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

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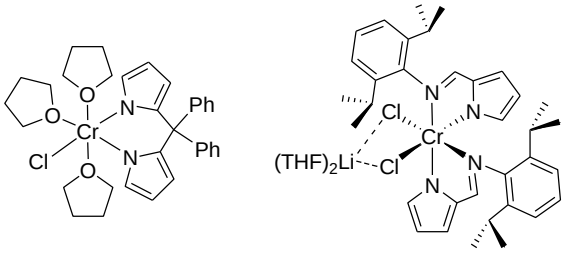
Chromium(III) complexes [$CrCl_2$(L)(THF)] based on monoanionic tridentate ligands [**2a**, L = {2-(C_4H_3N-2'-CH=N)C_2H_4NHPh}; **2b**, L = {5-*tert*-butyl-2-(C_4H_2N-2'-CH=N)C_2H_3NHPh}; **2c**, L = {2-(C_4H_3N-2'-CH=N)C_2H_4OPh}] have been prepared. Complexes **2a,b** were converted into the monomeric acetonitrile adducts [$CrCl_2$(L)(NCMe)] [**3a**, L = {2-(C_4H_3N-2'-CH=N)C_2H_4NHPh}; **3b**, L = {5-*tert*-butyl-2-(C_4H_2N-2'-CH=N)C_2H_3NHPh}] 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** and **3b**. Upon activation with methylaluminoxane (MAO), chromium precatalysts **2a** and **2c** showed good activity in ethylene oligomerization (TOF = 47.0–57.0 × 10^3 (mol ethylene)(mol Cr)$^{-1}$·h^{-1} at 80 °C), producing mostly oligomers (93.0–95.6 wt% of total products). On 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-C_4 (68.7 wt%) and α-C_6 (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-C_4 and increase in the α-C_8 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 (Cossee-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 NˆNˆN,[7] PˆNˆP,[8] SˆNˆS,[9] PˆN,[10] and NˆNˆP[11] 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.[12] Recently, Duchateau and co-workers evaluated the ethylene oligomerization capabilities of different dipyrrole-based ancillary ligands using different activation methods.[12a] Upon activation with triethylaluminum (TEA), chromium catalysts stabilized by dipyrrole-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 methylcyclohexane using dried-methylaluminoxane (DMAO) along with triisobutylaluminum (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 pyrrolide-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.[12d]



Duchateau et al.[12a] Gibson et al.[12d]

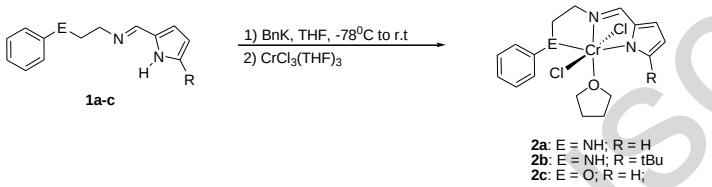
Chart 1. Examples of pyrrolide-based chromium complexes applied in ethylene oligo- and polymerization.

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In this work, we report a series of new chromium complexes supported by pyrrolide-imine-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 Pyrrolide-Imino-Amine/Ether Tridentate Ligands. The pyrrole-imino-amine/ether pro-ligands {ENN^R}H (E = NH, R = H, **1a**; E = NH, R = *t*Bu, **1b**; E = O, R = H, **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 IR, ^{1}H and ^{13}C NMR spectroscopy and combustion analysis. Treatment of **1a-c** with 1.0 equiv. of benzyl potassium and then $CrCl_3(THF)_3$ yielded the corresponding chromium complexes {ENN^R}$CrCl_2$(THF) (**2a**-**c**), which were isolated as red solids in moderate to good yields (63-83%) (Scheme 1). These compounds, which are air- and moisture-sensitive, show moderate solubility at room temperature in dichloromethane and THF, and are readily soluble in acetonitrile. The identity of **2a-c** was established on the basis of elemental analysis, IR spectroscopy, and magnetochemistry. Elemental analyses of complexes **2a-c** synthesized in THF are consistent with one molecule of THF occupying chromium's sixth coordination site. Magnetic moment measurements gave values (see the Experimental section) as expected for the d^3 electronic configuration of trivalent chromium in octahedral fields.[13]



cheme 1. Synthesis of {ENN^R}$CrCl_2$(THF) complexes.

Complexes **2a,b** were converted into the acetonitrile adducts Cr(L)Cl_2(NCMe) [**3a**, L = {2-(C_4H_3N-2'-CH=N)C_2H_4NHPh}; **3b**, L = {5-*tert*-butyl-2-(C_4H_2N-2'-CH=N)C_2H_3NHPh}] by reaction with acetonitrile at room temperature. The identity of **3a,b** was established on the basis of elemental analysis, IR spectroscopy, and by an X-ray diffraction study. In the solid state, **3a** and **3b** are monomeric with a six-coordinated chromium center in a slightly distorted octahedral geometry (Figures 1-2). The chromium center is chelated by the pyrrolide-imino-amine ligand in a tridentate meridional fashion, with the two chloride ligands occupying mutually *trans* positions and the acetonitrile molecule coordinated *trans* to the imino nitrogen donor. The Cr–N(pyrrole) bond distances [2.0239(13) Å for **3a** and 2.070(2) Å for **3b**] are close to the values previously reported for Cr(III) complexes having pyrrole unit.[12b,12d,14] The average Cr-Cl_{av} (2.318 Å for **3a** and 2.325 for **3b**) bond distances are comparable to those found in similar chromium(III) compounds having tridentate ligands such as $CrCl_3$L (L = bis(carbene)pyridine, Cr-Cl_{av} = 2.327 Å) and $CrCl_3${$HN(CH_2CH_2SEt)_2$} (Cr-Cl_{av} = 2.312 Å). The Cr–N(imine) bond distances in **3a** and **3b** (1.991(1), 1.986(2) Å, respectively) are in the range (1.984(3)-2.057(3) Å) of those determined for related phenoxy-based{ONN^R}$CrCl_2$(solvent) (solvent = MeCN, THF, pyridine) complexes.[1c,15] The chelate bite angles of the N-N-N ligand in **3a** [N-Cr-N, 80.26(5) º and 79.51(5) º] and in **3b** [N-Cr-N, 80.91(9) º and 78.56(9) º] compare well to those in $CrCl_3${bis[2-(3,5-dimethyl-l-pyrazolyl)ethyl]ether}[1d] [N-Cr-O, 85.54(5) º and 87.06(5) º], $CrCl_3${$HN(CH_2CH_2PPh_2)_2$}[8d] [P-Cr-N, 81.08(8) °, 82.07(8) °] and $CrCl_3${$HN(CH_2CH_2SR)_2$}[16] [S-Cr-N, 83.07(5) °, 82.90(5) °] complexes. The coordination of the acetonitrile ligand in **3a** and **3b** is distorted from linear geometry [Cr(1)–N(1)-C(2) = 173.35 ° and Cr(1)–N(31)-C(32) =164.24 °, respectively].[17]

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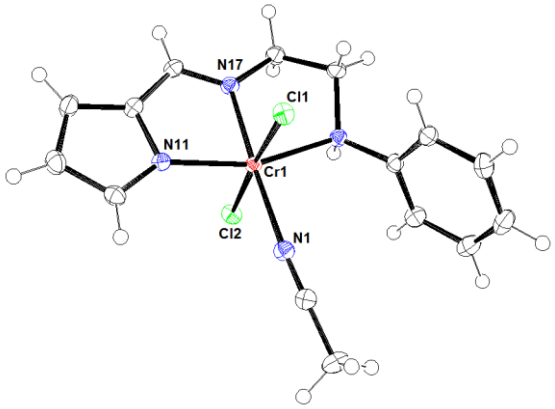


Figure 1. Molecular structure of **3a** (thermal ellipsoids drawn at 50% probability level). Selected bond distances (Å) and angles (deg): Cr(1)-N(17) = 1.9911(13), Cr(1)-N(11) = 2.0239, Cr(1)-N(1) = 2.0623(14), Cr(1)-N(20) = 2.1455(13), Cr(1)-C1(1) = 2.3030(4), Cr(1)-Cl(2) = 2.3339(4), N(17)-Cr(1)-N(11) = 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)-Cl(1) = 92.28(4), N(11)-Cr(1)-Cl(1) = 91.08(4), N(1)-Cr(1)-Cl(1) = 89.94(4), N(20)-Cr(1)-Cl(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), Cl(1)-Cr(1)-Cl(2) = 176.319(17).

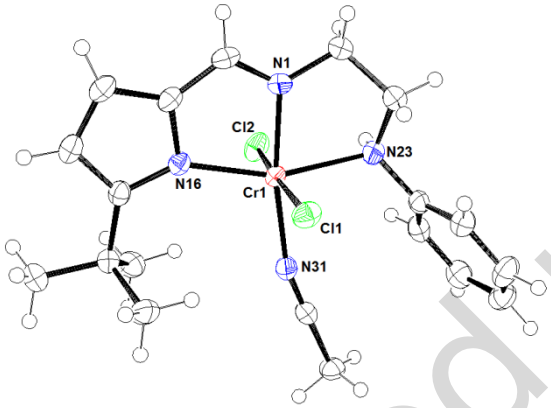


Figure 2. Molecular structure of **3b** (ellipsoids drawn at 50% probability level). Selected bond distances (Å) and angles (deg): Cr(1)-N(1) = 1.986(2), Cr(1)-N(16) = 2.070(2), Cr(1)-N(31) = 2.078(2), Cr(1)-N(23) = 2.181(2), Cr(1)-C1(1) = 2.3145(8), Cr(1)-Cl(2) = 2.3365(4), N(1)-Cr(1)-N(16) = 80.91(9), N(1)-Cr(1)-N(31) = 170.73(9), N(16)-Cr(1)-N(31) = 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)-Cl(1) = 91.55(7), N(16)-Cr(1)-Cl(1) = 92.33(6), N(31)-Cr(1)-Cl(1) = 86.96(7), N(23)-Cr(1)-Cl(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), Cl(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% $AlMe_3$, 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]

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Table 1. Ethylene Oligomerization with **2a-c**/MAO systems.[a]

Entry	Cat.	[Al/Cr]	TOF[b] ($10^3 \cdot h^{-1}$)	Oligomer distribution (wt%)[c] C_4 (α-C_4)	C_6 (α-C_6)	C_8 (α-C_8)	C_{10} (α-C_{10})	C_{12+}	Olig. (wt%)	PE (wt%)	Total product (mg)
1	**2a**	300	47.0	67.6 (97.2)	16.2 (88.9)	4.60 (73.9)	5.30 (60.2)	6.30	95.6	4.4	3450
2	**2b**	300	3.30	33.4 (80.0)	22.3 (78.0)	19.4 (62.0)	10.8 (70.0)	14.1	27.0	73.0	846
3	**2c**	300	57.0	63.2 (97.5)	16.7 (96.8)	5.4 (77.0)	2.8 (47.1)	10.7	93.0	7.0	4300
4	**2b**	500	73.5	69.7 (98.6)	22.4 (85.7)	5.6 (90.7)	1.7 (100)	0.70	97.6	2.4	5400
5	**2b**	1000	43.5	14.0 (96.5)	17.6 (96.9)	17.5 (88.4)	14.6 (88.3)	36.3	76.2	23.8	4000
6	**2a**	500	75.7	63.5 (97.0)	20.1 (97.2)	4.70 (94.5)	1.80 (74.4)	9.90	97.6	2.4	5430
7	**2a**	1000	62.5	14.8 (97.0)	18.2 (98.2)	17.7 (90.9)	14.3 (91.0)	35.0	80.6	19.4	5430
8[d]	**2a**	300	7.1	64.6 (94.0)	25.7 (88.9)	9.70 (75.1)	-	-	79.4	20.6	630
9[e]	**2a**	300	25.0	68.1 (94.0)	17.0 (86.8)	5.10 (75.0)	4.60 (61.8)	5.20	91.7	8.3	3820
10[f]	**2a**	300	17.3	66.5 (88.1)	15.9 (82.6)	5.70 (73.7)	5.10 (62.8)	6.80	87.5	10.5	4150
11[g]	**2a**	1000	-	-	-	-	-	-	-	100	2370

[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)$^{-1} \cdot h^{-1}$ as determined by quantitative GLC. [c] C_n, percentage of olefin with *n* carbon atoms in oligomers; α-C_n, percentage of terminal alkene in the C_n 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)$^{-1} \cdot h^{-1}$. 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)$^{-1} \cdot h^{-1}$]. 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 C_4 to C_{12+} 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-C_6 (17.4 wt%), α-C_8 (12.0 wt%), and α-C_{10} (7.6 wt%) and concomitant decrease in α-C_4 (26.7 wt%). Precatalyst **2c**, which bears a phenoxy 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-C_4 (61.6 wt%) and α-C_6 (16.2 wt%)], as illustrated in Figure 3.

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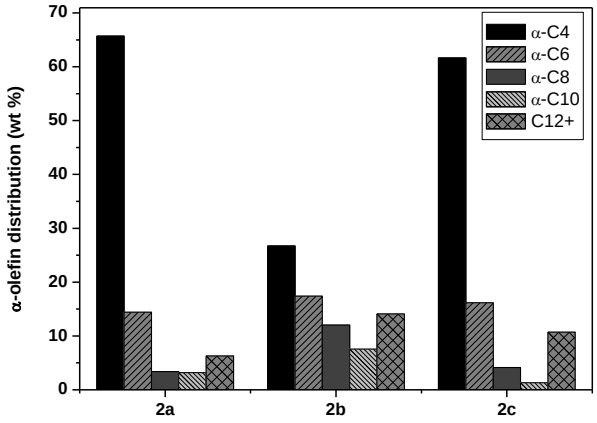


Figure 3. Selectivity of **2a-c**/MAO oligomerization systems for α-olefins (80 °C, 20 bar, MAO-to-Cr = 300).

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 α-olefins with a M_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 β-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.[1c,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 $[(Ph_3SiO)Cr^{III}Me]^+$ and $[(\eta^6\text{-toluene})Cr^{III}Me_2]^+$, generated from a disproportionation reaction, are the actual polymerization active species at lower [Al]/[Cr] ratios (≤100), while the divalent $[(\eta^6\text{-toluene})Cr^{II}Me]^+$ 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 α-olefins fractions [α-C_4 (**2a**: 61.6 wt%; **2b**: 68.7 wt%) and α-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 α-C_8 fraction. For instance, the activation of **2a** with 1000 equiv of MAO afforded only 14.3 wt% of α-C_4 and a significant improvement in the selectivity for α-C_8 (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 α-C_6 (22.8 wt%) and α-C_8 (7.3 wt%) were obtained, and no oligomers heavier than C_8 were produced.

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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 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 pyrrolide-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. $CrCl_3(THF)_3$, 2-phenoxyethanamine, *N*-phenylethylenediamine, and pyrrole-2-carboxyaldehyde 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-1*H*-pyrrole-2-carboxyaldehyde.[25] Ethylene (White Martins Co.) and argon were deoxygenated and dried through BTS columns (BASF) and activated molecular sieves prior to use. 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. ^1H and ^{13}C chemical shifts are reported in ppm vs. $SiMe_4$ and were determined by reference to the residual solvent peaks. Elemental analysis was performed by the Analytical Central Service of the Institute of Chemistry-USP (Brazil) and is the average of two independent determinations. Magnetic moment data were obtained on a Quantum Design SQUID MPMS magnetometer, operating with a constant magnetic field of 1000 Oe. Quantitative gas chromatographic analysis of ethylene oligomerization products was performed on a Agilent 7890A instrument with a Petrocol HD capillary column (methyl silicone, 100 m length, 0.25 mm i.d. and 0.5 µm film thickness) operating at 36 °C for 15 min followed by heating at 5 °C·min^{-1} until 250 °C; cyclohexane was used as internal standard.

2-(C_4H_3N-2'-CH=N)C_2H_4NHPh (1a). This ligand was prepared using a modification of the literature method.[26] To a stirred solution containing pyrrole-2-carboxyaldehyde (0.250 g, 2.63 mmol) in ethanol (75 mL), *N*-phenylethylenediamine (0.358 g, 2.63 mmol) was added. The reaction mixture was stirred for 72 h at 65 ºC. Evaporation of ethanol gave a brown solid residue, which was washed with pentane (3 × 10 mL), and recrystallized from ethanol/ether to give **1a** as an off-white solid (0.334 g, 60%). Mp: 78.8 ºC. ^1H NMR (300 MHz, $CDCl_3$, 25 ºC): δ 3.41 (t, $^3J_{HH}$ = 5.4 Hz, 2H, CH_2), 3.74 (t, $^3J_{HH}$ = 5.4 Hz, 2H, CH_2), 3.95 (s, 1H, N-H), 6.25 (dd, $^2J_{HH}$ = 2.7 and 3.5 Hz, 1H, 4-pyr), 6.49 (dd, $^2J_{HH}$ = 1.2 and 3.5 Hz, 1H, 3-pyr), 6.64 (d, $^2J_{HH}$ = 7.6 Hz, 2H, Ar-H), 6.71 (t, $^3J_{HH}$ = 7.3 Hz, 1H, Ar-H), 6.91 (s, 1H, 5-pyr), 7.18 (dd, $^2J_{HH}$ = 7.4 and 8.5 Hz, 2H, Ar-H), 8.07 (s, 1H, N=C-H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC): δ 44.74 (*C*H_2), 59.54 (*C*H_2), 110.0 ($C_{pyrrole}$), 113.24 ($C_{pyrrole}$), 114.74 (C_{aro}), 117.64 (C_{aro}), 122.14 (C_{aro}),, 129.36 (*C*$_{pyrrole}$), 130.19 (quat. *C*$_{pyrrole}$), 148.12 (quat. C_{aro}), 153.40 (*C*=N). IR (KBR, cm^{-1}): ν 3390 (w), 3151 (m), 3083 (w), 2965 (w), 2909 (w), 2838 (w), 1637 (s), 1599 (s), 1504 (s), 1464 (s), 1423 (s), 1373 (w), 1355 (m), 1311 (s), 1268 (m), 1131 (s), 1059 (m), 1037 (s), 991 (w), 977 (m), 920 (m), 904 (m), 879 (m), 748 (s), 696 (s), 610 (w), 511 (w). Anal. Calcd. for $C_{13}H_{15}N_3$: C, 73.21; H, 7.09; N, 19.70. Found: C, 73.04; H, 7.10; N, 19.69.

5-*tert*-Butyl-2-(C_4H_2N-2'-CH=N)C_2H_4(NH)Ph (1b). This product was prepared as described above for **1a**, starting from 5-*tert*-butyl-1*H*-pyrrole-2-carboxyaldehyde (0.500 g, 3.30 mmol) and *N*-phenylethylenediamine (0.450 g, 3.30 mmol). **1b** was was obtained as an off-white solid (0.694 g, 78%). Mp: 104.6 ºC. ^1H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 1.33 (s, 9H, C(CH_3)$_3$), 3.42 (dd, $^2J_{HH}$ = 5.7 and 11.4 Hz, 2H, CH_2), 3.73 (t, $^3J_{HH}$ = 5.7 Hz, 2H, CH_2), 3.96 (s, 1H, N-H), 5.99 (d, $^2J_{HH}$ = 3.6 Hz, 1H, 4-pyr), 6.39 (d, $^2J_{HH}$ = 3.5 Hz, 1H, 3-pyr), 6.66 (d, $^2J_{HH}$ = 7.9 Hz, 2H, Ar-H), 6.71 (t, $^3J_{HH}$ = 7.3 Hz, 1H, Ar-H), 7.18 (t, $^3J_{HH}$ = 7.8 Hz, Ar-H), 7.98 (s, 1H, N=C-H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC): δ 30.43 (C(*C*H_3)$_3$), 31.80 (*C*(CH$_3$)$_3$), 44.77 (*C*H_2), 59.65 (*C*H_2), 105.01 ($C_{pyrrole}$), 113.28 ($C_{pyrrole}$), 115.31 (C_{aro}), 117.58 (C_{aro}), 128.71 (quat. *C*$_{pyrrole}$), 129.33 (*C*$_{pyrrole}$), 147.07 (quat. *C*$_{aro}$), 148.20 (*C*$_{aro}$), 153.20 (*C*=N). IR (KBR, cm^{-1}): ν 3240 (m), 2965 (m), 2896 (w), 2884 (w), 2836 (w), 1635 (s), 1599 (s), 1566 (m), 1485 (s), 1465 (m), 1424 (m), 1360 (m), 1335 (w), 1307 (m), 1278 (m), 1258 (s), 1226 (m), 1157 (w), 1100 (m), 1054 (w), 1039 (s), 1022 (w), 922 (m), 901 (m), 880 (w), 849 (w), 817 (w), 787 (s), 755 (s), 696 (s), 600 (m), 512 (s), 421 (m). Anal. Calcd. for $C_{17}H_{23}N_3$: C, 75.80; H, 8.61; N, 15.60. Found: C, 75.66; H, 8.30; N, 15.22.

2-(C_4H_3N-2'-CH=N)C_2H_4OPh (1c). This product was prepared as described above for **1a**, starting from pyrrole-2-carboxyaldehyde (0.250 g, 2.63 mmol) and 2-phenoxyethylamine (0.360 g, 2.63 mmol). **1c** was obtained as an off-white solid (0.416 g, 87%). Mp: 91.1 ºC. ^1H NMR (300 MHz, $CDCl_3$, 25 ºC): δ 3.90 (t, $^3J_{HH}$ = 5.6, 2H, CH_2), 4.20 (t, $^3J_{HH}$ = 5.6 Hz, 2H, CH_2), 6.24 (dd, $^2J_{HH}$ = 2.7 and 3.5 Hz, 1H, 4-pyr), 6.51 (dd, $^2J_{HH}$ = 1.3 and 3.5, 1H, 3-pyr), 6.90–6.96 (m, 4 H, 5-pyr + 3 Ar-H), 7.25-7.30 (m, 2H, Ar-H), 8.15 (s, 1H, -CH=N-). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC): δ 59.72 (*C*H_2), 67.68 (*C*H_2), 109.85 ($C_{pyrrole}$), 114.62 ($C_{pyrrole}$), 114.80 (C_{aro}), 120.90 ($C_{pyrrole}$), 122.08 (C_{aro}), 129.54 (C_{aro}), 130.30 (quat. *C*$_{pyrrole}$), 153.83 (*C*=N), 158.91 (quat. *C*$_{aro}$). IR (KBR, cm^{-1}): ν 3430 (sh), 3135 (w), 3083 (w), 2967 (w), 2925 (w), 2901 (w), 2850 (w), 1637 (s), 1594 (m), 1492

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(m), 1454 (m), 1423 (m), 1367 (m), 1307 (w), 1243 (s), 1177 (w), 1132 (m), 1106 (w), 1085 (m), 1051 (m), 1037 (m), 927 (w), 902 (m), 750 (s), 694 (m), 607 (m), 512 (m). Anal. Calcd. for $C_{13}H_{14}N_2O$: C, 72.87; H, 6.59; N, 13.07. Found: C, 72.55; H, 7.02; N, 13.06.

[Cr{2-(C_4H_3N-2'-CH=N)C_2H_4(NH)Ph}(THF)Cl_2] (2a). A solution of benzyl potassium (0.122g, 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 $CrCl_3(THF)_3$ (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 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}): ν 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 $C_{17}H_{21}Cl_2CrN_3O$: C: 50.13, H: 5.44, N: 10.32. Found: C: 49.93, H: 5.54, N: 10.35.

[Cr{5-tert-butyl-2-(C_4H_2N-2'-CH=N)C_2H_4(NH)Ph}(THF)Cl_2] (2b). This product was prepared as described above for **2a**, starting from benzyl potassium (0.110 g, 0.94 mmol), **1b** (0.229 g, 0.85 mmol) and $CrCl_3(THF)_3$ (0.316 g, 0.85 mmol) in THF (10 mL) to give **2b** as a red solid (0.248 g, 63%). IR (ATR, cm^{-1}): ν 3196 (w), 2962 (w), 2950 (w), 2902 (w), 2859 (w), 1606 (m), 1593 (s), 1525 (w), 1489 (m), 1446 (m), 1396 (m), 1359 (m), 1271 (m), 1256 (m), 1230 (w), 1205 (w), 1105 (w), 1049 (s), 1004 (m), 985 (m), 977 (w), 954 (w), 848 (m), 801 (m), 788 (m), 758 (s), 707 (m), 694 (s), 657 (w), 626 (w), 577 (w), 532 (w), 501 (w). μ (BM) = 3.68. Anal. Calcd. for $C_{21}H_{30}Cl_2CrN_3O$: C: 54.43, H: 6.53, N: 9.07. Found: C: 54.13, H: 6.47, N: 8.85.

[Cr{2-(C_4H_3N-2'-CH=N)C_2H_4(O)Ph}(THF)Cl_2] (2c). This product was prepared as described above for **2a**, starting from benzyl potassium (0.120 g, 0.93 mmol), **1c** (0.199 g, 0.93 mmol) and $CrCl_3(THF)_3$ (0.346 g, 0.93 mmol) in THF (10 mL) to give **2c** as a red solid (0.315 g, 83%). IR (ATR, cm^{-1}): ν 2927 (w), 2870 (w), 1660 (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 $C_{17}H_{21}Cl_2CrN_2O_2$: C: 50.01, H: 5.18, N: 6.86. Found: C: 49.78, H: 5.11, N: 6.67.

[Cr{2-(C_4H_3N-2'-CH=N)C_2H_4(NH)Ph}(NCMe)Cl_2] (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 (*ca.* 5 mL), and then pentane (10 mL) was added to afford an orange precipitated. 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}): ν 32037 (w), 2919 (w), 2868 (w), 2265 (vw), 1671 (m), 1567 (s), 1491 (m), 1445 (m), 1396 (m), 1351 (w), 1338 (w), 133 (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 $C_{15}H_{17}Cl_2CrN_4$: C: 47.89, H: 4.55, N: 14.89. Found: C: 47.24, H: 4.09, N: 14.57.

[Cr{5-tert-butyl-2-(C_4H_2N-2'-CH=N)C_2H_4(NH)Ph}(NCMe)Cl_2] (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. ν 3191 (w), 2958 (w), 2954 (w), 2903 (w), 2855 (w), 2271 (vw), 1602 (m), 1587 (s), 1521 (w), 1483 (m), 1442 (m), 1393 (m), 1361 (m), 1272 (m), 1255 (m), 1232 (w), 1202 (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 $C_{19}H_{25}Cl_2CrN_4$: 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 APEXII Bruker-AXS diffractometer with graphite-monochromatized MoKa radiation (l = 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 SHELXL-97)[27] with the aid of the WINGX program.[28] 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)

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