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Chromium Complexes Supported by Phenyl Ether-Pyrazolyl [N,O] Ligands as Catalysts for the Oligo- and Polymerization of Ethylene

Jorge L.S. Milani | **Osvaldo L. Casagrande Jr**

Laboratory of Molecular Catalysis, Instituto de Química, Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves, 9500, Porto Alegre, RS, 91501-970, Brazil

Correspondence
Osvaldo L. Casagrande Jr., Laboratory of Molecular Catalysis, Instituto de Química, Universidade Federal do Rio Grande do Sul, Avenida Bento Gonçalves, 9500, RS, 90501-970, Brazil.
Email: osvaldo.casagrande@ufrgs.br

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A new series of Cr (III) complexes [Cr{1-(3-phenoxypropyl)-1H-pyrazole}Cl_3]$_2$ **(Cr1),** [Cr{1-(3-phenoxypropyl)-3,5-dimethyl-1H-pyrazole}Cl_3]$_2$ **(Cr2**), and [Cr {1-(3-phenoxypropyl)-3-phenyl-1H-pyrazole}Cl_3]$_2$ **(Cr3)** have been synthesized and characterized by elemental analysis, high-resolution mass spectrometry (HRMS) and IR spectroscopy. Upon activation with methylaluminoxane (MAO), chromium precatalysts **Cr2** and **Cr3** showed moderate activity in ethylene oligomerization [TOF = 17,900–29,200 mol (ethylene)·mol $(Cr)^{-1}\cdot h^{-1}$ at 80 °C] with Schultz-Flory distribution of oligomers (K = 0.54–0.66) and production of polymer varying from 2.8 to 6.7 wt.%. On the other hand, under identical oligomerization conditions, **Cr1**/MAO behaved as a polymerization catalyst generating predominantly polyethylene (63.7 wt%). The amount of 1-butene is the largest component in the liquid fraction suggesting that these precatalysts operate via a Cossee-Arlman mechanism. The catalytic activities, selectivity and product distribution are quite sensitive to the R-group at the 3- and 5-position of the pyrazolyl ring. Based on the electronic and steric effects of R- substituents, it is possible to stablish a trend of activity: **Cr2** (Pz^{Me2}) > **Cr3**(Pz^{Ph}) > **Cr1**(Pz). Moreover, the effect of oligomerization parameters (cocatalyst, temperature, [Al]/[Cr] molar ratio, time) on the activity and on the product distribution were examined.

KEYWORDS
bidentate ligands, chromium complexes, ethylene oligomerization, phenyl ether-pyrazolyl ligands, α-Olefins

1 | INTRODUCTION

Catalytic oligomerization of ethylene is an important industrial process in view of the importance of linear α-olefins (LAO) as versatile intermediates for many industrially substances such as linear low-density polyethylene (LLDPE), plasticizers, surfactants for detergents, base stock, additives for synthetic lubricants, and alcohols for plasticizers.[1–8] LAOs are generally produced with a broad range of olefins from C_4 to C_{20} featured by Schulz-Flory distributions manufactured by Shell, Ineos, SABIC, and Chevron-Phillips.[9–12] Among all the transition-metal-based catalysts, chromium catalysts have proven to be the most promising candidates for selective ethylene oligomerization.[13–16] In this way, significant efforts have been dedicated to the synthesis of new families of ligands based on a wide variety of donor-group combinations aiming to generate more efficient chromium catalyst systems that are capable of selectively forming α-olefins with high productivities.[17–81] In

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particular, chromium catalysts stabilized by pyrazolyl-based tridentate ligands have been successfully synthetized and their catalytic application in ethylene oligomerization explored in details.[51,81–91] Selected examples are presented in Chart 1. For instance, Tosoh Corporation reported chromium complex bearing tris(3,-5-dimethyl-1-pyrazolyl)methane ligand that, once activated with methylalumoxane (MAO), generate highly active oligomerization/polymerization species 526.0 x 10^3 (mol ethylene) (mol Cr)$^{-1}$·h^{-1} with selectivity for 1-hexene >99.5%.[81] In 2007, Casagrande, Carpentier and co-workers reported the synthesis of chromium (III) complexes of general formula [$CrCl_3$(NZN)] based on pyrazolyl tridentate ligands NZN (Z = N, O, S). Once activated with MAO, these precatalysts formed active catalysts for Schulz-Flory oligomerization to LAOs and low molecular weight polymer, with TOFs varying from 3.4 to 131.0 x 10^3 (mol ethylene) (mol Cr)$^{-1}$·h^{-1} at 80 ° C.[83]

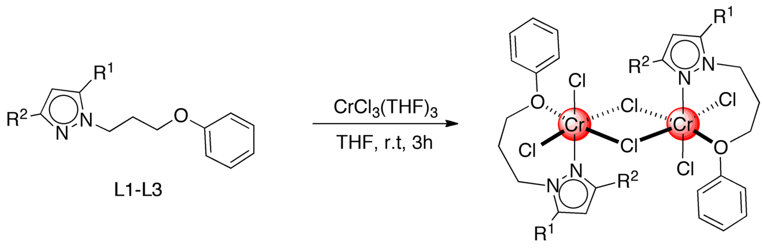
Braunstein, Hor and co-workers reported a series of active Cr (III) complexes with [NON] heteroscorpionate ligands derived from bis (pyrazol-1-yl)methane.[84] Activation by MAO resulted in highly selective toward trimerization (total C_6 selectivities >98.9%) to 1-hexene (>99.6%) with activity of 16,200 g/(g of Cr)·h. In 2010, Mountford et al. described the synthesis and structural characterization of Cr (II) and Cr (III) complexes containing N_2N' and N_2O donor heteroscorpionate ligands with secondary or tertiary amine side arms and phenyl ether, phenol or phenolate side arms.[87] Upon activation with MAO, all new chromium complexes are more active 27.5–116.0 x 10^3 (mol ethylene) (mol Cr)$^{-1}$·h^{-1} than Cr {HC $(pz^{Me2})_3$}Cl_3 (24.6 x 10^3 (mol ethylene) (mol Cr)$^{-1}$·h^{-1}) but invariably produce a width Schultz-Flory distribution of oligomers. Whereas most complexes display a typical *K* value between 0.59 and 0.67, with a *K* value of 0.37 Cr{$(pz^{Me2})_2$CHArOMe}Cl_3 (Chart 1) shows a significantly higher selectivity for 1-hexene (52.4%) and 1-octene (34.7%).

As alluded to above, the tridentate pyrazolyl ligands have been successfully used for the synthesis of active chromium catalysts towards production of α-olefins; however, to the best of our knowledge, there appear to be no known examples of chromium complexes bearing pyrazolyl-based bidentate ligands. Furthermore, the use of these bidentate ligands could provide an additional coordination site which can be useful to adjust the electronic and steric properties of the complexes towards selective tri- and tetramerization of ethylene. Thus, inspired by these works, and considering our results based on nickel complexes bearing phenyl ether-pyrazolyl bidentate ligand applied in selective dimerization of ethylene,[92] we have decided to carry out the synthesis of Cr (III) complexes, and investigate their catalytic performance in ethylene oligomerization. This paper will discuss the oligomerization results for these new systems, evaluating the role of the ligand, and the experimental parameters on the activity and selectivity.

2 | EXPERIMENTAL

2.1 | General considerations

All manipulations involving air- and/or moisture-sensitive compounds were carried out in an MBraun glovebox or under dry argon using standard Schlenk techniques. Toluene, THF, and hexane were dried over a Braun MB-SPS-800 solvent purification system. Other solvents were dried from the appropriate drying agents under argon before use. [$CrCl_3(THF)_3$] was purchased from Sigma-Aldrich and used as received. The ligands 1-(3-phenoxypropyl)-1H-pyrazole) (**L1**), 3,5-dimethyl-1-(3-phenoxypropyl)-1H-pyrazole (**L2**) and 1-(3-phenoxypropyl)-3-phenyl-1H-pyrazole, (**L3**) were prepared following the literature procedures.[92] 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), polymethylaluminoxane-improved performance (PMAO-IP) (AkzoNobel, 13.0 wt.% Al solution in toluene), EASC (Akzo Nobel) (2.1 wt.% Al solution in toluene) and trimethylaluminum (TMA) (Sigma-Aldrich, 2 M in



Cr1: $R^1 = R^2 = H$
Cr2: $R^1 = R^2 = Me$
Cr3: $R^1 = H$, $R^2 = Ph$

CHART 1 Examples of chromium complexes for oligomerization catalysis based on pyrazolyl ligands toluene) were used as received. Infrared spectra were performed on neat products using a FT-IR Bruker Alpha Spectrometer operating in the ATR mode. Elemental analyses were performed on a Perkin Elmer 2,400 Series II by the Analytical Central Service of the Institute of Chemistry-UFRGS (Brazil) and is the average of two independent determinations. High-resolution mass spectra of Cr (III) complexes (**Cr1**-**Cr3**) were obtained by electrospray ionization (ESI) in the positive mode in methanol or acetonitrile solutions using a Micromass Waters® Q-Tof spectrometer. Quantitative gas chromatographic analysis of ethylene oligomerization products was performed on a Agilent 7890A instrument equipped with a Petrocol HD capillary column (methyl silicone, 100 m length, 0.25 mm i.d. and film thickness of 0.5 μm) (36 °C for 15 min, then heating at 5 °C min^{-1} until 250 °C); cyclohexane was used as internal standard. Melting temperatures were determined by differential scanning calorimetry (DSC) with a Thermal Analysis Instruments DSC-Q20 using a heating rate of 10 °C min^{-1} after twice previous heating to 180 °C and cooling to 40 °C at 10 °C min^{-1}.

2.2 | Synthesis of the Cr (III) complexes

2.2.1 | [Cr{1-(3-phenoxypropyl)-1H-pyrazole}Cl$_3$]$_2$ (Cr1)

A solution of **L1** (0.200 g, 0.98 mmol) in THF (10 ml) was added dropwise over a period of 10 min to a solution of [CrCl$_3$(THF)$_3$] (0.330 g, 0.88 mmol) in THF (15 ml) at room temperature under constant stirring. The resulting solution was allowed to stir for 3 hr at room temperature and then the solvent was removed under vacuum. The solid residue was washed with diethyl ether (3 x 10 ml) to give, after drying, **Cr1** as a purple solid (0.290 g, 90%). IR (ATR, cm^{-1}): ν 3,274 (s), 3,119 (w), 3,037 (w), 2,957 (w), 2,875 (w), 1,626 (m), 1,599 (s), 1,586 (m), 1,493 (s), 1,472 (m), 1,455 (w), 1,421 (m), 1,293 (w), 1,266 (w), 1,241 (s), 1,173 (m), 1,152 (w), 1,104 (m), 1,081 (m), 1,050 (m), 944 (w), 908 (w), 887 (w), 864 (w), 783 (m), 756 (s), 693 (m), 609 (m), 514 (m). ESI-HRMS (CH$_3$OH, m/z): 323.9883 [M-Cl]$^+$ (calc. For $C_{12}H_{14}Cl_2CrN_2O$: 323.9888 g). Anal. Calcd. for $C_{24}H_{28}Cl_6Cr_2N_4O_2$: C: 39.97, H: 3.91, N: 7.77. Found: C: 39.52, H: 3.87, N: 7.13.

2.2.2 | [Cr{1-(3-phenoxypropyl)-3,5-dimethyl-1H-pyrazole}Cl$_3$]$_2$ (Cr2)

This complex was prepared as described above for **Cr1**, starting from **L2** (0.200 g, 0.72 mmol) and [CrCl$_3$(THF)$_3$] (0.240 g, 0.65 mmol) in THF (15 ml) to give **Cr2** as a purple solid (0.250 g, 86%). IR (ATR, cm^{-1}): ν 3,062(w), 3,039 (w), 2,933(m), 2,875 (w), 1,637 (m), 1,617 (m), 1,599 (m), 1,588 (w), 1,586 (w), 1,493 (m), 1,472 (m), 1,443 (w), 1,430 (w), 1,395 (w), 1,384 (w), 1,304 (w), 1,292 (m), 1,241 (m), 1,214 (w), 1,200 (w), 1,172 (w), 1,150 (w), 1,081 (w), 1,042 (w), 992 (m), 940 (w), 758 (m), 693 (w). ESI-HRMS (CH$_3$OH, m/z): 352.0197 g [M-Cl]$^+$ (calc. For $C_{14}H_{18}Cl_2CrN_2O$: 352.0201 g). Anal. Calcd. for $C_{28}H_{36}Cl_6Cr_2N_4O_2$: C: 43.26; H: 4.67; N: 7.21. Found: C: 43.12; H: 4.17; N: 6.88.

2.2.3 | [Cr{1-(3-phenoxypropyl)-3-phenyl-1H-pyrazole}Cl$_3$]$_2$ (Cr3)

This complex was prepared as described above for **Cr1**, starting from **L3** (0.220 g, 0.79 mmol) and [CrCl$_3$(THF)$_3$] (0.270 g, 0.72 mmol) in THF (15 mL) to give **Cr3** as a purple solid (0.270 g, 84%). IR (ATR, cm^{-1}): ν 3,240 (m), 2,973 (w), 2,901 (w), 2,872 (w), 1,600 (m), 1,584 (w), 1,546 (w), 1,517 (w), 1,492 (m), 1,467 (w), 1,458 (w), 1,450 (w), 1,339 (w), 1,299 (w), 1,243 (m), 1,227 (m), 1,171 (w), 1,097 (w), 1,079 (w), 1,040 (m), 1,011 (m), 919 (w), 854 (s), 755 (m), 688 (m), 512 (w). ESI-HRMS (CH$_3$OH, m/z): 400.0198 g [M-Cl]$^+$ (calc. For $C_{18}H_{18}Cl_2CrN_2O$: 400.0201 g). Anal. Calcd. for $C_{36}H_{36}Cl_6Cr_2N_4O_2$: C: 49.51; H: 4.15; N: 6.41. Found: C: 48.78; H: 4.18; N: 6.13.

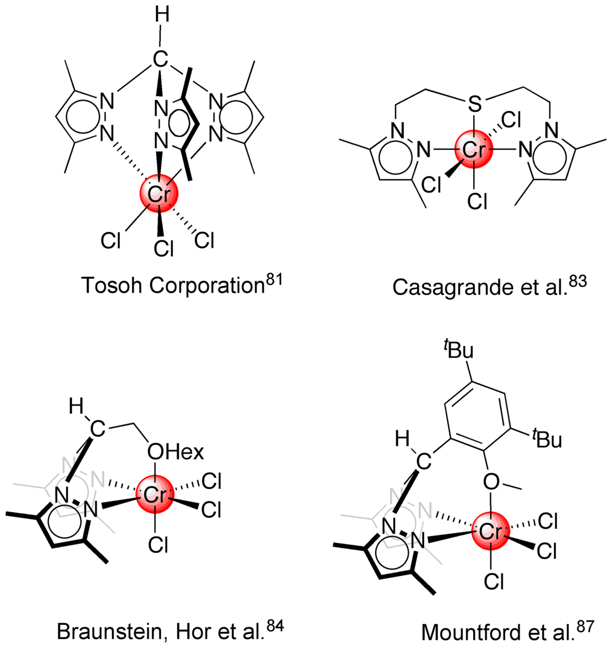
2.3 | Ethylene oligomerization

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 hr 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 hr.

3 | RESULTS AND DISCUSSION

3.1 | Synthesis and characterization of chromium complexes bearing phenyl ether-pyrazolyl ligands

The phenyl ether-pyrazolyl ligands (**L1-L3**) were readily synthesized by reaction of 3-bromopropyl phenyl ether with sodium pyrazolate in DMF/THF in moderate to good yields (60–85%).[92] The ligands obtained were fully characterized by analytical and spectroscopic methods. The reaction between $CrCl_3(THF)_3$ and 1.1 equiv of **L1-L3** in THF at room temperature afforded the chromium complexes **Cr1-Cr3** as purple solids in good yields (84–90%) as shown in Scheme 1. All chromium complexes, 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 these complexes was established on the basis of combustion elemental analysis, IR spectroscopy and high-resolution mass spectrometry (HRMS). Upon reaction with $CrCl_3(THF)_3$, either $[CrCl_3(N,O)(THF)]$ or the dimer $[Cr(N,O)Cl_3]_2$ were expected, both of which would maintain the favored hexacoordination of chromium (III)[14,24,27,28,45,46]; however, the elemental analyses of complexes **Cr1-Cr3** confirmed the formation of dimeric species of general formula $[CrCl_2(N,O)(\mu\text{-}Cl)]_2$. Furthermore, the ESI-HRMS results indicated the formation of $[M\text{-}Cl]^+$ ions for all chromium complexes (Figures S1-S3).



SCHEME 1 Synthesis of chromium (III) complexes supported by phenyl ether-pyrazolyl ligands

3.2 | Ethylene Oligomerization studies

Ethylene oligomerization was investigated using chromium complexes **Cr1-Cr3** in toluene at 80 °C, 20 bar constant ethylene pressure, and using MAO containing 20 wt.% $AlMe_3$ as cocatalyst. Relevant data are compiled in Table 1. All experiments were at least duplicated, the error in terms of activity and product selectivity values was estimated to be approximately ±5%. Initial studies, carried out at 80 °C with [Al]/[Cr] = 300, showed that these catalyst systems were moderately active, affording a nonselective distribution of α-olefins with turnover frequencies (TOFs) in the range of 6,500–29,200 mol (ethylene)·mol $(Cr)^{-1}\cdot h^{-1}$ over 15-min runs as presented in Figure 1. In addition, analyses of the data showed that the activity and product distribution were dependent on the R substituent at the 3- and 5-position of the pyrazolyl ring.

The highest activity among the three chromium catalysts screened was reached with **Cr2** [TOF = $29{,}200 \times 10^3$ (mol ethylene) (mol $Cr)^{-1}$ h^{-1}] which is *ca* 4.5 times more active than **Cr1** [TOF = 6,500 (mol ethylene) (mol $Cr)^{-1}$ h^{-1}]. The activity data found for this class of chromium precatalysts are comparable to those for other chromium complexes stabilized by pyrazolyl-based ligands.[38,84]

To compare the steric properties of **Cr1-Cr3**, topographic steric maps were generated using the SambVca 2.1 software, and metrical data from the optimized structures (Figure 2). The results are compiled assuming a 3.50 Å for the sphere radius, omitted hydrogen atoms and scaled bond radii by 1.17, as recommended.[93,94] Particularly, it was found that **Cr1** and **Cr2** have similar percent buried volume ($\%V_{Bur}$) [$\%V_{Bur}$ = 64.3 for **Cr1**; $\%V_{Bur}$ = 66.8 for **Cr2**] suggesting that the presence methyl groups at the 3- and 5-position of the pyrazolyl ring does not cause a significant increase in steric protection around the Cr metal center. In this respect, the higher activity of **Cr2** can be tentatively associated with the higher electron-donating ability of 3,5-dimethyl-pyrazolyl unit when compared with unsubstituted pyrazolyl, thus generating a more stable catalytic species.[95] These results are in line with previously reported using MAO-activated metal complexes bearing pyrazolyl ligands.[38,92,96]

As presented in Figure 2, the presence of sterically demanding Ph group in **Cr3** resulted in a higher percent buried volume ($\%V_{Bur}$ = 70.0) with respect to **Cr1**. Considering the comparable electron-withdrawing ability of Pz^{Ph} and Pz, we guess that the catalytic activity of **Cr3** is not driven by electronic effects of the phenyl group.[95,97–99] Thus, the presence of the phenyl group at 3-position of the pyrazolyl ring might be able to promote

TABLE 1 Ethylene Oligomerization with **Cr1**-**Cr3** precatalyst systems[a]

Oligomer distribution (wt.%)[c]												
Entry	**Cat.**	**Time (min)**	**[Al/Cr]**	**TOF**[b] **($10^3 \cdot h^{-1}$)**	**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	**Cr1**	15	300	6.5	25.3 (93.8)	22.6 (93.0)	21.7 (82.9)	16.1 (91.4)	14.3	36.3	63.7	1,240
2	**Cr2**	15	300	29.2	72.2 (97.4)	19.9 (92.9)	5.6 (100)	2.3 (100)	0.0	97.2	2.8	2,100
3	**Cr3**	15	300	17.9	43.4 (96.4)	30.5 (95.3)	16.0 (91.6)	6.9 (90.0)	3.2	93.3	6.7	1,340
4	**Cr3**	15	1,000	24.8	12.3 (92.6)	17.8 (93.2)	20.0 (91.9)	16.1 (93.6)	33.8	68.6	31.4	2,503
5	**Cr3**	15	1,500	97.2	13.6 (93.4)	15.3 (93.6)	13.7 (93.9)	11.3 (91.2)	46.1	76.5	23.5	8,870
6[d]	**Cr3**	15	300	8.1	16.8 (96.7)	20.9 (96.9)	18.6 (98.9)	15.0 (85.6)	28.7	49.1	50.9	1,140
7	**Cr3**	5	300	52.2	68.3 (94.2)	19.6 (90.1)	6.3 (89.2)	2.7 (75.7)	3.2	94.8	5.2	1,280
8	**Cr3**	30	300	11.3	54.9 (96.4)	22.1 (89.2)	11.3 (83.0)	4.1 (100.0)	7.6	94.1	5.9	1,680
9[e]	**Cr3**	15	300	13.5	9.1 (89.6)	14.9 (91.9)	16.2 (90.6)	14.2 (91.6)	45.6	37.4	62.6	2,700

[a] Reaction conditions unless specified otherwise: 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, yielding reproducible results within ±5%.

[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] PMAO-IP as cocatalyst.

[e] $T = 100$ °C.

a better steric protection around the chromium metal center, and thus improve the catalyst performance (entry 1vs 3). Based on these results, it is possible to establish a trend of activity: **Cr2**(Pz^{Me2}) > **Cr3**(Pz^{Ph}) > **Cr1**(Pz), which is similar to that one found for nickel complexes bearing the same class of ligands.[92]

Except for **Cr1**, all other two chromium precatalysts **Cr2** and **Cr3** activated with MAO afforded mostly oligomers (93.3–97.2 wt.% of total products) ranging from C_4 to C_{12}^+ with a distinct distribution for α-olefins and production of polymer varying from 2.8 to 6.7 wt.%. Contrasting result was found using **Cr1** where the replacement of the methyl on the pyrazolyl rings by hydrogen decreases significantly the selectivity and favors the formation of PE which corresponds to 63.7 wt.% of the total amount of products. A similar behavior was observed in $CrCl_3[Pz^RCH_2NCH_2Ph]$.[86] In this case, such selectivity switch (oligomers vs polymer) can be tentatively associated to formation of different active species, and in particular the catalytically active oxidation states of chromium (I, II, and III).[71,81,100–103]

The pyrazolyl-type moiety has also a significant impact on the product distribution in the liquid fraction as can be seen in Figure 3. For instance, **Cr1** precatalyst led to a more balanced distribution of oligomers [α-C_4 (41.3 mol%), α-C_6 (24.4 mol %), and α-C_8 (15.7 mol%)] while those containing more sterically demanding pyrazolyl group (**Cr2-Cr3**) are centered in lighter α-olefins fractions with a considerable amount of 1-butene (58.0–82.3 mol %). However, enriched fraction in α-C_6 (26.9 mol %) is obtained using **Cr3**.

The oligomer distributions obtained by the **Cr1 – Cr3**/MAO systems follow a Schulz–Flory distribution as presented in Figure 4. The amount of 1-butene is the largest component in the liquid fraction suggesting that these precatalysts operate via a Cossee-Arlman

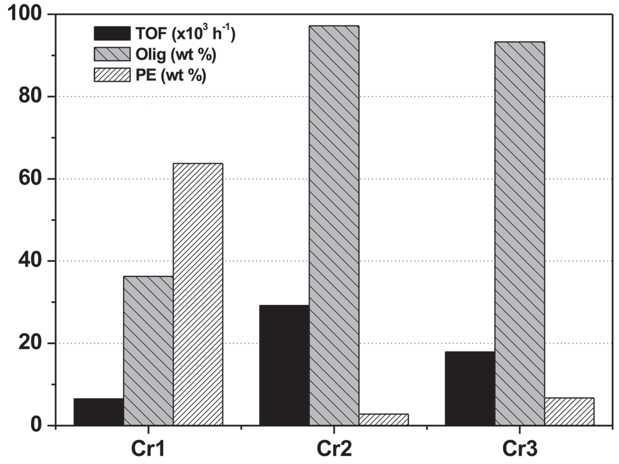


FIGURE 1 Influence of the nature of chromium precatalyst Cr1-Cr3 on TOF and selectivity for oligomers (T = 80 °C, 20 bar, time = 15 min, [Al]/[Cr] = 300)

mechanism.[16,104] The K values calculated from a plot of log [mol%] vs carbon number was higher for **Cr1** ($K_{\text{C4-C10}} = 0.82$) than for **Cr2** ($K_{\text{C4-C10}} = 0.54$) and **Cr3** ($K_{\text{C4-C10}} = 0.66$) as expected taking into account the higher amounts of heavier olefins and polymer produced by **Cr1**.

The DSC curve of the polymer produced by **Cr1** showed a single melting transition at 131.5 °C, and a relatively high crystallinity (70%). Conversely, the polymers produced by **Cr2-Cr3** displayed two endothermic peaks at in the range of 63.4–125.4 °C suggesting the production of linear oligoethylenes with low molecular weight (Figures S4-S6). Similar results were observed with other catalytic systems based on chromium complexes bearing bi- and tridentate ligands.[37,38,105–107]

To establish the optimal oligomerization conditions, precatalyst **Cr3** was selected as test precatalyst varying the oligomerization parameters such as [Al]/[Cr] molar ratio, cocatalyst type, reaction temperature and run time. The results are collected in Table 1 (entries 4–9). The precatalyst **Cr3** was found to be inactive upon activating with different cocatalysts such as aluminum sesquichloride (EASC), TMA and triethylaluminum (TEA) presumably due to the low Lewis acidity of these activators.

The [Al]/[Cr] molar ratio was adjusted from 300 to 1,500 (entries 3, 4–5, Table 1). Increasing the [Al]/[Cr] ratio from 300 to 1,500 equiv had a beneficial effect on the catalytic activity (TOF = 97,200 (mol ethylene) (mol Cr)$^{-1}$ h^{-1}) with a significant decrease in the production of 1-butene (from 58.03 to 18.4–30.2 mol %), and production of enriched fractions in C_{12}^{+} (from 1.5 to 17.3–31.7 mol %) (Figures S7-S8 and S10). Furthermore, the level of polymer formation increased substantially [from 6.7 to 23.5–31.4 wt.%] as well as the K values ($K_{1000} = 0.91$; $K_{1500} = 0.85$) (Figure S11).

Activation of **Cr3** with PMAO-IP instead of MAO resulted in slightly improvement in activity (8,100 (mol ethylene) (mol Cr)$^{-1}$ h^{-1}). The total mass of products (oligomers + polymer) is quite similar in both cases (compare entries 3 and 6) suggesting no occurrence of deactivation pathway. The production of a larger amount of polymer (50.9 wt.%) compared to that one using MAO (6.7 wt.%) strongly suggest that the amount of "free" TMA present in the reaction medium is not enough to generate reduced catalytically active chromium species (Cr^{I}/Cr^{II}), which are assumed to be responsible for the nonselective oligomerization behavior. However, we cannot rule out the possibility that the absence of "free" TMA could also decrease the chain-transfer rate of the growing chain from the catalyst to the aluminum, and thus resulting in a formation of higher quantity of polyethylene.[27,108,109] The role of Al activators on catalytic performance of chromium catalysts in homogeneous ethylene oligomerization has been recently studied by Tromp, Brückner and coworkers.[110,111] With regards to product distribution within the liquid fraction, **Cr3**/PMAO-IP catalytic system leads to a more balanced distribution of oligomers, with a drastic decreases in α-C_4 (30.20 mol %) and increase in α-C_8 (16.80 mol %) and α-C_{10} (10.80 mol %) fractions (Figures S9 and S10).

The optimal operating temperature for this class of precatalysts is 80 °C. At 100 °C the precatalyst still operating but with slightly lower activity (13,500 mol (ethylene)·mol (Cr)$^{-1}$·h^{-1}), probably due to the partial deactivation of the active species and the lower solubility of ethylene in toluene at 100 °C. At same time, **Cr3** produced a significant amount of polymer (1.69 g, 62.6 wt. % of the total mass of products) with activity of 676 kg of PE/mol[Cr]·h. This result suggests that different temperature stabilities exist for the catalytic species involved in ethylene oligomerization and polymerization reactions, respectively. Thus, we guess that higher temperature favored the catalytic species involved in polymerization reactions; however, we cannot rule out that other catalytically active species are being generated at 100 °C. At this temperature, the production of 1-butene dropped to 18.07 mol % with a significant improvement in the formation of the α-C_8 (from 10.16 to 16.33 mol %) and α-C_{10} (from 3.44 to 11.56 mol %) fractions. A plot of log (mol %) versus carbon number shows a Schulz-Flory distribution with a K value of 0.91. (Figures S10 and S11).

The product distribution and productivity were monitored at different time intervals (5, 15 and 30 min) with

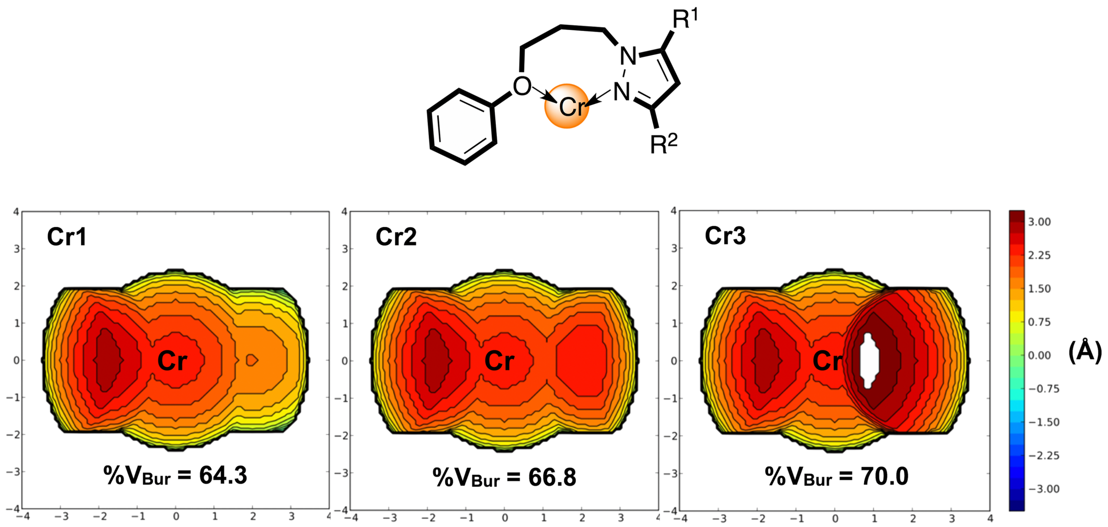


FIGURE 2 Steric maps of chromium complexes Cr1-Cr3 bearing phenyl ether-pyrazolyl ligands

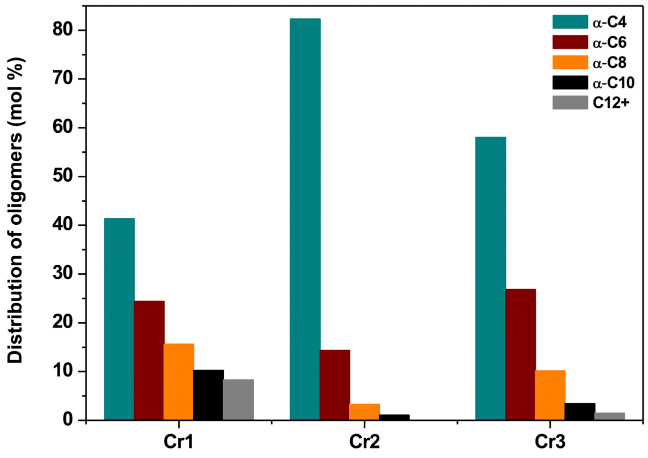
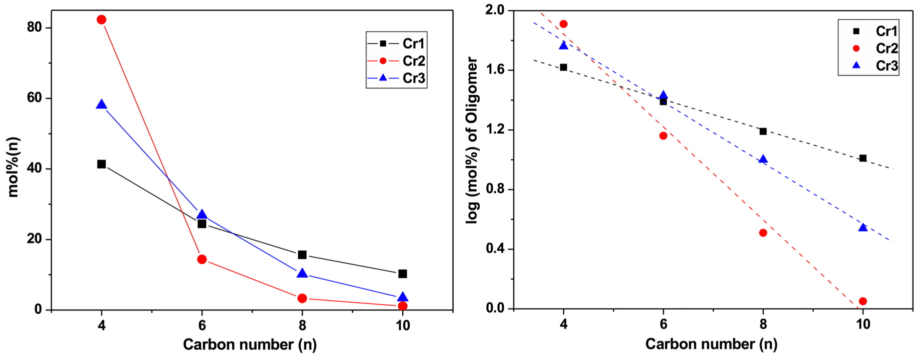


FIGURE 3 Selectivity of Cr1-Cr3/MAO oligomerization systems for α-olefins (T = 80 °C, 20 bar of ethylene, time = 15 min, [Al]/[Cr] = 300)

[Al]/[Cr] molar ratio of 300 and the temperature at 80 °C for investigating the lifetime of the active species. (entries 3, 7 and 8). On prolonging the reaction time from 5 to 15 min, it was not observed a significant variation in total mass of products (oligomers and polymer), which are comparable considering an average error of ± 5% as presented in Figure 5.

When the oligomerization time was prolonged, the total mass of products increased (from 1.28 to 1.68 g) indicating that **Cr3** had a minimal catalytic lifetime of 30 min. It is noteworthy to mention that the ratio between the mass of oligomers/polymer does not change significantly suggesting that the nature of the active species remains unchanged along of 30 min. Furthermore, no significant variation in the selectivities for α-olefins was observed over a 5–30 min period (92.6–94.8 wt.%), indicating that parallel chain isomerization processes are a minor pathway in these oligomerization reactions (Figures S12 and S13). On the other hand, the reaction time has some influence on the oligomer distribution. Thus, on extending the reaction time seems to favor the production of higher amounts of 1-hexene and 1-octene and reduction of the amount of 1-butene.

FIGURE 4 Oligomers distribution produced by Cr1-Cr3/MAO oligomerization systems (C4-C10) (80 °C, 20 bar, [Al/[Cr] = 300). (a) Schulz–Flory α-olefin distribution in molar percentage and (b) plot of the log (mol%) of vs carbon number



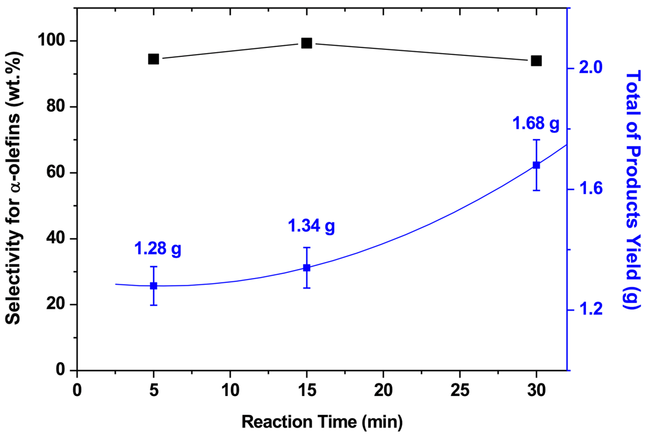


FIGURE 5 Monitoring of selectivities and productivities as a function of time in the ethylene oligomerization reaction promoted by the Cr3/MAO system (T = 80 °C, 20 bar of ethylene, [MAO]/[Cr] = 300)

4 | CONCLUSIONS

A new class of chromium complexes bearing a phenyl ether-pyrazolyl bidentate ligands have been reported. When activated with MAO, these catalyst systems show moderate activity in ethylene oligomerization affording Schulz–Flory olefin distribution. Variations in electronic and steric effects on the pyrazolyl group can significantly affect the activity and selectivity, as well as the product distribution (oligomers versus polymers). Thus, the higher electron-donating ability of 3,5-dimethyl-pyrazolyl unit afforded the highest activity among the three chromium catalysts screened. The contrasting catalytic behavior of **Cr1** that acts as ethylene polymerization catalyst and **Cr2-Cr3** that afforded mostly oligomers can be associate to the influence of pyrazolyl unit on the formation of different active species, and in particular the catalytically active oxidation states of chromium. Furthermore, the **Cr1** precatalyst led to a more balanced distribution of oligomers while those containing more sterically demanding pyrazolyl group (**Cr2-Cr3**) are centered in lighter α-olefins fractions. Oligomerization studies involving **Cr3** showed that the use of higher MAO loading positively affected the catalytic activity with a significant decrease in the production of 1-butene; however the presence of higher amounts of MAO increased substantially the amounts of heavier fractions C_{12}^{+} and polymer. The use of PMAO-IP instead of MAO led to a slight improvement in the TOF with the production of oligomer/polymer ratio close to 1. This may suggest that the very low amount of “free” TMA in the reaction medium is not enough to generate reduced chromium species (Cr^{I}/Cr^{II}), which is assumed to be responsible for the nonselective oligomerization behavior.

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AUTHOR CONTRIBUTIONS

OSVALDO CASAGRANDE: Conceptualization; data curation; formal analysis; investigation; methodology; supervision. **Jorge Milani:** Conceptualization; formal analysis; methodology.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

ORCID

Osvaldo L. Casagrande Jr https://orcid.org/0000-0002-9855-6159

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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