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Article

Synthesis, Characterization and Ethylene Oligomerization Studies of Chromium Complexes Bearing Imino-Furfural Ligands

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Uma série de complexos de cromo(III) contendo ligantes imina-furfural (**Cr1**-**Cr4**) foram sintetizados e caracterizados por espectrometria de massas de alta resolução (HRMS). Todos os pré-catalisadores de cromo, ativados com metilaluminoxano (MAO), apresentaram atividade moderada na oligomerização do etileno [frequência de rotação (TOF) = 11.800-23.200 mol(etileno) mol(Cr)$^{-1}$ h^{-1})] produzindo oligômeros na faixa de C_4-C_{12+} e com boa seletividade para olefinas-α. Os pré-catalisadores de cromo(III) formados *in situ* pela combinação do ligante imina-furfural **L^1** com [CrCl$_3$(THF)$_3$] ou [Cr(acac)$_3$] apresentaram baixas atividades, produzindo oligômeros juntamente com quantidades variáveis de polietileno. A utilização de diferentes compostos de cromo e cocatalisadores influenciam a atividade bem como a seletividade para a produção de olefinas-α, o que sugere que diferentes espécies catalíticas são formadas.

A series of chromium(III) complexes bearing imino-furfural ligands (**Cr1**-**Cr4**) were synthesized and characterized by high-resolution mass spectrometry (HRMS). All chromium precatalysts, activated with methylaluminoxane (MAO), exhibited moderate to high activities for ethylene oligomerization [turnover frequency (TOF) = 11,008-23,200 mol(ethylene) mol(Cr)$^{-1}$ h^{-1})] producing oligomers in the range C_4-C_{12+} with good selectivity for α-olefins. The *in situ* chromium precatalysts formed by mixing imino-furfural ligand **L^1** with [CrCl$_3$(THF)$_3$] or [Cr(acac)$_3$] showed low activities, producing oligomers together with varying amounts of polyethylene. The use of different chromium sources and cocatalysts influences the activity as well as the selectivities toward α-olefin production, which suggests that different active species are formed.

Keywords: imino-fufural ligands, chromium complexes, ethylene oligomerization

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 comprehension of this industrially relevant catalytic process.[1-7] 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.).[8-10] A nonselective oligomerization is closely reminiscent of a polymerization randomly truncated at the early stages of the chain growth (Cossee-Arlman mechanism).[11]

Among the transition-metal-based catalysts, chromium catalysts occupy a unique position, since they provide both selective (commercially viable tri-, and tetramerization catalytic systems)[12-14] and nonselective ethylene oligomerization. Typical examples are the Chevron Phillips trimerization catalyst,[15] the first and sole trimerization system to be successfully commercialized, and the few existing tetramerization systems with 1-octene selectivities in the range of 70%.[16,17]

In the past years, several well-defined ethylene oligomerization chromium catalysts bearing N^N^N,[18-22] P^N^P,[23-36] S^N^S,[37-40] P^N[41-43] ligands have been reported. Such bi- and tridentate ligands play a central role in stabilizing

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a particular oxidation state and consequently in determining the catalytic behavior (selective *vs.* nonselective). Particularly, the BP Chemicals and Sasol PNP-chromium complexes (PNP = $PhCH_2N(CH_2CH_2PPh_2)_2$), stabilized by neutral $RN(PAr_2)_2$ ligands, have marked a milestone in this field. These catalysts oligomerize ethylene with high selectivity toward either 1-hexene or 1-octene, depending on the ligand substituents (Ar = 2-OMe–C_6H_4, C_6H_5, respectively).[16,44,45] Further replacements of the heteroatom combinations or modifications of the ligand frameworks also produced highly selective ethylene trimerization catalysts.[46-50]

More recently, Gambarotta and co-workers[51] reported chromium complexes bearing a series of pyridine-phosphine ligands and their catalytic behavior in 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. 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. It has been demonstrated that minor differences in the ligand structure can result in remarkable changes not only in catalytic activity but also in selectivity toward α-olefins *vs.* polyethylene and distribution of oligomeric products. Ligand $PyCH_2N(Me)P^{i}Pr_2$, 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.[51]

In this work, we report a series of chromium complexes supported by imino-furfural ligands and investigated their catalytic behavior for ethylene oligomerization. We also discuss the performance of *in situ*-generated catalysts evaluating the effect of chromium sources and cocatalyst type on their activity and selectivity towards the production of α-olefins.

Experimental

General procedures

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. $[CrCl_3(THF)_3]$, $[Cr(acac)_3]$, 2-phenoxyethanamine, 5-methylfurfural, 2-phenoxybenzenamine, 2-methoxybenzylnamine, and furfural were purchased from Sigma-Aldrich and used as received. Ethylene (White Martins Co.) and argon were deoxygenated and dried through BTS columns (BASF) and activated molecular sieves prior to use. Methylaluminoxane (MAO) (Witco, 5.21 wt.% Al solution in toluene), polymethylaluminoxane-improved performance (PMAO-IP) (Akzo Nobel, 13.0 wt.% Al solution in toluene) was used as received. Ethylaluminum sesquichloride (EASC) (Akzo Nobel) was used with the previous dilution (2.1 wt.% Al solution in toluene). Infrared spectra (IR) were performed on a Bruker FT-IR Alpha Spectrometer. ^1H and $^{13}C\{^1H\}$ nuclear magnetic resonance (NMR) spectra were recorded on a Varian Inova 300 spectrometer operating at 25 °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. High-resolution mass spectra (HRMS) of chromium precatalysts (**Cr1**-**Cr4**) were obtained by electrospray ionization (ESI) in the positive mode in $CHCl_3$ solutions using a Waters Micromass® Q-Tof spectrometer. Quantitative gas chromatographic analysis of ethylene oligomerization products was performed on an Agilent 7890A instrument with a Petrocol HD capillary column (methyl silicone, 100 m length, 0.25 mm i.d. and film thickness of 0.5 μm) operating at 36 °C for 15 min followed by heating at 5 °C min^{-1} until 250 °C; cyclohexane was used as the internal standard.

Synthesis of the imino-furfural proligands

N-((5-Methylfuran-2-yl)methylene)-2-phenoxyethanamine (**L^1**): A solution of 5-methylfurfural (0.44 g, 4.00 mmol) in ethanol (8 mL) was added to a solution of 2-phenoxyethanamine (0.55 g, 4.00 mmol) in ethanol (20 mL) and stirred at room temperature for 3 days. Then, the solvent was evaporated under reduced pressure to afford an orange solid that was washed with hexane and dried under vacuum. The resulting orange solid was crystallized in ether (0.79 g - 86%); m.p. 70 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 2.37 (s, 3H), 3.95 (t, 2H, *J* 5.8 Hz), 4.28 (t, 2H, *J* 5.8 Hz), 6.08 (d, 1H, *J* 3.4 Hz), 6.64 (d, 1H, *J* 3.2 Hz), 6.92 (m, 3H, *J* 8.9 Hz), 7.26 (t, 2H, *J* 9.2 Hz), 8.08 (s, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 13.9, 60.3, 67.1, 108.0, 114.6, 116.7, 120.7, 129.3, 149.9, 151.4, 155.8, 158.7; IR (neat) ν_{max}/cm^{-1} 3111 (w), 2936 (w), 2878 (w), 2836 (w), 1647 (s), 1586 (m), 1531 (m), 1498 (m), 1455 (m), 1435 (m), 1335 (m), 1246 (s), 1165 (m), 1080 (m), 1056 (m), 1022 (m), 947 (m), 904 (m), 813 (m), 780 (w), 761 (s), 695 (m), 614 (w), 510 (w); elemental analysis for $C_{14}H_{15}NO_2$ (229.11): C, 73.34; H, 6.59; N, 6.11%; found: C, 73.36; H, 6.96; N, 6.19%.

_N_-((5-Methylfuran-2-yl)methylene)-2-phenoxybenzenamine (L^2): This product was prepared by following a procedure similar to what was described above for **L^1**, starting from 5-methylfurfural (1.00 g, 9.10 mmol), and 4-phenoxybenzenamine (1.69 g, 9.10 mmol). **L^2** was obtained as a brown solid (2.41 g, 96%); m.p. 94 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.38 (s, 3H), 6.11 (d, 1H, *J* 3.4 Hz), 6.76 (d, 1H, *J* 3.2 Hz), 6.93-7.18 (m, 7H), 7.28 (t, 2H, *J* 7.5 Hz), 8.22 (s, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 13.9, 108.6, 118.3, 118.6, 119.9, 122.3, 122.7, 124.1, 126.1, 129.4, 143.7, 148.7, 149.6, 150.5, 156.7, 157.5; IR (neat) ν_{max}/cm^{-1} 3117 (m), 2941 (m), 2874 (m), 2832 (m), 1649 (s), 1587 (s), 1535 (m), 1498 (m), 1464 (m), 1435 (m), 1393 (w), 1369 (w), 1289 (w), 1246 (s), 1174 (m), 1108 (w), 1084 (m), 1056 (m), 1022 (m), 1004 (m), 965 (w), 947 (m), 899 (m), 809 (m), 756 (s), 690 (m), 610 (w), 514 (w); elemental analysis for $C_{18}H_{15}NO_2$ (277.11): C, 77.96; H, 5.45; N, 5.05%; found: C, 77.45; H, 5.70; N, 5.20%.

2-Methoxyphenyl-_N_-((5-methylfuran-2-yl)methylene) methanamine (L^3): This product was prepared by following a procedure similar to what was described above for **L^1**, starting from 5-methylfurfural (0.57 g, 5.2 mmol) and 2-methoxybenzylnamine (0.71 g, 5.2 mmol). After purification by chromatographic column on silica gel (petroleum ether/ethyl acetate, 90:10), **L^3** was obtained as a dark brown oil (1.15 g, 97%); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.35 (s, 3H), 3.82 (s, 3H), 4.78 (s, 2H), 6.06 (d, 1H, *J* 3.2 Hz), 6.60 (d, 1H, *J* 3.2 Hz), 6.85 (1H, d, $^3J_{HH}$ 8.2 Hz), 6.93 (1H, t, $^3J_{HH}$ 7.4 Hz), 7.22-7.30 (2H, m), 8.01 (1H, s); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 13.5, 54.8, 58.9, 107.6, 109.8, 115.6, 120.1, 126.7, 127.9, 129.4, 149.9, 150.0, 154.9, 156.9; IR (neat) ν_{max}/cm^{-1} 3120 (w), 3017 (w), 2960 (w), 2841 (w), 1635 (m), 1584 (m), 1580 (m), 1498 (s), 1464 (s), 1388 (w), 1346 (w), 1289 (m), 1241 (s), 1203 (w), 1184 (w), 1132 (w), 1046 (w), 1022 (m), 961 (w), 756 (m), 728 (w), 604 (w), 462 (w); elemental analysis for $C_{14}H_{15}NO_2$ (229.11): C, 73.34; H, 6.59; N, 6.11%; found: C, 72.98; H, 6.55; N, 6.14%.

_N_-((Furan-2-yl)methylene)-2-phenoxybenzenamine (L^4): This product was prepared by following a procedure similar to what was described above for **L^1**, starting from furfural (1.84 g, 19.2 mmol), and 2-phenoxybenzenamine (3.51 g, 18.9 mmol). **L^4** was obtained as a yellow solid (3.50 g, 70%); m.p. 89 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.50 (s, 1H), 6.89 (d, 1H, *J* 3.3 Hz), 6.97-7.06 (m, 4H), 7.12-7.16 (m, 3H), 7.29 (t, 2H, *J* 7.8 Hz), 7.57 (s, 1H), 8.34 (s, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 112.0, 116.1, 118.2, 120.1, 122.1, 124.1, 126.5, 129.4, 143.3, 145.53, 148.7, 149.8, 151.9, 157.5; IR (neat) ν_{max}/cm^{-1} 3002 (m), 2929 (m), 2884 (m), 2836 (m), 1646 (s), 1580 (m), 1570 (m), 1492 (s), 1460 (m), 1440 (m), 1388 (m), 1374 (m), 1289 (m), 1246 (s), 1179 (w), 1113 (w), 1022 (m), 937 (w), 795 (m), 756 (s), 610 (w), 581 (w), 505 (w); elemental analysis for $C_{14}H_{15}NO_2$ (263.09): C, 77.55; H, 4.98; N, 5.32%; found: C, 77.81; H, 4.99; N, 5.45%.

Synthesis of chromium precatalysts

$[L^1CrCl_2(\mu\text{-}Cl)]_2$ (Cr1): To a solution of $[CrCl_3(THF)_3]$ (0.21 g, 0.56 mmol) in tetrahydrofuran (THF) (10 mL) was added a solution of **L^1** (0.14 g, 0.63 mmol) in THF (10 mL) and the resulting solution was stirred for 3 h at room temperature. The solvent was removed, and the resulting brown solid residue was washed with Et_2O (3 × 5.0 mL). Complex **Cr1** was obtained as a brown solid (0.14 g, 67%); ESI-HRMS ($CHCl_3$) *m/z* calcd. for $C_{14}H_{15}NO_2{}^{35}Cl_2{}^{52}Cr$ [M–Cl]$^+$: 350.9885; found: 350.9886.

$[L^2CrCl_2(\mu\text{-}Cl)]_2$ (Cr2): This compound was prepared according to the method described for **Cr1** using $[CrCl_3(THF)_3]$ (0.28 g, 0.75 mmol) and **L^2** (0.23 g, 0.83 mmol). Precatalyst **Cr2** was obtained as a brown solid (0.32 g, 98%); ESI-HRMS ($CHCl_3$) *m/z* calcd. for $C_{18}H_{15}NO_2{}^{35}Cl_2{}^{52}Cr$ [M–Cl]$^+$: 398.9885; found: 398.9886.

$[L^3CrCl_2(\mu\text{-}Cl)]_2$ (Cr3): This compound was prepared according to the method described for **Cr1** using $[CrCl_3(THF)_3]$ (0.27 g, 0.73 mmol) and **L^3** (0.19 g, 0.85 mmol). Precatalyst **Cr3** was obtained as a brown solid (0.16 g, 56%); ESI-HRMS ($CHCl_3$) *m/z* calcd. for $C_{14}H_{15}NO_2{}^{35}Cl_2{}^{52}Cr$ [M–Cl]$^+$: 350.9885; found: 350.9886.

$[L^4CrCl_2(\mu\text{-}Cl)]_2$ (Cr4): This compound was prepared according to the method described for **Cr1** using $[CrCl_3(THF)_3]$ (0.33 g, 0.89 mmol) and **L^4** (0.23 g, 1.00 mmol). Precatalyst **Cr4** was obtained as a red solid (0.34 g, 91%); ESI-HRMS ($CHCl_3$) *m/z* calcd. for $C_{17}H_{13}NO_2{}^{35}Cl_2{}^{52}Cr$ [M–Cl]$^+$: 384.9728; found: 384.9723.

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 desired ethylene pressure. After 15 min, 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 gas-liquid chromatography (GLC).

Crystal structure determination

Diffraction data for **L**^{1} and **L**^{2} were collected at 150(2) K using a Bruker APEX CCD diffractometer with graphite monochromated MoKα radiation (λ = 0.71073 Å). A combination of ω and φ scans was carried out to obtain at least a unique data set. The crystal structures were solved by direct methods; the remaining atoms were located from difference Fourier synthesis followed by full-matrix least-squares refinement based on F^2 (programs SIR97)[52] and then refined with full-matrix least-square methods based on F2 (SHELXL-97)[53] with the aid of the WINGX program.[54] All non-hydrogen atoms were refined with anisotropic displacement parameters. H atoms were finally included in their calculated positions. Crystal data and details of data collection and structure refinement for **L**^{1} and **L**^{2} can be obtained, free of charge, from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif (CCDC 1015675 and 1015679).

Theoretical calculations

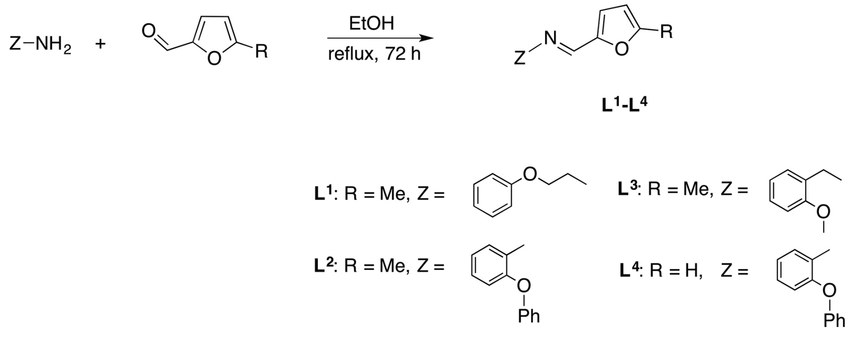
Full unconstrained geometry optimizations of all species were performed at density functional theory (DFT) level using the B3LYP hybrid functional formed by the three parameter fit of the exchange-correlation potential suggested by Becke[55] and the gradient-corrected correlation functional of Lee, Yang and Parr.[56] The polarized Dunning-Huzinaga DZ basis set[57,58] was used for the hydrogen, carbon, nitrogen, oxygen and chloride atoms. For the chromium atom the inner shell electrons were represented by the Los Alamos effective core potential (LANL2) of Hay and Wadt[59,60] and the valence electrons were explicitly included using the associated DZ basis set. All calculations were performed with the Gaussian 09 program using standard procedures and parameters.[61]

Results and Discussion

The imino-furfural proligands **L**^{1}-**L**^{4} were readily synthesized by Schiff base condensations between the corresponding primary amines and the corresponding furfural in refluxing ethanol (Scheme 1). These proligands were characterized by IR, ^{1}H and ^{13}C NMR spectroscopy, elemental analysis, and by an X-ray diffraction study for proligands **L**^{1} and **L**^{2}. The ^{1}H NMR spectra of **L**^{1}-**L**^{4} in $CDCl_3$ at room temperature exhibit resonances in the region δ 8.01-8.34 ppm assigned to the imine proton (HC=N), with the corresponding ^{13}C NMR resonances for the carbons of the imine moieties at ca. δ 157 ppm. In the solid state, the IR spectra of imina-furfural proligands showed the vibration modes of the imine (C=N) unit at 1635-1649 cm^{-1}.

Single crystals of the proligands **L**^{1} and **L**^{2} suitable for crystal X-ray diffraction analysis were obtained by slow evaporation from pentane solution. Crystal data and structure refinement are summarized in Table S1 (see Supplementary Information). The molecular geometry and atom-labeling scheme are shown in Figures 1 and 2. The molecular structures of **L**^{1}-**L**^{2} show that the geometry around the C=N bond is essentially co-planar, with phenyl/alkyl units *trans* to the furfural moiety. The C=N bond length in **L**^{1} and **L**^{2} are similar (1.2735(15) and 1.283(2) Å) and compare well with those observed for related Schiff base ligands.[62,63]

The reaction of [$CrCl_3(THF)_3$] with 1.1 eq. of imino-furfural proligands (**L**^{1}-**L**^{4}) in THF at room temperature affords the corresponding chromium complexes (**Cr1**-**Cr4**) which were isolated as brown or red-colored solids



Scheme 1. Preparation of imino-furfural proligands.

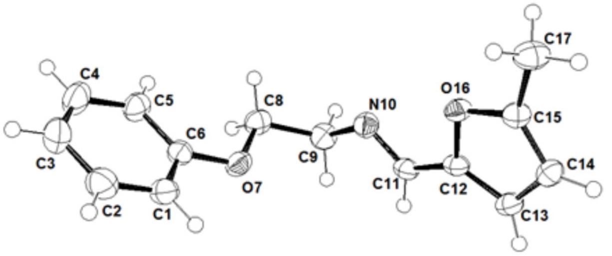


Figure 1. ORTEP representation of the molecular solid-state structure of $\mathbf{L}^1$. Ellipsoids are drawn at the 50% probability level. All hydrogen atoms are omitted for clarity. Select bond distances (Å): C(6)–O(7) = 1.3724(15), C(9)–N(10) = 1.4572(16), C(11)–N(10) = 1.2735(15), C(12)–C(11) = 1.4396(17), C(12)–O(16) = 1.3768(13) and C(15)–O(16) = 1.3732(14).

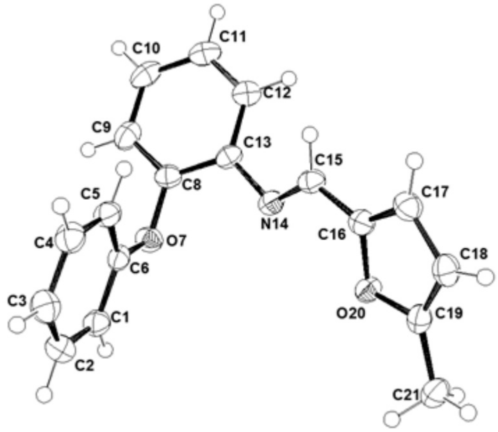


Figure 2. ORTEP representation of the molecular solid-state structure of $\mathbf{L}^2$. Ellipsoids are drawn at the 50% probability level. All hydrogen atoms are omitted for clarity. Select bond distances (Å): C(6)–O(7) = 1.3813(19), C(16)–C(15) = 1.431(2), C(15)–N(14) = 1.283(2), C(16)–O(20) = 1.3784(18), C19–O20 = 1.3736(17), N14–C15 = 1.283(2) and C13–N14 = 1.4180(19).

in moderate to good yields (typically 56-98%). These precatalysts are very moisture sensitive and therefore satisfactory CHN analyses were difficult to obtain. Hence, the identity of **Cr1**-**Cr4** was established on the basis of ESI-HRMS (which indicated the formation of $[M–Cl]^+$ ions without the presence of THF molecules coordinated to the metal center). Attempts to recrystallize complexes **Cr1**-**Cr4** from dichloromethane/petroleum ether resulted in amorphous materials, unfortunately not suitable for a single crystal X-ray diffraction analysis.

We performed DFT calculations in order to estimate the preferable coordination mode of the imine-furfural ligand $\mathbf{L}^2$ to generate the chromium precatalyst **Cr2**. Initial DFT theoretical study carried out assuming the formation of monomeric species with $\mathbf{L}^2$ acting as a tridentate ligand failed to generate a stable structure. The most stable structure was achieved with $\mathbf{L}^2$ acting as a bidentate ligand without coordination of furfural to the metal center as presented in Figure 3. Furthermore, the bidentate behavior of imino-furfural proligands is also supported by cobalt[64] and titanium[65] complexes, in which it was observed that the furfural unit did not coordinate to the metal center due to its low Lewis basicity. Based on the results mentioned above, we speculate that the 5-coordinated Cr species converts to the most stable 6-coordinated ones after the dimerization process, generating dimeric species as shown in Scheme 2. It should be pointed out that the use of bidentate ligands in the synthesis of chromium complexes promotes the formation of dimeric or monomeric species.[41-43] However, in the latter case these monomeric species usually exhibit THF or CH_3CN in the coordination sphere of the chromium atom.

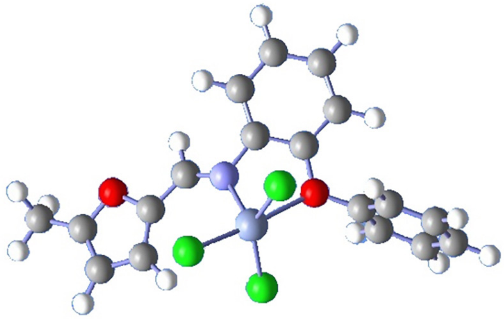
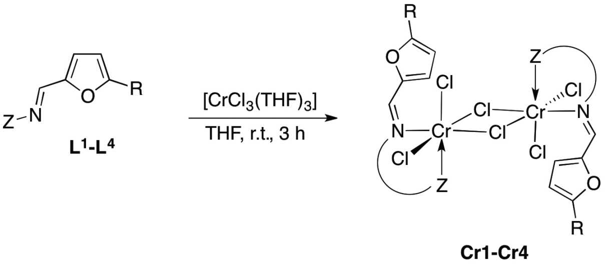


Figure 3. DFT-optimized coordination mode of imine-furfural proligand for **Cr2**.



Scheme 2. Synthesis of chromium complexes supported by the imino-furfural proligands.

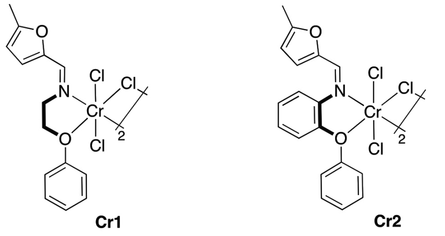
All chromium complexes were tested for ethylene oligomerization at 80 °C, 20 bar of ethylene pressure, and using MAO as cocatalyst. Table 1 summarizes the results of reactions carried out using 10 μmol of precatalyst in 40 mL of toluene. All chromium complexes investigated have been found to generate active systems for the linear oligomerization of ethylene with turnover frequencies (TOFs) varying from 11,800 to 23,200 mol(ethylene) $mol(Cr)^{-1}$ h^{-1}. Among the catalytic systems herein, the **Cr1**/MAO system shows the highest activity of up to 23,200 mol(ethylene) $mol(Cr)^{-1}$ h^{-1} (Table 1, entry 1). The activity results found for this class of chromium precatalysts are much lower, comparable to chromium complexes stabilized by N,P-bidentate ligands,[41-43] indicating that the imino-furfural ligands do not provide the formation of very stable active species.

Table 1. Ethylene Oligomerization with **Cr1**-**Cr4**/MAO systems[a]

entry	Cat.	TOF[b] / 10^3 h^{-1}	Oligomer distribution / wt.%[c]					Olig. / wt.%	PE / wt.%	Total product / mg	α_{av}[d]
			C_4 (α-C_4)	C_6 (α-C_6)	C_8 (α-C_8)	C_{10} (α-C_{10})	C_{12+}				
1	**Cr1**	23.2	15.5 (94.0)	18.5 (95.0)	21.1 (77.0)	14.5 (85.0)	30.4	81.8	18.2	2690	0.64
2	**Cr2**	11.8	11.9 (89.0)	16.3 (89.0)	24.2 (72.0)	16.3 (67.0)	31.3	70.2	29.8	1710	0.70
3	**Cr3**	13.7	14.4 (91.0)	16.4 (91.0)	19.8 (80.0)	17.1 (66.0)	32.3	76.0	24.0	1710	0.68
4	**Cr4**	16.6	15.4 (90.0)	18.4 (90.0)	18.6 (92.0)	16.4 (76.0)	31.2	86.9	13.1	1840	0.67

[a]Reaction conditions: toluene = 40 mL, [Cr] = 10 µmol, oligomerization time = 15 min, P(ethylene) = 20 bar, T = 80 °C, MAO ([Al]/[Cr] = 300). The results shown are representative of at least duplicate experiments; [b]mol of ethylene converted (mol of Cr)$^{-1}$ 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]k = mol C_{n+2} / mol C_n; averaged *k* value over the carbon rangesC_6-C_{10}.

The activity of ethylene oligomerization is substantially affected by the ligand environment. For instance, precatalyst **Cr1** containing ethylenic bridge unit is ca. 2.0 times more active than **Cr2** that contains phenyl moiety (Scheme 3). This result suggests that the presence of a weak electron-donating group (phenyl unit) increases the Lewis acidity of Cr(III) and thus destabilizes the active species.



Scheme 3.

All chromium complexes **Cr1**-**Cr4** produce oligomers ranging from C_4 to C_{12+} with a good selectivity for α-olefins. As shown in Figure 4, the selectivities for 1-alkenes afforded by these precatalysts are similar. This indicates that the pendant *O*-donor group plays no significant influence in this series on the product distribution. However, it should be pointed out that precatalysts **Cr2** and **Cr4** having more rigid pendant *O*-donor moiety, exhibited higher 1-octene selectivity (**Cr2**: 17.4 wt.%; **Cr4**: 17.1 wt.%) compared to other precatalysts. The distributions of obtained oligomers deviate little from Schulz-Flory behavior, which is characteristic of the constant α, where α represents the probability of chain propagation (α = rate of propagation / ((rate of propagation) + (rate of chain transfer)) = (moles of C_{n+2}) / (moles of C_n)).[66-68]

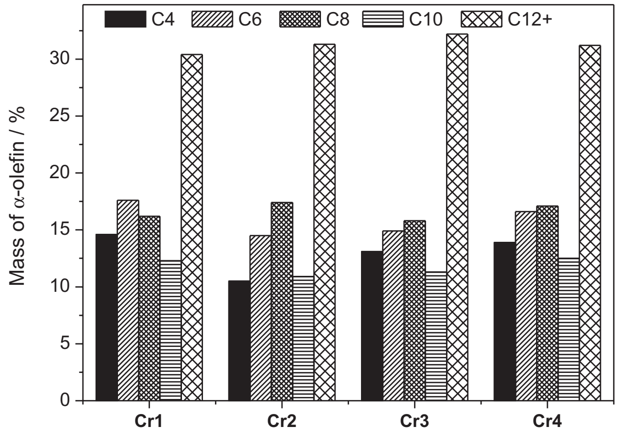


Figure 4. Selectivity of **Cr1**-**Cr4**/MAO oligomerization systems for α-olefins (80 °C, 20 bar, MAO-to-Cr = 300).

A major advantage of chromium-based selective ethylene oligomerization catalysts stabilized by neutral ancillary ligands is that they can effectively be generated *in situ* by mixing the ancillary ligand with an appropriate chromium precursor and the cocatalyst.[69-71] This approach avoids the process complexity and cost of preparing a procatalyst Cr-ligand complex while still obtaining an active and selective catalyst. However, attempts to apply similar *in situ* complexation with $\mathbf{L^1}$ were less successful.

In this preliminary study, $\mathbf{L^1}$ was mixed with [$CrCl_3(THF)_3$] or [$Cr(acac)_3$] in dry toluene and stirred for at least 4 h at room temperature before each run. First, the effect of different chromium precursors on the catalytic behavior was investigated. The results, with comparison against **Cr1**, are shown in Table 2. While the *in situ* activation method resulted in poor activities, it is clear that the change in chromium sources causes different selectivities toward α-olefins production, which suggests that the different active species are formed as presented in Figure 5. The use of [$CrCl_3(THF)_3$] led to improved selectivities for the α-C_4 (14.5 to 31.6 wt.%) and α-C_6 (17.6 to 25.6 wt.%) fractions and only small amount of higher olefins (C_{12}^+: 7.7 wt.%) along with a higher amount of PE (28.3 wt.%). On the other hand, the use of chlorine-free chromium exhibited higher selectivity for production of α-olefins (90 wt.%) with almost 45% related to C_{12}^+ fraction.

Melting and crystallization of the polyethylenes produced by Cr/$\mathbf{L^1}$ under MAO activation were measured

Table 2. Catalyst performance with different **Cr/L^1** procatalyst sources^a

entry	Cat.	Cocat.	TOF^b / (10^3 h^{-1})	Oligomer distribution / wt.%^{c}					Olig. / wt.%	PE / wt.%	Total product / mg
				C_4 (α-C_4)	C_6 (α-C_6)	C_8 (α-C_8)	C_{10} (α-C_{10})	C_{12+}			
1	**Cr1**	MAO	23.2	15.5 (94.0)	18.5 (95.0)	21.1 (77.0)	14.5 (85.0)	30.4	81.8	18.2	2690
5	[CrCl$_3$(THF)$_3$]/**L^1**	MAO	3.1	34.0 (93.0)	33.3 (77.0)	16.0 (100.0)	9.0 (67.0)	7.7	71.7	28.3	293
6	[Cr(acac)$_3$]/**L^1**	MAO	6.4	12.5 (90.0)	17.4 (81.7)	14.2 (90.0)	11.2 (88.0)	44.7	90.0	10.0	500
7^d	[Cr(acac)$_3$]/**L^1**	EASC	1.1	40.0 (89.0)	21.9 (72.0)	16.6 (85.0)	17.7 (88.0)	3.8	23.5	76.5	340
8	[Cr(acac)$_3$]/**L^1**	PMAO-IP	2.5	17.9 (97.0)	22.3 (93.0)	20.7 (88.0)	12.7 (96.0)	26.4	40.9	59.1	440

^{a}Reaction conditions: **L^1** was mixed with [Cr(acac)$_3$] or [CrCl$_3$(THF)$_3$] in dry toluene and stirred for at least 4 h at room temperature before each run. Toluene = 40 mL, [Cr] = 10 µmol, oligomerization time = 15 min, P(ethylene) = 20 bar, T = 80 °C ([Al]/[Cr] = 300). The results shown are representative of at least duplicate experiments; ^{b}mol of ethylene converted (mol of Cr)$^{-1}$ 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}([Al]/[Cr] = 100). EASC: ethylaluminum sesquichloride; PMAO-IP: polymethylaluminoxane-improved performance.

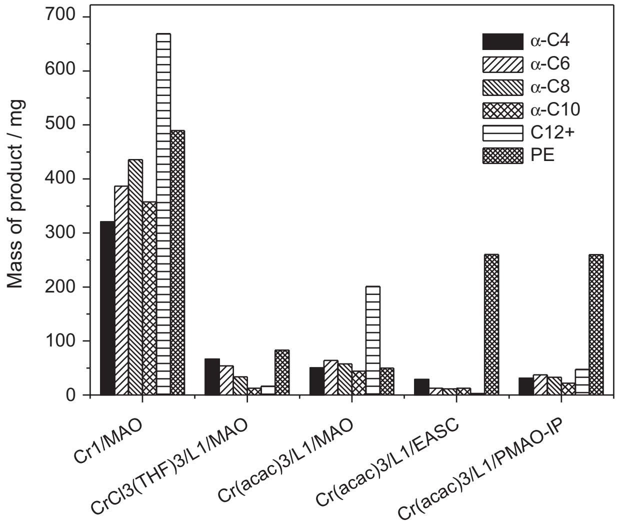


Figure 5. Influence of the chromium sources and cocatalyst type on the distribution of products. Toluene = 40 mL, [Cr] = 10 µmol, oligomerization time = 15 min, P_{C2H4} = 20 bar, T = 80 °C.

by means of thermal analysis (differential scanning calorimetry, DSC) as a function of chromium sources. The use of [CrCl$_3$(THF)$_3$] generates high-density polyethylene with melting temperature of 133 °C and crystallinity in the range of 44%. On the other hand, the use of [Cr(acac)$_3$] produces a highly branched polyethylene (BPE) with one endothermic peak at 123 °C and crystallinity of only 8% (see Supplementary Information). In this case, we assume that the formation of BPE arises from incorporation of the *in situ* produced α-olefins into the growing polymer chain.

A recent study on the Sasol Cr/PNP system shed light on the role of the cocatalyst during catalysis, suggesting that the selectivity can be affected remarkably by the strength of the interaction between the chromium center and the aluminum species.[72] Thus, the influence of cocatalyst on the catalytic behavior was subsequently investigated. The *in situ* catalytic testing using [Cr(acac)$_3$]/**L^1** in toluene varying the cocatalyst type (EASC and PMAO-IP) showed some interesting differences (Table 2).

Using EASC instead of MAO shifted the system to ethylene polymerization with substantial production of polyethylene (76.5 wt.%) (Table 2, entry 7) and only 23.5 wt.% of the total amount of products corresponds to linear α-olefins. In this case, a very small amount of C_{12}^+ was detected (3.80 wt.%). The use of PMAO-IP also promotes the formation of a substantial amount of PE and a production of lower amount of α-olefins (40.9 wt.%). However, an improvement in the selectivity for 1-hexene and 1-octene formation was observed compared to the use of EASC, as shown in Figure 4. In both cases, the DSC curves show the formation of high-density polyethylenes (HDPE) with melting temperatures in the range of 132-134 °C and crystallinities around of 60% (see Supplementary Information).

Conclusions

In summary, a new set of chromium(III) complexes based on imino-furfural ligands has been prepared and evaluated for ethylene oligomerization under MAO activation. DFT calculations suggest a bidentate coordination mode for this class of ligand, which can generate dimeric Cr species. The selectivities for 1-alkenes afforded by these precatalysts are similar, suggesting that the pendant O-donor group plays no significant influence in this series on the product distribution. However, the presence of the ethylenic bridge unit in **L^1** generates more catalyst activity as compared to the one containing the phenyl moiety (**L^2**), suggesting that the presence of a weak electron-donating group (phenyl unit) increases the Lewis acidity of Cr^{3+} and thus destabilizing the active species and decreasing the catalyst lifetime. The *in situ* activation method resulted in poor activities, which is most likely the result of the poor solubility of the catalysts in toluene. The use of different chromium sources and cocatalyst influences the activity as well as the selectivities toward α-olefin production, which suggests that different active species are formed.

Supplementary Information

Supplementary data (DSC curves of the polyethylenes) are available free of charge at http://jbcs.sbq.org.br as PDF file.

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