of anionic ligands have been utilized in the synthesis of active chromium species. In particular, studies involving pyrrolyl-based chromium catalyst systems have shown that different catalytic behavior can be achieved depending on the nature of the ancillary ligand and the reaction conditions.¹¹ Recently, Duchateau and co-workers evaluated the ethylene oligomerization capabilities of different dipyroyle-based ancillary ligands using different activation methods.¹² Upon activation with triethylaluminum (TEA), chromium catalysts stabilized by dipyroyle-based ligands showed a lower activity and selectivity compared to the Chevron-Phillips trimerization system. However, unprecedented increases in both activity and selectivity were observed by carrying out the oligomerization in methycyclohexane using dried-methylaluminoxane (DMAO) along with trisobutylaluminum (TiBA) [1:2 ratio] as cocatalyst system under mild conditions, even for the Chevron-Phillips system itself. On the other hand, Gibson and co-workers reported some chromium complexes supported by two pyrrolid-imine ligands that behave as ethylene polymerization catalysts upon treatment with an excess of a range of aluminum activators converting ethylene to high molecular weight polyethylene.¹²

![Chart 1. Examples of pyrrolide-based chromium complexes applied in ethylene oligo- and polymerization.](chart.png)

Duchateau et al.¹²a

Gibson et al.¹²d
In this work, we report a series of new chromium complexes supported by pyrroline-imino-amine/ether tridentate ligands. Their catalytic behavior for ethylene oligomerization upon activation with MAO has been investigated. We discuss the performance of these catalysts, evaluating the role of the ligand, and the experimental parameters on the activity and on the product distribution (oligomer/PE ratio).

Results and discussion

Synthesis of Chromium Complexes Bearing Monoanionic Pyrroline-Imino-Amine/Ether Tridentate Ligands. The pyrrole-imine-amine/ether pro-ligands \( \text{ENN}^N \text{H} \) \( \text{E} = \text{NH}, \text{R} = \text{H}, \text{1a}; \text{E} = \text{NH}, \text{R} = \text{tBu}, \text{1b}; \text{E} = \text{O}, \text{R} = \text{H}, \text{1c} \) were readily synthesized by Schiff base condensations between the corresponding primary amines and pyrrole-2-carboxaldehyde in refluxing methanol. These pro-ligands were characterized by amine/ether pro-ligands {ENN}.

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Figure 1. Molecular structure of 3a (thermal ellipsoids drawn at 50% probability level). Selected bond distances (Å) and angles (deg): Cr(1)-N(17) = 1.9911(13), Cr(1)-N(11) = 2.0239, Cr(1)-N(1) = 2.0623(14), Cr(1)-N(20) = 2.1455(13), Cr(1)-C1(1) = 2.3030(4), Cr(1)-Cl(2) = 2.3339(4), N(17)-Cr(1)-N(11) = 80.26(5), N(17)-Cr(1)-N(1) = 175.66(5), N(11)-Cr(1)-N(1) = 103.43(5), N(17)-Cr(1)-N(20) = 79.51(5), N(11)-Cr(1)-N(20) = 159.77(5), N(1)-Cr(1)-N(20) = 96.77(5), N(17)-Cr(1)-C1(1) = 92.28(4), N(11)-Cr(1)-C1(1) = 91.08(4), N(1)-Cr(1)-C1(1) = 89.94(4), N(20)-Cr(1)-C1(1) = 89.88(4), N(17)-Cr(1)-Cl(2) = 90.50(4), N(11)-Cr(1)-Cl(2) = 91.77(4), N(1)-Cr(1)-Cl(2) = 87.13(4), N(20)-Cr(1)-Cl(2) = 88.26(4), C1(1)-Cr(1)-Cl(2) = 176.31(17).

Figure 2. Molecular structure of 3b (ellipsoids drawn at 50% probability level). Selected bond distances (Å) and angles (deg): Cr(1)-N(1) = 1.986(2), Cr(1)-N(16) = 2.070(2), Cr(1)-N(31) = 2.078(2), Cr(1)-N(23) = 2.181(2), Cr(1)-C1(1) = 2.3145(8), Cr(1)-Cl(2) = 2.3365(4), N(1)-Cr(1)-N(16) = 80.91(9), N(1)-Cr(1)-N(31) = 170.73(9), N(1)-Cr(1)-N(23) = 108.28(9), N(1)-Cr(1)-N(23) = 78.56(9), N(16)-Cr(1)-N(23) = 159.32(9), N(31)-Cr(1)-N(23) = 92.31(9), N(1)-Cr(1)-C1(1) = 91.55(7), N(16)-Cr(1)-C1(1) = 92.33(6), N(31)-Cr(1)-C1(1) = 86.96(7), N(23)-Cr(1)-C1(1) = 90.71(7), N(1)-Cr(1)-Cl(2) = 91.58(7), N(16)-Cr(1)-Cl(2) = 93.43(4), N(31)-Cr(1)-Cl(2) = 89.10(4), N(23)-Cr(1)-Cl(2) = 84.69(4), C1(1)-Cr(1)-Cl(2) = 173.82(3).

Ethylene Oligomerization Studies. Chromium complexes 2a-c were tested in ethylene oligomerization using as cocatalyst methylaluminoxane (MAO) containing 20 wt% AlMe3 at 80 °C and 20 bar constant ethylene pressure. Table 1 summarizes the results of reactions carried out using 10 μmol of precatalyst in 40 mL of toluene. All experiments were at least duplicated, yielding reproducible results within ±5%. The three chromium complexes were found to generate active systems for the linear oligomerization of ethylene with turnover frequencies (TOFs) varying from 3,300 to 57,000 mol(ethylene)·mol(Cr)-1·h-1. Among the catalytic systems studied herein, the 2c/MAO system showed the highest activity of up to 57,000 mol(ethylene)·mol(Cr)-1·h-1 (Table 1, entry 3). The activity data found for this class of chromium precatalysts are comparable to those for other chromium complexes stabilized by tridentate ligands.1
Table 1. Ethylene Oligomerization with 2a-c/MAO systems.a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cat.</th>
<th>[Al/Cr]</th>
<th>TOPb (10^3 h⁻¹)</th>
<th>Oligomer distribution (wt%)c</th>
<th>Olig. (wt%)</th>
<th>PE (wt%)</th>
<th>Total product (mg)</th>
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<tr>
<td>1</td>
<td>2a</td>
<td>300</td>
<td>47.0</td>
<td>C₄ (α-C₄) = 67.6, C₆ (α-C₆) = 16.2, C₈ (α-C₈) = 4.60, C₁₀ (α-C₁₀) = 5.30, C₁₂+ (α-C₁₂+) = 6.30</td>
<td>95.6</td>
<td>4.4</td>
<td>3450</td>
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<tr>
<td>2</td>
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<td>3.30</td>
<td>(97.2) (88.9) (73.9) (60.2)</td>
<td>27.0</td>
<td>73.0</td>
<td>846</td>
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<tr>
<td>3</td>
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<td>300</td>
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<td>(80.0) (78.0) (62.0) (70.0)</td>
<td>10.7</td>
<td>93.0</td>
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<tr>
<td>4</td>
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<td>0.70</td>
<td>97.6</td>
<td>5400</td>
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<tr>
<td>5</td>
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<td>1000</td>
<td>43.5</td>
<td>(98.6) (85.7) (90.7) (100)</td>
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<td>23.8</td>
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<td>(97.0) (98.2) (90.9) (91.0)</td>
<td>79.4</td>
<td>20.6</td>
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<td>2a</td>
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<td>11g</td>
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<td>(88.1) (82.6) (73.7) (62.8)</td>
<td>100</td>
<td>-</td>
<td>2370</td>
</tr>
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</table>

a Reaction conditions: toluene = 40 mL, [Cr] = 10 μmol, oligomerization time = 15 min, P(ethylene) = 20 bar (kept constant), T = 80 °C, MAO. The results shown are representative of at least duplicated experiments. b Mol of ethylene converted (mol of Cr)⁻¹·h⁻¹ as determined by quantitative GLC. c Cₙ, percentage of olefin with n carbon atoms in oligomers; α-Cₙ, percentage of terminal alkene in the Cₙ fraction, as determined by quantitative GLC. d T = 100 °C; e time = 30 min; f time = 45 min. g TMA-depleted methylaluminoxane as cocatalyst.

The catalytic activities and selectivities are substantially affected by the ligand environment. Thus, pre-catalyst 2a produced mostly oligomers (95.6 wt% of total products) with an activity of 47,000 (mol ethylene)(mol Cr)⁻¹·h⁻¹. Quite different results were found for 2b where the presence of a bulky tert-butyl group leads to a dramatic decrease in activity [3,300 (mol(ethylene)·mol(Cr)⁻¹·h⁻¹)]. This complex, when activated with MAO, is in fact primarily a polymerization system; in this case, the amount of oligomers in the liquid fraction was only 27.0 wt% of the total amount of products, and the polymer fraction jumped from 4.4 to 73.0 wt% (entry 1 vs. 2). With regards to selectivity within the liquid fraction, chromium complexes 2a and 2b produced oligomers ranging from C₄ to C₁₂⁺, with a good selectivity for α-olefins. The presence of a sterically demanding group in 2b led to a more balanced distribution of oligomers with enriched fractions in α-C₆ (17.4 wt%), α-C₈ (12.0 wt%), and α-C₁₀ (7.6 wt%) and concomitant decrease in α-C₄ (26.7 wt%). Precatalyst 2c, which bears a phenoxo group instead of a phenylamine unit, afforded a higher activity in comparison to 2a, with a similar oligomer distribution centered on lighter α-olefins fractions [α-C₄ (61.6 wt%) and α-C₆ (16.2 wt%)], as illustrated in Figure 3.
The polymer produced by 2a/MAO has been characterized by DSC analysis and NMR spectroscopy (entry 1). The DSC trace showed three melting temperature peaks in the range of 65-121 °C. The $^1$H and $^{13}$C($^1$H) NMR analyses revealed linear oligomers with vinyl end-groups, that is, essentially linear $\alpha$-olefins with a $M_\text{n}$ value around 800 g mol$^{-1}$ as determined by $^1$H NMR spectroscopy (see the Supporting Information). $^{18}$ Apparently, the steric effect of the pyrrolide-imino-amine ligand is not sufficient to prevent associative displacement of the growing oligomeric chain, and the electron deficiency of the chromium center facilitates the chromium-induced abstraction of a $\beta$-hydride from the growing alkyl chain; these combined reasons result in a rapid chain transfer process and production of low-molecular-weight polymer chains. $^{19}$ Similar results were observed with other catalytic systems based on chromium complexes bearing tridentate ligands. $^{20}$

On the other hand, the steric protection of the tert-butyl group in 2b promotes the formation of a polymer, which is essentially linear, with a single melting transition at 131 °C and a relatively high crystallinity (50%).

The influence of reaction conditions, namely the [Al]/[Cr] molar ratio, temperature and pre-activation period, on the catalytic performance of the 2a-b/MAO systems was investigated (Table 1, entries 4-10). Increasing the [Al]/[Cr] molar ratio from 300 to 500 equiv positively affected the catalytic performance of both chromium precatalysts. In particular, the activation of 2b with 500 equiv led to a remarkable increase in the catalytic activity, that is 22-fold higher than that observed using 300 equiv. At the same time, a higher amount of MAO led almost exclusively to the production of oligomers (97.6 wt% of total products). Similar observations related to the effect of MAO loading on the performance of chromium catalysts have been reported by Eisen et al. $^{21}$ A triphenylsiloxy chromium(II) complex showed an unexpected transformation from ethylene polymerization to ethylene nonselective oligomerization upon increasing the [Al]/[Cr] molar ratio from 100 to 200. A recent combined experimental and computational approach of this system has shown that such selectivity switch can be associated to the nature of the active species, and in particular the chromium oxidation state: it was proposed that the trivalent complexes [(Ph$_3$SiO)Cr($^\text{III}$)Me]$^+$ and [(η$^6$-toluene)Cr($^\text{III}$)Me]$^+$, generated from a disproportionation reaction, are the actual polymerization active species at lower [Al]/[Cr] ratios (≤100), while the divalent [(η$^6$-toluene)Cr($^\text{II}$)Me]$^+$ species would achieve ethylene nonselective oligomerization at higher [Al]/[Cr] molar ratios (≥200). $^{22}$ The activation of both chromium precatalysts 2a-b with 500 equiv of MAO afforded a similar oligomer distribution based on the production of lighter $\alpha$-olefins fractions [$\alpha$-C$_4$ (2a: 61.6 wt%, 2b: 68.7 wt%) and $\alpha$-C$_6$ (2a: 17.9 wt%, 2b: 19.2 wt%)]. A further increase of the amount of MAO ([Al]/[Cr] = 1000) resulted in a decreased oligomer production, whereas it promoted the formation of higher amounts of polymer. Furthermore, the use of higher MAO loading resulted in a drastic decrease in 1-butene and improvement towards formation of the $\alpha$-C$_8$ fraction. For instance, the activation of 2a with 1000 equiv of MAO afforded only 14.3 wt% of $\alpha$-C$_8$ and a significant improvement in the selectivity for $\alpha$-C$_6$ (3.4 to 16.1 wt%).

Interestingly, the activation of 2a using trimethylaluminum (TMA)-depleted methylaluminoxane (DMAO) as cocatalyst (1000 equiv), a switch in the catalytic behavior was observed. The catalyst produced a large amount of polyethylene along with traces of light oligomers (entry 11). The fact that activation of 2a with DMAO exclusively produces PE implies that most probably the reducing power of DMAO is not sufficient to generate the divalent chromium species, which is assumed to be responsible for nonselective oligomerization behavior. Recent work on selective ethylene oligomerization has also highlighted that the type of activator may have a profound influence on the oligomerization selectivity and activity. $^{10c, 12a, 23}$

The optimal operating temperature for this class of pre-catalysts is 80 °C. At 30 °C, neither oligomers nor PE were detected. At a temperature of 100 °C, the oligomerization activity of the 2a/MAO dropped significantly. The pronounced decrease in the catalytic activity at higher temperatures might reflect faster thermal deactivation of the catalyst. $^{4, 12a}$ Conversely, the amount of polymer produced increased with increasing temperature (4.4 at 80 °C vs. 20.6 wt% at 100 °C). However, while the selectivity for 1-butene remained almost unchanged (65.7 wt%), enriched fractions in $\alpha$-C$_6$ (22.8 wt%) and $\alpha$-C$_4$ (7.3 wt%) were obtained, and no oligomers heavier than C$_8$ were produced.
To investigate the relationship between the oligomerization time and the catalytic activity and product distribution, ethylene oligomerization reactions were conducted for 15, 30, and 45 min, using the 2a/MAO system with a [Al]/[Cr] molar ratio of 300 at 80 °C. The productivity obviously decreased with prolonged reaction time (compare entry 1 with entries 9 and 10); however it is important to note that 2a undergoes almost complete deactivation after 15 min. Furthermore, increasing the oligomerization time led to a slight increase in the amount of polymer (4.4 to 12.5 wt%), indicating that the polymerization active species are more robust than those achieving oligomerization.

Conclusions

Chromium complexes bearing monoanionic pyrroli-de-imino-amine/ether ligands have been synthesized and have shown, upon activation with MAO, distinct catalytic performance for ethylene oligomerization. Variations in the ligand structure induced a significant change in catalytic behavior. Steric effects in the pyrrole moiety play a pronounced role in controlling the oligomer/PE ratio while tuning of electronic effects, using either a phenylamine or a phenoxy unit, has a higher impact on the catalytic activity. The use of higher MAO loading positively affected the catalytic performance of these chromium precatalysts. Furthermore, in the case of 2b, the use of higher amounts of MAO causes a dramatic shift in catalyst performance from polymerization to ethylene oligomerization that may tentatively be associated to the predominant presence of Cr(II) catalytically active species in the reaction medium.

Experimental

General considerations. All manipulations involving air- and/or water-sensitive compounds were carried out in an MBraun glovebox or under dry argon using standard Schlenk techniques. Solvents were dried from the appropriate drying agents under argon before use. CrCl$_3$(THF)$_2$, 2-phenoxynanethyamine, and pyrrole-2-carboxaldehyde were purchased from Sigma-Aldrich and used as received. The following compounds were synthesized according to literature procedures: benzyl potassium (BnK),$^{24}$ 5-tert-butyl-1H-pyrrole-2-carboxaldehyde, 25 Ethylene (White Martins Co.) and argon were deoxygenated and dried through BTS columns (BASF) and activated with MAO (Witco, 5.21 wt% Al solution in toluene, 20% TMA) was used as received. Infrared spectra were performed on a FT-IR Bruker Alpha Spectrometer. NMR spectra of diamagnetic compounds were recorded on Bruker AC-300 and AM-500 spectrometers.

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General considerations. All manipulations involving air- and/or water-sensitive compounds were carried out in an MBraun glovebox or under dry argon using standard Schlenk techniques. Solvents were dried from the appropriate drying agents under argon before use. CrCl$_3$(THF)$_2$, 2-phenoxynanethyamine, and pyrrole-2-carboxaldehyde were purchased from Sigma-Aldrich and used as received. The following compounds were synthesized according to literature procedures: benzyl potassium (BnK),$^{24}$ 5-tert-butyl-1H-pyrrole-2-carboxaldehyde, 25 Ethylene (White Martins Co.) and argon were deoxygenated and dried through BTS columns (BASF) and activated with MAO (Witco, 5.21 wt% Al solution in toluene, 20% TMA) was used as received. Infrared spectra were performed on a FT-IR Bruker Alpha Spectrometer. NMR spectra of diamagnetic compounds were recorded on Bruker AC-300 and AM-500 spectrometers.
[Cr(2-(CH₃N-2'-Z=CH-N(C₆H₄)(NH)Ph)(THF)Cl)] (2a). A solution of benzyl potassium (0.122 g, 0.94 mmol) in THF (5 mL) was added dropwise to a stirring solution of 1a (0.200 g, 0.94 mmol) in THF (5 mL) at −78 °C. The resulting solution was allowed to stir for 4 h at room temperature and then added to a solution of CrCl₂(THF)₃ (0.350 g, 0.94 mmol) in THF (10 mL). The reaction mixture was stirred overnight at room temperature and then pentane (10 mL) was added, resulting in precipitation of potassium chloride (KCl) as a fine solid. The solution was filtered by cannula, the solvent was removed in vacuo, and the crude product was washed with diethyl ether (ca. 15 mL) to give, after drying, 2a as a red solid (0.265 g, 69%). Anal. IR (ATR, cm⁻¹): v 3207 (w), 2924 (w), 2872 (w), 1666 (m), 1580 (s), 1494 (m), 1442 (m), 1392 (m), 1357 (w), 1342 (w), 1316 (w), 1294 (m), 1240 (w), 1193 (w), 1099 (w), 1033 (s), 984 (w), 866 (m), 797 (m), 746 (s), 690 (s), 605 (s), 482 (w). μ (BM) = 3.72. Anal. Calcd. for C₂₉H₂₅ClCrN₃: C: 54.43, H: 5.53, N: 9.07. Found: C: 54.13, H: 5.47, N: 8.85.

[Cr(5-tert-butyl-2-(CH₃N-2'-Z=CH-N(C₆H₄)(NH)Ph)(THF)Cl)] (2c). This product was prepared as described above for 2a, starting from benzyl potassium (0.110 g, 0.93 mmol), 1c (0.229 g, 0.85 mmol) and CrCl₂(THF)₃ (0.316 g, 0.85 mmol) in THF (10 mL) to give 2c as a red solid (0.248 g, 63%). IR (ATR, cm⁻¹): v: 3207 (w), 2924 (w), 2872 (m), 1666 (m), 1576 (s), 1493 (m), 1438 (m), 1394 (m), 1342 (m), 1311 (m), 1240 (s), 1168 (s), 1037 (s), 1009 (m), 851 (s), 740 (s), 692 (s). Anal. Calcd. for C₂₉H₂₅ClCrN₃O₂: C: 50.01, H: 5.18, N: 8.68. Found: C: 49.78, H: 5.11, N: 6.67.

[Cr(2-(CH₃N-2'-Z=CH-N(C₆H₄)(N(C₆H₅))Cl)] (3a). A solution of 2a (0.124 g, 0.33 mmol) in acetonitrile (15 mL) was allowed to stir for 4 h at room temperature. The resulting orange solution was concentrated to ca. 5 mL, and then pentane (10 mL) was added to afford an orange precipitated product. The product was collected by filtration, washed with pentane (ca. 15 mL) to give, after drying, 3a as an orange solid (0.117 g, 95%). Analytically pure crystals of 3a suitable for X-ray diffraction were obtained by recrystallization from a concentrated acetonitrile solution. Anal. IR (ATR, cm⁻¹): v: 3207 (w), 2919 (w), 2868 (w), 2265 (ww), 1671 (m), 1567 (s), 1491 (m), 1445 (m), 1396 (m), 1351 (w), 1338 (w), 1328 (w), 1298 (m), 1237 (w), 1187 (w), 1091 (w), 1036 (s), 981 (w), 868 (m), 793 (m), 742 (s), 687 (s), 601 (s), 482 (w). Anal. Calcd. for C₃₀H₂₆Cl₂CrN₃: C: 74.89, H: 4.55, N: 14.89. Found: C: 74.24, H: 4.09, N: 14.57.

[Cr(5-tert-butyl-2-(CH₃N-2'-Z=CH-N(C₆H₄)(N(C₆H₅))(NCMe)Cl)] (3b). This product was prepared as described above for 3a, starting from 2b (0.138 g, 0.32 mmol) in acetonitrile (10 mL) to give 3b as a dark red solid (0.128 g, 93%). Analytically pure crystals of 3b suitable for X-ray diffraction were obtained by recrystallization from a concentrated acetonitrile solution. v: 3191 (w), 2958 (w), 2954 (w), 2903 (w), 2855 (w), 2771 (w), 1602 (m), 1587 (s), 1521 (w), 1483 (m), 1442 (m), 1393 (m), 1361 (m), 1272 (m), 1255 (m), 1232 (w), 1104 (w), 1047 (s), 1005 (m), 983 (m), 973 (w), 952 (w), 851 (m), 807 (m), 786 (m), 757 (s), 706 (m), 698 (s), 655 (w), 627 (w), 576 (w), 531 (w), 500 (w). Anal. Calcd. for C₃₀H₂₆Cl₂CrN₃: C: 52.79, H: 5.83, N: 12.96. Found: C: 52.22, H: 5.46, N: 12.31.

**Ethylene oligomerization.** All ethylene oligomerization tests were performed in a 100 mL double-walled stainless Parr reactor equipped with mechanical stirring, internal temperature control and continuous feed of ethylene. The Parr reactor was dried in an oven at 120 °C for 5 h prior to each run, and then placed under vacuum for 30 min. A typical reaction was performed by introducing toluene (30 mL) and the proper amount of cocatalyst into the reactor under an ethylene atmosphere. After 20 min, the toluene catalyst solution (10 mL, [Cr] = 10 μmol) was injected into the reactor under a stream of ethylene and then the reactor was immediately pressurized. Ethylene was continuously fed in order to maintain the ethylene pressure. After the desired time, the reaction was stopped by cooling the system to −60 °C and depressurizing. An exact amount of cyclohexane was introduced (as an internal standard) and the mixture was analyzed by quantitative GLC. The polymer was separated by filtration, washed with small portions of acidic ethanol, then ethanol and water, and the resulting material was dried in a vacuum oven at 60 °C for 12 h.

**X-ray Diffraction Analyses.** Suitable single-crystals of 3a and 3b were grown from concentrated acetonitrile solutions at room temperature and were mounted onto a glass fiber using the “oil-drop” method. Crystal data for compounds 3a and 3b can be found in the Supporting Information. Selected bond lengths and angles are given in the Figure captions. Diffraction data were collected at 150(2) K using an APEX2 Bruker-AXS diffractometer with graphite-monochromatized MoKα radiation (λ = 0.71073 Å). A combination of w and f scans was carried out to obtain at least a unique data set. The crystal structures were solved by direct methods, remaining atoms were located from difference Fourier synthesis followed by full-matrix least-squares refinement based on F2 (programs SIR97 and SHEXL-97) with the aid of the WINGX program. Except nitrogen linked hydrogen atom that was introduced in the structural model through Fourier difference maps analysis, H atoms were finally included in their calculated positions. Relevant collection and refinement data are given in Table S1 (Supporting Information). Crystal data and details of data collection and structure refinement can be obtained from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif (CCDC 1402488, 1402489).
Notes and references

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