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Chromium Catalysts Based on Tridentate Pyrazolyl Ligands for Ethylene Oligomerization

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A set of chromium(III) complexes $\text{CrCl}_3(\text{L})$ based on tridentate ligands (**1**, L = bis[2-(3,5-dimethylpyrazolyl)ethyl]amine; **2**, L = bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]benzylamine; **3**, L = bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl] ether; **4**, L = bis[2-(3-phenyl-1-pyrazolyl)ethyl] ether; **5**, L = bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl] sulfide) have been prepared and characterized by elemental analysis, ESI-HRMS, and an X-ray diffraction study for **3**. Upon activation with methylaluminoxane (MAO), these precatalysts show high activity in ethylene oligomerization ($\text{TOF} = (3.4\text{--}131.0) \times 10^3$ (mol ethylene) $(\text{mol Cr})^{-1} \text{ h}^{-1}$ at 80 °C), producing α -olefins in the range $\text{C}_4\text{--C}_{14+}$ with high selectivity. The catalytic performances are substantially affected by the ligand environment, especially the bridge donor atom, and reaction conditions. Under optimized conditions ($[\text{Cr}] = 10 \mu\text{mol}$, 80 °C, 40 bar ethylene, MAO-to-Cr = 300), precatalyst **5** leads to $\text{TOF} = 131.0 \times 10^3 \text{ h}^{-1}$ and selectivity for α -olefins in the range 89–97%.

Introduction

The pursuit of ethylene oligomerization catalysts capable of selectively producing α -olefins has been a major focus of research in recent decades, due to their importance in a variety of industrial processes. Among linear α -olefins, special attention has been devoted to the production of 1-hexene and 1-octene, which are mostly used as co-monomers in the production of linear low-density polyethylene (LLDPE).¹ For this purpose, several ethylene tri- and tetramerization catalyst systems have been developed, most of which are based on chromium catalysts bearing NNN,² PNP,³ and SNS⁴ ligands. Such tridentate ligands are quite prone to steric and electronic modifications, allowing the formation of highly active chromium catalytic species capable of producing 1-hexene⁵ and 1-octene^{3c,6} with high selectivity.

In recent years we have been interested in studying the potential applications of tridentate nitrogen-, oxygen-, or sulfur-bridged bis(pyrazolyl) ligands (NZN) in the oligo/polymerization

catalysis field. Thus, we have previously communicated a new class of pentacoordinated Ni^{II} complexes based on these tridentate Z-bridged bis(pyrazolyl) ligands (Z = O, N, S), which act as highly selective and efficient precatalysts for ethylene dimerization in the presence of methylaluminoxane (MAO).⁷ Also, we have used bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine in the synthesis of Al, Zn, and Mg complexes and used them as initiators for lactide polymerization.⁸ Herein, we report the synthesis and characterization of Cr^{III} complexes bearing NZN

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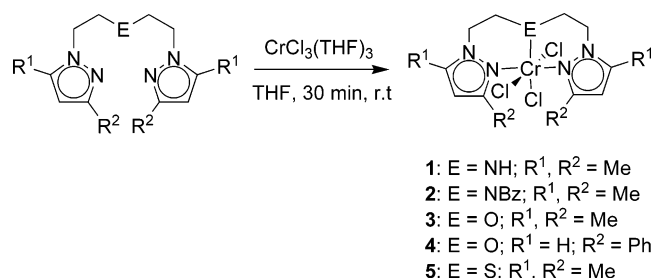
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Scheme 1



tridentate ligands, which, in association with MAO, afford active catalysts for the selective production of α -olefins in the range C₄–C₁₄+. We also show the effect of the central donor atom and the pyrazolyl substituents on turnover frequency (TOF), selectivity for α -olefins, and product distributions.

Results and Discussion

Synthesis and Characterization of Bis(Pyrazolyl)–Cr(III) Complexes. The reaction of CrCl₃(THF)₃ with 1.1 equiv of tridentate nitrogen-, oxygen-, or sulfur-bridged bis(pyrazolyl) ligands (NZN)⁹ in THF at room temperature affords the corresponding complexes CrCl₃(NZN) (**1**–**5**) (Scheme 1), which were isolated as green- or red wine-colored solids in high yields (typically 87–92%). These complexes show moderate solubility at room temperature in dichloromethane, THF, and ethyl acetate and are readily soluble in acetonitrile. The identity of **1**–**5** was established on the basis of elemental analysis and ESI-high-resolution mass spectrometry (which indicated the formation of [M – Cl]⁺ or [M – 2Cl]⁺ ions), and by an X-ray diffraction study for complex **3**.

Crystals of complex **3** suitable for an X-ray diffraction study were grown from a concentrated acetonitrile solution at –4 °C. Crystal data and structure refinement for **3** are summarized in Table 1, and selected bond distances and angles are listed in Table 2. The molecular geometry and atom-labeling scheme are shown in Figure 1. The crystal structure of **3** confirms both the monomeric nature of the complex and κ^3 -coordination of the NON ligand. The geometry around the chromium atom is best described as slightly distorted octahedral with the chlorine ligands in a *mer* disposition. The Cl–Cr–Cl and N–Cr–N angles are 94.84(2)°, 176.27(2)°, and 88.23(2)° and 172.51(6)°, respectively. The chelate bite angles of the N–O–N ligand in **3** [N–Cr–O, 85.54(5)° and 87.06(5)°] compare similarly to those in CrCl₃{HN(CH₂CH₂PPh₂)₂}^{3b} [P–Cr–N, 81.08(8)°, 82.07(8)°] and CrCl₃{HN(CH₂CH₂SR)₂}^{4a} [S–Cr–N, 83.07(5)°, 82.90(5)°] complexes. On the other hand, these bite angles are smaller than those found in nickel(II) and copper(I) complexes having similar bis(pyrazolyl) tridentate ligands, i.e., NiCl₂{HN(CH₂CH₂Pz^{Me2})₂} [N–Cr–N, 95.55(8)°, 94.12(8)°]⁷ and Cu{O(CH₂CH₂Pz^{Me2})₂}BF₄ [N–Cu–O, 94.05(17)°, 95.91-

Table 1. Crystal Data and Structure Refinement for **3**·CH₃CN.

empirical formula	C ₁₆ H ₂₅ Cl ₃ CrN ₅ O
fw	461.76 g mol ^{–1}
temp	100 K
wavelength	0.71073 Å
cryst syst	Triclinic
space group	P1̄, (no. 2)
unit cell dimens	<i>a</i> = 8.5821(2) Å, α = 110.1040(10)° <i>b</i> = 9.5447(2) Å, β = 90.7560(10)° <i>c</i> = 13.1028(3) Å, γ = 97.3420(10)°
volume	997.76(4) Å ³
Z	2
density (calcd)	1.537 Mg m ^{–3}
absorp coeff	0.991 mm ^{–1}
<i>F</i> (000)	478
cryst size	0.18 × 0.09 × 0.05 mm
θ range for data collection	3.00 to 31.01°
index ranges	–12 ≤ <i>h</i> ≤ 12, –13 ≤ <i>k</i> ≤ 13, –18 ≤ <i>l</i> ≤ 18
no. of reflns collected	25 620
no. of indep reflns	6350 [<i>R</i> _{int} = 0.0333]
completeness to θ = 27.75°	99.7%
refinement method	full-matrix least-squares on <i>F</i> ²
no. of data/restraints/params	6350/0/239
goodness-of-fit on <i>F</i> ²	1.090
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0293, <i>wR</i> ₂ = 0.0903
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0399, <i>wR</i> ₂ = 0.1286
largest diff peak and hole	0.777 and –1.370 e·Å ^{–3}

Table 2. Selected Bond Lengths [Å] and Angles [deg] for **3**·CH₃CN

Cr(1)–O(3)	2.0757(12)	Cr(1)–N(11)	2.1163(14)
Cr(1)–N(21)	2.1221(14)	Cr(1)–Cl(1)	2.2864(5)
Cr(1)–Cl(2)	2.3189(5)	Cr(1)–Cl(3)	2.3437(5)
O(3)–Cr(1)–N(11)	85.54(5)	O(3)–Cr(1)–N(21)	87.06(5)
N(11)–Cr(1)–N(21)	172.51(6)	O(3)–Cr(1)–Cl(1)	176.34(4)
N(11)–Cr(1)–Cl(1)	92.23(4)	N(21)–Cr(1)–Cl(1)	95.22(4)
O(3)–Cr(1)–Cl(2)	88.06(4)	N(11)–Cr(1)–Cl(2)	89.73(4)
N(21)–Cr(1)–Cl(2)	88.88(4)	Cl(1)–Cr(1)–Cl(2)	94.836(17)
O(3)–Cr(1)–Cl(3)	88.96(4)	N(11)–Cr(1)–Cl(3)	92.28(4)
N(21)–Cr(1)–Cl(3)	88.72(4)	Cl(1)–Cr(1)–Cl(3)	88.227(17)
Cl(2)–Cr(1)–Cl(3)	176.269(18)		

(18)°].^{9a} The Cr–N distances in **3** [2.1221(14), 2.1163(14) Å] are longer than those in the corresponding copper(I) complex Cu{O(CH₂CH₂Pz^{Me2})₂} [1.877(5), 1.874(4) Å].^{9a} Conversely, the Cr–O distance of 2.0757(12) Å in **3** is shorter than that in the latter copper complex (2.197(4) Å). These differences in the bond distances between chromium(III) and copper(I) are mainly associated with the oxidation state and ionic radii of the metal centers. The average Cr–Cl_{av} (2.316 Å) bond distances are comparable to those found in similar chromium(III) compounds having tridentate ligands such as CrCl₃L (L = bis-(carbene)pyridine, Cr–Cl_{av} = 2.327 Å)^{5b} and CrCl₃{HN(CH₂CH₂SEt)₂} (Cr–Cl_{av} = 2.312 Å).^{4a}

Ethylene Oligomerization. The ethylene oligomerization behavior of complexes **1**–**5** was investigated in toluene with MAO activation. Representative results are summarized in Table 3. Initial studies carried out at 80 °C under 20 bar with [Al]/[Cr] = 300 showed that these catalytic systems are active for the linear oligomerization/polymerization of ethylene.

The catalytic activities and selectivities are substantially affected by the ligand environment. Thus, precatalyst **1** exclusively produces polyethylene (PE) with an activity of 10 373 (mol ethylene) (mol Cr)^{–1}·h^{–1}. The DSC shows that the PE produced under these conditions is essentially linear (*T*_m = 136 °C). This strongly suggests that no oligomers were produced during the oligomerization reaction. Attempts to carry out GPC analysis failed since this PE is insoluble under standard analysis

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Table 3. Ethylene Oligomerization with 1–5/MAO Systems^a

entry	cat. (amount, μmol)	MAO (equiv)	TOF ^b (10 ³ ·h ⁻¹)	oligomer distribution (wt %) ^c						oligomers (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 (α-C ₁₂)	C ₁₄₊			
1	1 (30.0)	300								0	100	2182
2	2 (30.0)	300	11.4	10.7 (100)	15.2 (100)	16.1 (87.2)	13.8 (87.6)	11.4 (92.4)	16.8	83.8	16.2	2717
3	3 (30.0)	300	41.2	12.3 (98.0)	16.2 (100)	17.9 (91.0)	15.2 (90.4)	11.5 (91.4)	20.9	94.0	6.0	9501
4	4 (30.0)	300	26.7	10.4 (97.4)	15.5 (95.1)	15.9 (98.8)	14.3 (97.5)	11.9 (92.6)	21.5	89.5	10.5	6020
5	5 (30.0)	300	29.0	15.6 (96.0)	20.1 (95.4)	18.9 (90.1)	11.8 (93.7)	6.9 (91.7)	8.0	81.3	18.7	7485
6 ^d	3 (30.0)	300	13.7	16.2 (94.5)	19.3 (93.5)	17.3 (87.7)	11.4 (89.1)	7.2 (90.3)	6.2	77.6	22.4	3512
7	3 (11.8)	100	3.40	15.6 (76.8)	17.2 (69.8)	20.2 (66.8)	17.3 (52.2)	12.9 (49.4)	7.9	91.1	8.9	292
8	3 (10.9)	300	47.4	14.1 (93.8)	15.6 (91.2)	21.0 (76.1)	15.1 (92.0)	11.6 (91.6)	12.5	89.9	10.1	4037
9	3 (10.2)	1000	69.6	23.8 (92.4)	22.9 (90.5)	18.3 (88.0)	12.2 (86.0)	11.6 (88.5)	3.1	91.9	8.1	5414
10	5 (10.0)	300	66.2	18.0 (94.3)	18.8 (95.8)	16.4 (93.7)	12.8 (92.0)	10.4 (65.3)	8.9	85.3	14.7	5437
11 ^e	5 (10.0)	300	131.0	9.7 (94.3)	14.3 (95.8)	17.7 (93.7)	16.3 (92.0)	12.0 (91.1)	14.9	84.9	15.1	11865
12 ^f	5 (10.0)	300	28.2	19.1 (96.2)	24.0 (97.4)	21.1 (88.7)	12.8 (95.7)	8.2 (93.1)	8.6	93.8	6.2	2107

^a Reaction conditions: toluene = 50 mL, oligomerization time = 15 min, *P*(ethylene) = 20 bar, *T* = 80 °C. The results shown are representative of at least duplicated experiments. ^b Moles 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 Preactivation of Cr complex with MAO under ethylene atmosphere (1 bar) for 10 min followed by pressurizing of reactor with ethylene (20 bar) for 15 min (see ref 12). ^e *P*(ethylene) = 40 bar; *T* = 100 °C.

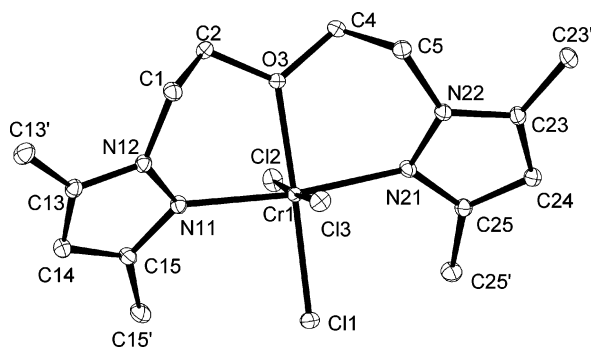


Figure 1. Molecular structure of compound **3** (thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity).

procedures (trichlorobenzene, 145 °C), a characteristic that likely calls for very high molecular weights.

The amount of PE produced can be dramatically reduced using complex **2**, which bears an *N*-benzyl-substituted ligand. In this case, distributions of oligomers¹⁰ constituted mostly of 1-alkenes are produced with up to 84 wt % selectivity, and polyethylene is a minor product (16 wt %) (entry 1). Thus, the N–H functionality does not appear to be essential for high activity and selectivity with this ligand system. Quite different results have been found for CrCl₃{RN(CH₂CH₂PPh₂)₂} precatalysts,^{5a} where the substitution of the NH bridge by a methyl or benzyl group leads to a dramatic decrease in both activity and selectivity; in these cases, the amounts of PE produced jumped to 30 and 66 wt %, respectively, instead of virtually no PE for the NH-bridged catalyst. Other studies carried out using Cr catalysts based on bis(diphenylphosphino)amine ligands have demonstrated that the oligomerization product selectivity as well as the activity tendencies are connected to the structure and size of the N–R functionality.^{3c,g,h} Our results and the above-mentioned studies confirm that the nature of the donor group [PR₂, SR, Pz^R] as well as the substituent on the central bridging

nitrogen have an influence on the formation of ethylene oligomers and/or polyethylene.^{3c,g,h,5a} Furthermore, the chelating ring size of these tridentate nitrogen-, oxygen-, or sulfur-bridged bis(pyrazolyl) ligands (NZN) (formation of six-membered-ring complexes) may in part explain why these catalysts (**2**–**5**) are not selective for tri/tetramerization of ethylene (*vide infra*).^{10,11}

Along the same line, the selectivity for oligomers is increased up to 94 wt % on using complex **3**, which bears an O-bridged ligand (entry 2). Varying the central donor atom in tridentate 3,5-dimethyl-substituted bis(pyrazolyl) ligands NZN^{Me,Me} (Z = N, O, S) also has a significant effect on catalyst activity. Relatively high turnover frequencies (TOFs) in the range 11 400–29 000 h⁻¹ are obtained with N- and S-based ligands (entries 1 and 4), while the catalyst system derived from the NON complex **3** gives an improved TOF of 41 200 h⁻¹ (entry 2). The introduction of relatively bulky phenyl substituents (as compared to methyl groups) leads to a noticeable decrease in catalytic activity in (NON)Cr(III) systems based on complexes **3** and **4** (compare entries 2 and 3).

All chromium complexes **2**–**5** produce oligomers ranging from C₄ to C₁₄₊ with a high selectivity for α-olefins. As shown in Figure 2, the selectivities for 1-alkenes afforded by precatalysts **2**–**4** derived from N- and O-bridged ligands are very similar. This indicates that the central donor atoms and also the pyrazolyl R² substituents have no significant influence in this series on the product distribution. Similar trends have been observed for ethylene oligomerization with MAO-activated nickel complexes bearing analogous tridentate ligands.⁷ Enriched fractions in α-C₄ (15.0 wt %), α-C₆ (19.2 wt %), and α-C₈ (17.0 wt %) are obtained using the catalyst system derived from **5** that contains a sulfur-bridged ligand, with a concomitant decrease in the α-C₁₀ (11.1 wt %), α-C₁₂ (6.3 wt %), and C₁₄₊ fractions (8.0 wt %).

On the basis of these encouraging preliminary results, complexes **3** and **5** were selected for further optimization,

(10) Those Cr–NZN catalysts produce olefins that do not strictly follow Schulz–Flory distributions. As a matter of fact, a single α value, which represents the probability of chain transfer [rate of propagation/(rate of propagation + rate of chain transfer)] for a Schulz–Flory distribution, cannot accurately describe most of the observed distributions. However, individual α values determined from the data reported in Table 3 [α = mol of C_{n+2}/mol C_n] all fall in the range 0.5–0.9 [0.64 ± 0.12]. This observed inconsistency of the Schulz–Flory parameters hampers an accurate analysis of the reaction parameters (time, pressure, nature of the complex, ...).

(11) A six-membered-ring chromium catalyst (**1c**) was reported to produce 27 wt % of hexenes with a selectivity for 1-hexene of 99%. Blumh, M. E.; Walter, O.; Döring, M. *J. Organomet. Chem.* **2005**, 690, 713.

(12) Considering the poor solubility of complex **3** in toluene, a preactivation procedure was attempted to possibly generate higher amounts of active species. Thus, complex **3** was first dissolved and preactivated in a MAO/toluene solution under ethylene atmosphere (1 bar) for 10 min, and then oligomerization was carried out under 20 bar. However, we observed that this procedure led to lower TOF values (13 700 h⁻¹; compare entries 2 and 5), suggesting that catalyst deactivation takes place.

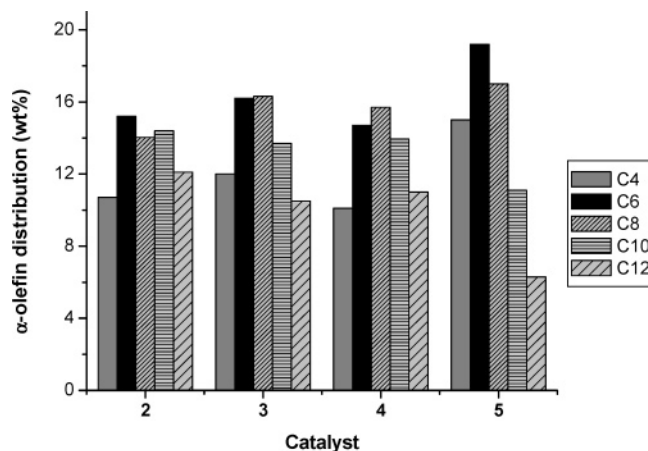


Figure 2. Selectivity of 2–5/MAO oligomerization systems for α -olefins (80 °C, 20 bar, MAO-to-Cr = 300).

investigating the influence of cocatalyst type, preactivation period, catalyst concentration, [Al]/[Cr] ratio, temperature, and ethylene pressure. A series of tests using complex **5** revealed that low loading of precatalyst in this system led to high activity. For instance, with 10.0 μmol of chromium complex (i.e., [Cr] = 0.2×10^{-3} M), a high TOF of 66 200 h^{-1} was obtained (entry 9). This effect can be associated with an easier solubilization of the precatalyst in toluene solution;¹² however, a decrease of excessive exotherms during the oligomerization reaction, which would induce catalyst decay, cannot be ruled out.

Activation of **3** with other Lewis acid cocatalysts, including diethylaluminum chloride (DEAC), and trimethylaluminum (TMA) produced neither oligomers nor polymer in significant amounts, presumably due to the low Lewis acidity of these compounds. However, it should be pointed out that the use of perfluoroaryl boranes, along with alkyl metal complexes or alkylating agents, has been shown to be a highly effective alternative to the use of MAO.^{3c,i}

The influence of the MAO loading on the catalyst behavior has been studied. When activated with 100 equiv of MAO, complex **3** gave a relatively low activity (TOF = 3400 h^{-1} , entry 6), which was increased upon using 300 equiv (TOF = 47 400 h^{-1} , entry 7) and even further with 1000 equiv (TOF = 69 600 h^{-1} , entry 8). At the same time, increasing the amount of MAO from 300 to 1000 equiv led to slightly improved selectivities for the α -C₄ (13.2 to 22.0 wt %) and α -C₆ (14.2 to 20.7 wt %) fractions.

Increasing the ethylene pressure resulted in much higher TOF values, most likely as an effect of increased ethylene concentration in solution. For instance, the activity of the **5**/MAO system is significantly enhanced from 20 to 40 bar, giving a maximal TOF of 131 000 h^{-1} (entry 10). The ethylene pressure does not affect the total amount of PE formed (ca. 15 wt %, compare entries 9 and 10), at least in the 20–40 bar range.

Taking into account the higher activity of systems based on **5**, this complex was chosen to investigate the effect of temperature on TOF and oligomer distributions. The optimal operating temperature for this class of precatalysts is 80 °C. At 60 °C, neither oligomers nor PE was detected, while at 100 °C partial catalyst deactivation was observed. However, the selectivity for 1-alkene remains almost unchanged (compare entries 9 and 11). In fact, even at high temperature (100 °C), the **5**/MAO catalyst system remains highly selective toward α -olefins (up to 88.7%) and only 6 wt % of the product formed was PE. We may reasonably assume that favored formation of α -olefins rather than polyethylene at 100 °C is a consequence of enhanced

rates of chain transfer and/or β -H elimination. Furthermore, it should be pointed out that the PE produced at 100 °C, in contrast to the PE produced with **1** at 80 °C (vide supra), is highly branched (BPE), the DSC curve of which displays two endothermic peaks at 74 and 124 °C (see Supporting 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.

In summary, a new set of chromium(III) complexes based on tridentate ligands has been prepared and evaluated for ethylene oligomerization under MAO activation. The central atom donor was found to play a significant role in the catalytic activity and product distribution. Substitution of the central nitrogen donor by a benzyl group appears to be an essential attribute of this ligand class for high activity and minimization of the amount of PE produced. This is in sharp contrast to related classes of precatalysts such as $\text{CrCl}_3\{\text{HN}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2\}$ ^{3b,5a} and $\text{CrCl}_3\{\text{HN}(\text{CH}_2\text{CH}_2\text{SR})_2\}$.^{4a} Replacement of the central bridging nitrogen with a sulfur donor atom affords a catalyst that exhibits higher TOF and higher selectivity for α -C₄–C₈. At this stage, we can only speculate that the absence of significant selectivity of precatalysts **2**–**5** for tri/tetramerization of ethylene may be in part associated with the formation of six-membered-ring complexes. Promising investigations of related NZN ligands that induce the formation of five-membered-ring chromium complexes are underway and will be reported in due course.

Experimental Section

General Procedures. All manipulations were performed using standard vacuum line and Schlenk techniques under a purified argon atmosphere. Et₂O, THF, and toluene were distilled from sodium benzophenone ketyl under argon and degassed by freeze–thaw–vacuum cycles prior to use. $\text{CrCl}_3(\text{THF})_3$ was prepared as previously reported.¹³ The ligands bis[2-(3,5-dimethylpyrazolyl)ethyl]amine, [bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]benzylamine], bis[2-(3,5-dimethylpyrazolyl)ethyl] ether, bis[2-(3,5-dimethylpyrazolyl)ethyl] sulfide, and bis[2-(5-phenylpyrazolyl)ethyl] ether were prepared by literature procedures.^{7,9} Ethylene (White Martins Co.) and argon were deoxygenated and dried through columns of BTS (BASF) and activated molecular sieves (3 Å) prior to use. PMAO-IP (Akzo, 12.9 wt % Al solution in toluene) was used as received. Elemental analyses were performed by the Analytical Central Service of the Institute of Chemistry-UFRGS (Brazil) and by the Microanalytical Laboratory at the Institute of Chemistry of Rennes and are the average of two independent determinations. ESI-HRMS of Cr complexes was performed on a Perkin-Elmer Sciex API-I single quadrupole spectrometer; the instrument was operated at atmospheric pressure in the positive-ion mode (5 kV). Quantitative gas chromatographic analysis of the products of oligomerization reactions was performed on a Varian 3400CX 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 and then heating at 5 °C min^{-1} until 250 °C, using cyclohexane as an internal standard.

$\text{CrCl}_3\{\text{bis}[2-(3,5\text{-dimethylpyrazolyl)ethyl}]\text{amine}\}$ (1**).** To a solution of bis[2-(3,5-dimethylpyrazolyl)ethyl]amine (120 mg, 0.46 mmol) in THF (10 mL) was added a solution of $\text{CrCl}_3(\text{THF})_3$ (54.9 mg, 0.14 mmol) in THF (15 mL), and the resulting solution was stirred for 30 min at room temperature. The solvent was removed until ca. one-third remained and 10 mL of pentane added to complete precipitation. The product was collected by filtration, washed with pentane, and dried *in vacuo*. Yield: 52.8 mg (89%).

(13) Boudjouk, P.; So, J.-H. *Inorg. Synth.* **1992**, 29, 108.

Anal. Calcd for $C_{14}H_{23}N_5Cl_3Cr$ (%): C, 40.06; H, 5.52; N, 16.69. Found (%): C, 39.88; H, 5.56; N, 16.44. ESI-HRMS: 347.0972 $[M - 2Cl]^+$ (calcd for $C_{14}H_{23}N_5ClCr$, 347.0969).

$CrCl_3[bis[2-(3,5\text{-dimethyl-1-pyrazolyl})ethyl]benzylamine]$ (2). This compound was prepared according to the method described for **1** using $CrCl_3(THF)_3$ (83.2 mg, 0.22 mmol) and bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]benzylamine (85.2 mg, 0.24 mmol). Complex **2** was obtained as a green solid (112 mg, 92%). Anal. Calcd for $C_{21}H_{29}N_5Cl_3Cr$ (%): C, 49.47; H, 5.73; N, 13.74. Found (%): C, 49.13; H, 5.61; N, 13.11. ESI-HRMS: 473.1171 $[M - Cl]^+$ (calcd for $C_{21}H_{29}N_5Cl_2Cr$, 473.1189).

$CrCl_3[bis[2-(3,5\text{-dimethyl-1-pyrazolyl})ethyl] ether]$ (3). This compound was prepared according to the method described for **1** using $Cr(THF)_3Cl_3$ (101.5 mg, 0.26 mmols) and bis[2-(3,5 dimethyl-1-pyrazolyl)ethyl] ether (77.5 mg, 0.29 mmol). Complex **3** was recovered as a red wine-colored solid (98.4 mg, 90%). Anal. Calcd for $C_{14}H_{22}N_4OCl_3Cr$ (%): C, 39.97; H, 5.27; N, 13.32. Found (%): C, 39.24; H, 5.03; N, 12.66. ESI-HRMS: 384.0554 $[M - Cl]^+$ (calcd for $C_{14}H_{22}N_4OCl_2Cr$, 384.0577).

$CrCl_3[bis[2-(3\text{-phenyl-1-pyrazolyl})ethyl] ether]$ (4). This compound was prepared according to the method described for **1** using $Cr(THF)_3Cl_3$ (148 mg, 0.39 mmol) and bis[2-(3-phenyl-1-pyrazolyl)-ethyl] ether (155 mg, 0.43 mmol). Complex **4** was obtained as a red wine-colored solid (175 mg, 87%). Anal. Calcd for $C_{22}H_{22}N_4OCl_3Cr$ (%): C, 51.13; H, 4.29; N, 10.84. Found (%): C, 50.87; H, 4.08; N, 10.55. ESI-HRMS: 480.0556 $[M - Cl]^+$ (calcd for $C_{22}H_{22}N_4OCl_2Cr$, 480.0575).

$CrCl_3[bis[2-(3,5\text{-dimethyl-1-pyrazolyl})ethyl] sulfide]$ (5). This compound was prepared according to the method described for **1** using $Cr(THF)_3Cl_3$ (298 mg, 0.79 mmol) and bis[2-(3,5-dimethylpyrazolyl)ethyl] sulfide (243 mg, 0.87 mmol). Complex **5** was obtained as a green-gray solid (299 mg, 87%). Anal. Calcd for

$C_{14}H_{22}N_4SCl_3Cr$ (%): C, 38.50; H, 5.08; N, 12.83. Found (%): C, 38.01; H, 4.96; N, 12.13. ESI-HRMS: 400.0324 $[M - Cl]^+$ (calcd for $C_{14}H_{22}N_4SCl_2Cr$, 400.0347).

General Oligomerization Procedure. Ethylene oligomerization reactions were performed in a 100 mL double-walled stainless steel Parr reactor equipped with mechanical stirring, internal control of temperature, and continuous feed of ethylene. A 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 in the reactor, under ethylene atmosphere, toluene (40 mL) and the proper amount of MAO cocatalyst. After 15 min the catalyst solution 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 at the desired value. After 15 min, the reaction was stopped by cooling the system at -20 °C, depressurizing, and introducing 1 mL of ethanol. An exact amount of cyclohexane was introduced (as internal standard), and the mixture was analyzed by quantitative GLC.

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Supporting Information Available: Complete crystallographic data (CIF file) for **3**, typical GLC analyses of oligomerization mixtures, and DSC curve of branched polyethylene produced at high temperature. This material is free of charge via the Internet at <http://pubs.acs.org>.

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