

## Substituted Tridentate Pyrazolyl Ligands for Chromium and Nickel-Catalyzed Ethylene Oligomerization Reactions. Effect of Auxiliary Ligand on Activity and Selectivity

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Dois novos complexos de cromo(III) contendo ligantes tridentados  $[\text{CrCl}_3(\text{L})]$  (**1a**, L = bis[2-(3-fenil-1-pirazol)etil]amina; **2a**, L = bis[2-(3-metil-5-fenil-1-pirazol)etil]sulfeto) foram preparados e caracterizados por análise elementar. Após ativação com metilaluminoxano (MAO), estes pré-catalisadores mostraram altas frequências de rotação nas reações de oligomerização do etileno sob condições otimizadas (FRs =  $22,9\text{-}36,4 \times 10^3 \text{ mol C}_2\text{H}_4 (\text{mol Cr}^{\text{III}})^{-1} \text{ h}^{-1}$ ,  $[\text{Cr}] = 10,0 \mu\text{mol}$ ,  $80^\circ\text{C}$ , 20 bar de etileno,  $[\text{Al}]/[\text{Cr}] = 300$ , tempo de oligomerização = 20 min), produzindo olefinas- $\alpha$  no intervalo de  $\text{C}_4\text{-C}_{14+}$  com alta seletividade (67,71-73,47%). Os desempenhos catalíticos são afetados substancialmente pelos grupos presentes nos ligantes, especialmente os substituintes nas posições 3 e 5 dos anéis pirazol. Em paralelo, o emprego de complexos de níquel(II) tais como  $\text{NiCl}_2\{\text{bis}[2\text{-}(3,5\text{-dimetil-1-pirazol)metil}] \text{benzilamina}\}$  (**3**) e  $\text{NiCl}_2\{\text{bis}[2\text{-}(3,5\text{-dimetil-1-pirazol)etil}]\text{éter}\}$  (**5**) em reações de oligomerização conduzidas na presença de trifetilfosfina ( $\text{PPh}_3$ ) resultou em sistemas catalíticos altamente ativos com frequências de rotação (FRs) variando de 36,4 a  $154,2 \times 10^3 \text{ mol C}_2\text{H}_4 (\text{mol Ni}^{\text{II}})^{-1} \text{ h}^{-1}$ . A presença deste ligante auxiliar tem um impacto significativo na produção seletiva de olefinas- $\alpha$ , diminuindo substancialmente a quantidade de buteno-1 com concomitante aumento da quantidade das frações de butenos-2. Tentativas de cristalização do complexo de níquel **3** resultaram na formação de um composto de níquel tetrametálico  $[\{(\text{L})(\mu_3\text{-Cl})\text{NiCl}\}_4]$  (**4**, L = 1-anilinoetil-3,5-dimetil-1-pirazol) o qual foi caracterizado por difratometria de raios X.

Two new chromium(III) complexes  $[\text{CrCl}_3(\text{L})]$  based on tridentate ligands (**1a**, L = bis[2-(3-phenyl-1-pyrazolyl)ethyl]amine; **2a**, L = bis[2-(3-methyl-5-phenyl-1-pyrazolyl)ethyl]sulfide) have been prepared and characterized by elemental analysis. Upon activation with methylaluminoxane (MAO), these pre-catalysts showed high turnover frequencies for ethylene oligomerization under optimized conditions (TOFs =  $22.9\text{-}36.4 \times 10^3 \text{ mol C}_2\text{H}_4 (\text{mol Cr}^{\text{III}})^{-1} \text{ h}^{-1}$ ,  $[\text{Cr}] = 10.0 \mu\text{mol}$ ,  $80^\circ\text{C}$ , 20 bar ethylene, MAO:Cr = 300, oligomerization time = 20 min), producing  $\alpha$ -olefins in the range  $\text{C}_4\text{-C}_{14+}$  with high selectivity (67.71-73.47%). The catalytic performances are substantially affected by the ligand environment, especially the substituents at the 3- and 5-positions of the pyrazolyl rings. In parallel, the use of nickel complexes such as  $\text{NiCl}_2\{\text{bis}[2\text{-}(3,5\text{-dimethyl-1-pyrazolyl)methyl}] \text{benzylamine}\}$  (**3**) and  $\text{NiCl}_2\{\text{bis}[2\text{-}(3,5\text{-dimethyl-1-pyrazolyl)ethyl}]\text{ether}\}$  (**5**) in oligomerization reactions carried out in the presence of triphenylphosphine ( $\text{PPh}_3$ ) afforded highly active catalytic systems with turnover frequencies (TOFs) varying from 36.4 to  $154.2 \times 10^3 \text{ mol C}_2\text{H}_4 (\text{mol Ni}^{\text{II}})^{-1} \text{ h}^{-1}$ . The presence of this auxiliary ligand has a strong impact on the selectivity towards the production of  $\alpha$ -olefins, decreasing substantially the amount of 1-butene with a concomitant increase of the 2-butene fractions. Attempts to crystallize the nickel complex **3** afforded the tetrametallic  $[\{(\text{L})(\mu_3\text{-Cl})\text{NiCl}\}_4]$  (**4**, L = 1-anilinomethyl-3,5-dimethylpyrazole) which was characterized by X-ray diffraction analysis.

**Keywords:** ethylene oligomerization, tridentate bis(pyrazolyl) ligands, nickel complexes, chromium complexes

## Introduction

The pursuit of ethylene oligomerization catalysts capable of producing selectively  $\alpha$ -olefins has been a major focus of research in recent decades, due to their importance in a variety of industrial processes. Depending on the chain length of the alkene, they can be used for production of various materials. The most important ones are linear low-density polyethylene (LLDPE) ( $C_4$ - $C_{10}$ ), poly- $\alpha$ -olefins ( $C_4$ ,  $C_{10}$ ), plasticizers ( $C_6$ - $C_{10}$ ), lubricants ( $C_8$ - $C_{10}$ ), lube oil additives ( $C_{12}$ - $C_{18}$ ), and surfactants ( $C_{12}$ - $C_{20}$ ).<sup>1</sup> For this purpose, several oligomerization catalyst systems have been developed, most of which are based on nickel<sup>2</sup> and chromium catalysts<sup>3</sup> bearing bi- and tridentate ligands.

In recent years we have been interested in studying the potential applications of tridentate ligands in the oligomerization catalysis field. We have thus previously communicated new classes of Ni<sup>II</sup><sup>4,5</sup> and Cr<sup>III</sup><sup>6,7</sup> complexes based on these tridentate pyrazolyl ligands, which act as highly selective and highly active pre-catalysts for ethylene oligomerization in the presence of methylaluminoxane (MAO) as co-activator. More recently, we have introduced a new set of Ni<sup>II</sup> complexes based on NZN ligands that form stable 5-membered chelate rings and which, in association with an alkylaluminum (MAO or AlEt<sub>2</sub>Cl), show high activity in ethylene oligomerization (TOF =  $1.7\text{--}104.5 \times 10^3$  mol(ethylene) mol(Ni)<sup>-1</sup> h<sup>-1</sup>), giving predominantly 1-butene (70-94% yield).<sup>8</sup> Herein, we report the synthesis and characterization of two new Cr<sup>III</sup> complexes, CrCl<sub>3</sub>{bis[2-(3-phenyl-1-pyrazolyl)ethyl]amine} (**1a**), and CrCl<sub>3</sub>{bis[2-(3-methyl-5-phenyl-1-pyrazolyl)ethyl]sulfide} (**2a**), which, in association with MAO, afford active catalysts for the selective production of  $\alpha$ -olefins in the range C<sub>4</sub>-C<sub>14+</sub>. Furthermore, studies on the influence of the auxiliary ligand triphenylphosphine (PPh<sub>3</sub>) on turnover frequency (TOF), selectivity for  $\alpha$ -olefins, and product distribution using 5- and 6-membered ring nickel complexes NiCl<sub>2</sub>{bis[2-(3,5-dimethyl-1-pyrazolyl)methyl]benzylamine} (**3**) and NiCl<sub>2</sub>{bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]ether} (**5**) are also reported.

## Experimental

### General procedures

All manipulations were performed using standard vacuum line and Schlenk techniques under a purified argon atmosphere. Et<sub>2</sub>O, thf and toluene were distilled from sodium-benzophenone ketyl under argon and degassed by freeze-thaw-vacuum cycles prior to use. 3-Phenylpyrazole<sup>9</sup> and [CrCl<sub>3</sub>(thf)<sub>3</sub>]<sup>10</sup> were prepared by literature procedures.

NiCl<sub>2</sub>·6H<sub>2</sub>O and triphenylphosphine (PPh<sub>3</sub>), both from Aldrich, were used as received. Ethylene (White Martins Co.) and argon were deoxygenated and dried through columns of BTS (BASF) and activated molecular sieves (3A) prior to use. PMAO-IP (methylaluminoxane, Akzo, 12.9 wt.% Al solution in toluene) and diethylaluminum chloride (DEAC) (Aldrich, 1.8 mol L<sup>-1</sup>, 25 wt.% toluene solution) were used as received. Elemental analyses were performed by the Analytical Central Service of the Institute of Chemistry-UFRGS (Brazil) and are the average of two independent determinations. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on a Varian Inova 300 spectrometer operating at 25 °C. Chemical shifts are reported in ppm vs. SiMe<sub>4</sub> and were determined by reference to the residual solvent peaks. Infrared spectra were performed on a FTIR Bruker Alpha Spectrometer. Quantitative gas chromatographic analysis of ethylene oligomerization products 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  $\mu$ m) operating at 36 °C for 15 min followed by heating at 5 °C min<sup>-1</sup> until 250 °C; cyclohexane was used as internal standard.

### Synthesis and characterization of tridentate pyrazolyl ligands

#### 1-(2-hydroxyethyl)-3-methyl-5-phenylpyrazole

A solution of 2-hydroxyethylhydrazine (4.64 g, 60.9 mmol) in absolute ethanol (10 mL) was added dropwise to a stirred solution of 1-phenyl-1,3-butanedione (10.01 g, 61.7 mmol) in absolute ethanol (30 mL). The temperature of the reaction mixture was kept below 10 °C. After the addition of the hydrazine, the reaction mixture was allowed to warm to room temperature and stirred for another 2 h. The solvent was then evaporated under reduced pressure to give a white solid composed by a mixture of two different isomers: 1-(2-hydroxyethyl)-3-methyl-5-phenylpyrazole (isomer A) and 1-(2-hydroxyethyl)-3-phenyl-5-methylpyrazole (isomer B). The pure form of isomer A was obtained after several washings with diethyl ether (4×15 mL) (6.36 g, 52%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.47 (s, 3H, CH<sub>3</sub>), 3.93 (t, 2H, <sup>3</sup>J<sub>HH</sub> 4.8 Hz, 2H, CH<sub>2</sub>), 4.26 (t, <sup>3</sup>J<sub>HH</sub> 4.7 Hz, 2H, CH<sub>2</sub>), 6.22 (s, 1H, CH), 7.24-7.79 (m, 5H, CH<sub>ar</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 13.4, 50.4, 61.9, 105.6, 128.5, 130.5, 144.9, 148.2. IR (KBr)  $\nu_{\text{max}}$ /cm<sup>-1</sup>: 3390s, 2947m, 2813w, 2788w, 1955w, 1903w, 1890w, 1664s, 1620s, 1595s, 1504s, 1460s, 1427s, 1380s, 1307m, 1236w, 1070m, 929w, 869w, 781m and 707s. mp 91 °C.

#### 1-(2-chloroethyl)-3-methyl-5-phenylpyrazole hydrochloride

A solution of 1-(2-hydroxyethyl)-3-methyl-5-phenylpyrazole (4.4 g, 19.8 mmol) and thionyl chloride

(2.90 mL, 39.9 mmol) in chloroform (25 mL) was allowed to reflux for 4 h. The volatiles were then evaporated under reduced pressure, and the resulting residue was washed with sodium bicarbonate solution (5%) to give a yellow oil (3.87, 89%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.61 (s, 3H, CH<sub>3</sub>), 4.13 (t, <sup>3</sup>J<sub>HH</sub> 6.6 Hz, 2H, CH<sub>2</sub>), 4.75 (t, <sup>3</sup>J<sub>HH</sub> 6.6 Hz, 2H, CH<sub>2</sub>), 6.3 (s, 1H, CH), 7.22-7.74 (m, 5H, CH<sub>ar</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ (ppm) 13.2, 42.1, 49.8, 105.8, 128.5, 130.3, 144.9, 148.3. IR (KBr) ν<sub>max</sub>/cm<sup>-1</sup>: 3060w, 2960m, 2928m, 2862w, 1967w, 1892w, 1824w, 1770w, 1602w, 1548m, 1494s, 1454s, 1425m, 1384m, 1307m, 1271m, 1166w, 1122w, 1072w, 1035w, 997m, 916w, 796m, 763s, 698s and 663s.

#### *Bis[2-(3-phenyl-1-pyrazolyl)ethyl]amine (I)*

Under an argon atmosphere, 3-phenylpyrazole (2.71 g, 18.7 mmol) was slowly added to a suspension of NaH (1.2 g, 50 mmol) in dry dmf (50 mL). The mixture was stirred at room temperature for 2 h. To the resulting solution, a solution of bis(2-chloroethyl)amine (1.66 g, 9.3 mmol) in dry dmf (10 mL) was added dropwise under stirring. The mixture was allowed to stir for 2 h at 70 °C, cooled and treated cautiously with H<sub>2</sub>O (15 mL) to decompose excess NaH. The solvents were then evaporated under reduced pressure. The residue was extracted with ethyl acetate (4×40 mL), washed with 10% NaOH (2×30 mL), H<sub>2</sub>O (2×30 mL), and then dried over MgSO<sub>4</sub>. The solvent was evaporated to give a yellow oil (2.60 g, 77%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 3.12 (t, <sup>3</sup>J<sub>HH</sub> 5.7 Hz, 4H, CH<sub>2</sub>), 4.36 (t, <sup>3</sup>J<sub>HH</sub> 5.7 Hz, 4H, CH<sub>2</sub>), 6.52 (d, <sup>2</sup>J<sub>HH</sub> 2.3 Hz, 2H, CH), 7.40-7.85 (m, 12 H, CH<sub>ar</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ (ppm) 48.2, 51.9, 102.4, 125.3, 127.8, 128.3, 131.0, 133.3, 151.4. IR (KBr) ν<sub>max</sub>/cm<sup>-1</sup>: 2948s, 2852s, 1957w, 1884w, 1812w, 1753w, 1664w, 1604m, 1525m, 1504s, 1461s, 1409s, 1355s, 1326m, 1226s, 1134m, 1076s, 1049m, 948m, 919m, 846w, 756s, 698s, 659w, 626w and 509w.

#### *Bis[2-(3-phenyl-5-methyl-1-pyrazolyl)ethyl]sulfide (2)*

A solution of 1-(2-chloroethyl)-3-methyl-5-phenyl pyrazole hydrochloride (5.07 g, 19.8 mmol) and sodium hydroxide (0.5 g, 12.5 mmol) in aqueous ethanol (50%, 100 mL) was treated with Na<sub>2</sub>S·9H<sub>2</sub>O (2.98 g, 12.4 mmol). The solution was allowed to reflux for 3 h, cooled and evaporated under reduced pressure. Water was added (20 mL), the product was extracted with dichloromethane (4×15 mL), and the organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub>. The volatiles were evaporated under reduced pressure to give a yellow oil (2.98 g, 75%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.32 (s, 6 H, CH<sub>3</sub>), 3.84 (t, <sup>3</sup>J<sub>HH</sub> 7.2 Hz, 4H, CH<sub>2</sub>), 4.23 (t, <sup>3</sup>J<sub>HH</sub> 7.2 Hz, 4H, CH<sub>2</sub>), 6.17 (s, 2H, CH), 7.25-7.67 (m, 10 H, CH<sub>ar</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ (ppm) 13.5, 31.8, 48.5, 105.9,

128.8, 129.2, 129.8, 130.7 144.0, 148.5. IR (KBr) ν<sub>max</sub>/cm<sup>-1</sup>: 3060m, 2960m, 2925s, 2864m, 1955w, 1892w, 1814w, 1764w, 1606m, 1548s, 1496s, 1454s, 1423s, 1303s, 1278m, 1218m, 1180w, 1118w, 1074m, 1035m, 993s, 954w, 919w, 794m, 767s, 700s, 675m, 635w and 549m.

#### *CrCl<sub>3</sub>[bis[2-(3-phenyl-1-pyrazolyl)ethyl]amine] (Ia)*

To a solution of bis[2-(3-phenyl-pyrazol)ethyl]amine (0.32 g, 0.90 mmol) in thf (10 mL), a solution of [CrCl<sub>3</sub>(thf)<sub>3</sub>] (0.30 mg, 0.80 mmol) in thf (15 mL) was added, and the resulting mixture was stirred for 30 min at room temperature. The solvent was removed until ca. 1/3 remained and 10 mL of pentane was added to complete precipitation. The product was collected by filtration, washed with pentane and dried in vacuo. Complex **1a** was obtained as a green solid. Yield: 0.38 g (92%). Compound **1a**, elemental analysis: Found C, 50.71; H, 4.33; N, 12.96. Calc. for C<sub>22</sub>H<sub>23</sub>Cl<sub>3</sub>CrN<sub>5</sub>: C, 51.23; H, 4.49; N, 13.58%.

#### *CrCl<sub>3</sub>[bis[2-(3-methyl-5-phenyl-1-pyrazolyl)ethyl]sulfide] (2a)*

This compound was prepared according to the method described for **1a** using [CrCl<sub>3</sub>(thf)<sub>3</sub>] (0.26 g, 0.70 mmol) and bis[2-(3-methyl-5-phenyl-1-pyrazolyl)ethyl]sulfide (0.33 g, 0.80 mmol). Complex **2a** was obtained as a light red wine coloured solid (0.36 g, 90%). Compound **2a**, elemental analysis: Found: C, 50.88; H, 4.25; N, 9.76. Calc. for C<sub>24</sub>H<sub>26</sub>Cl<sub>3</sub>CrN<sub>4</sub>S: C, 51.39; H, 4.67; N, 9.99%.

#### *NiCl<sub>2</sub>{bis[2-(3,5-dimethyl-1-pyrazolyl)methyl]benzylamine} (3)<sup>8</sup>*

To a solution of NiCl<sub>2</sub>·6H<sub>2</sub>O (130 mg, 0.56 mmol) in thf (10 mL), a solution of bis[2-(3,5-dimethyl-1-pyrazolyl)methyl]benzylamine (200 mg, 0.62 mmol) in thf (10 mL) was added, and the resulting mixture was stirred for 24 h at room temperature. Volatiles were removed under reduced pressure, and the resulting green solid residue was washed with Et<sub>2</sub>O (2×10 mL) to afford **3** as a green solid (189 mg, 75%). Compound **3**, elemental analysis: Found C, 46.51; H, 5.90; N, 14.07. Calc. for C<sub>19</sub>H<sub>25</sub>Cl<sub>2</sub>N<sub>5</sub>Ni·2H<sub>2</sub>O: C, 46.66; H, 5.98; N, 14.32%.

#### *[(1-anilinomethyl-3,5-dimethylpyrazole)(μ<sub>3</sub>-Cl)NiCl<sub>4</sub>] (4)*

A solution of **3** (18 mg) in CH<sub>2</sub>Cl<sub>2</sub> (7 mL) was kept at room temperature for five days, resulting in a few green crystals of **4**, which were separated from the solution and proved suitable for X-ray diffraction analysis.

#### *NiCl<sub>2</sub>[bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]ether] (5)<sup>4</sup>*

To a solution of NiCl<sub>2</sub>·6H<sub>2</sub>O (116 mg, 0.49 mmol) in thf (10 mL), a solution of bis[2-(3,5-dimethyl-pyrazol)ethyl]

ether (128 mg, 0.49 mmol) in thf (10 mL) was added, and the resulting mixture was stirred for 3 h at room temperature. Volatiles were removed under reduced pressure, and the resulting turquoise solid residue was washed with Et<sub>2</sub>O (2×10 mL) to afford a turquoise blue solid (175 mg, 91%). Compound **5**, elemental analysis: Found C, 39.98; H, 6.00; N, 12.83. Calc. for C<sub>14</sub>H<sub>22</sub>Cl<sub>2</sub>N<sub>4</sub>NiO·2H<sub>2</sub>O: C, 39.29; H, 6.12; N, 13.09%.

#### General oligomerization procedure

A 100 mL double-walled stainless Parr reactor equipped with mechanical stirring and internal control of temperature was evacuated and filled three times with argon and twice with ethylene. Freshly distilled toluene (30 mL) and the proper amount of MAO or DEAC were added into the vessel under a stream of ethylene. After 15 min, the toluene catalyst solution (10 mL) was injected. The reactor pressure was kept constant throughout the oligomerization process (20 bar) by manually controlled addition of ethylene. After the desired time, the reaction was stopped by cooling the system to -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.

#### X-ray crystallographic studies

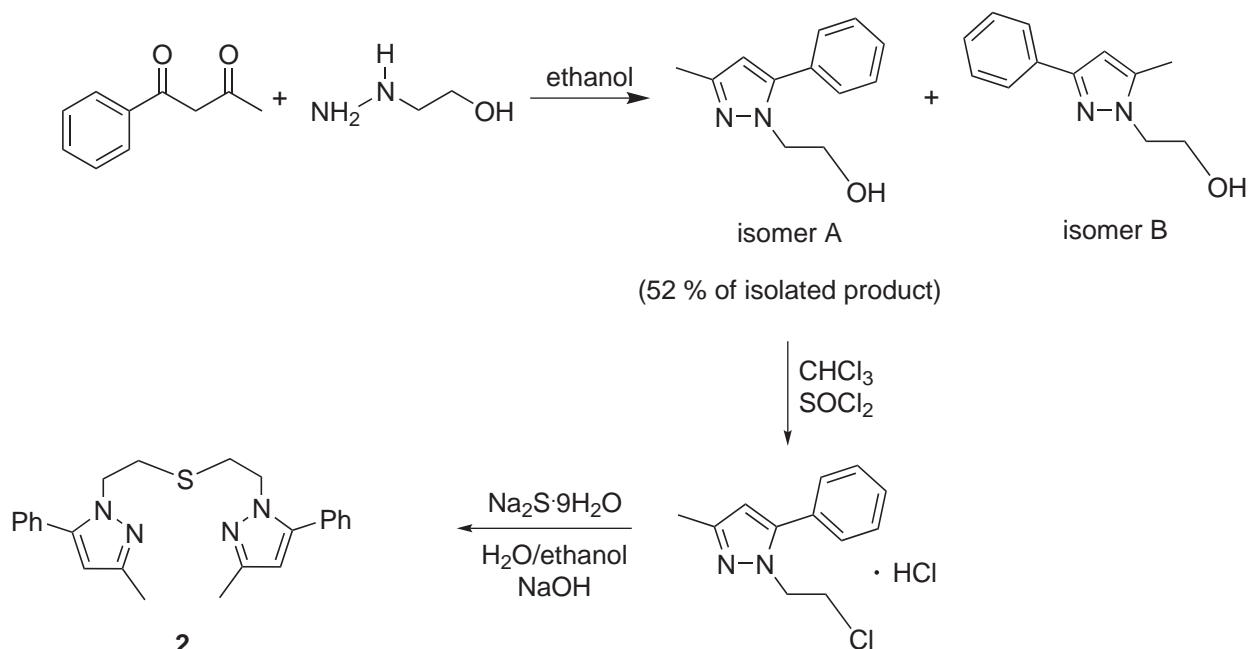
A suitable single crystal of **2** was mounted onto a glass fiber using the “oil-drop” method. Diffraction data

were collected at 100 K using an APEXII Bruker-AXS diffractometer with graphite-monochromatized Mo-K<sub>α</sub> radiation ( $\lambda = 0.71073 \text{ \AA}$ ). A combination of  $\omega$ - and  $\phi$ -scans was carried out to obtain at least a unique data set. The structure was solved by direct methods using the SIR97 program,<sup>11</sup> and then refined with full-matrix least-square methods based on F<sup>2</sup> (SHELX-97)<sup>12</sup> with the aid of the WINGX program.<sup>13</sup> Many hydrogen atoms could be found from the Fourier difference map. Carbon-bound hydrogen atoms were placed at calculated positions and forced to ride on the attached carbon atom. The hydrogen atom contributions were calculated but not refined. All non-hydrogen atoms were refined with anisotropic displacement parameters.

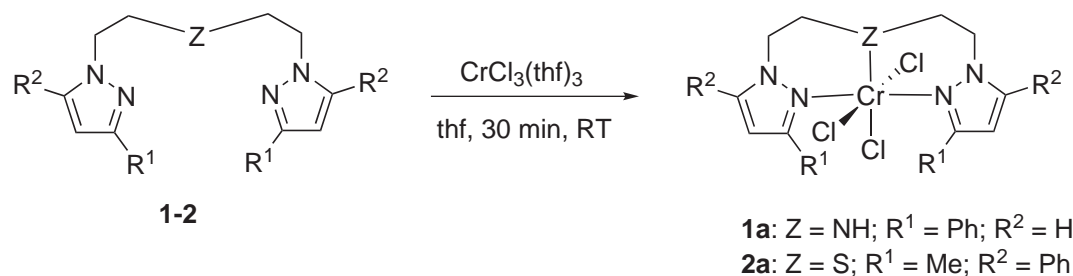
## Results and Discussion

#### Synthesis, characterization of substituted bis(pyrazolyl)-Cr<sup>III</sup> complexes and their use in oligomerization reactions

The substituted tridentate nitrogen-bridged bis(pyrazolyl) ligand (**1**) used in this study was readily prepared in high yield through adaptation of literature procedures (see Experimental). The synthesis of tridentate ligand **2** was achieved starting from commercially available 1-phenyl-1,3-butanedione and 2-hydroxyethylhydrazine. The initial step procedure promotes the formation of two different isomers (Scheme 1) whereas the isomer A was obtained in pure form (52% yield) after workup. The identity of isomer A was established on the basis of multinuclear



Scheme 1.



Scheme 2.

nuclear magnetic resonance (NMR) and heteronuclear multiple bond correlation (HMBC) experiments (see HMBC spectra in supporting information). Chlorination of the isomer A with thionyl chloride in  $\text{CHCl}_3$  gave 1-(2-chloroethyl)-3-methyl-5-phenyl pyrazole in 77% yield. The latter compound reacted with  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$ /ethanol to give the substituted sulfur-bridged tridentate ligand (**2**) in 75% yield.

The reaction of  $[\text{CrCl}_3(\text{thf})_3]$  with 1.1 equivalent of tridentate nitrogen-, or sulfur-bridged bis(pyrazolyl) ligands (**1** and **2**) in thf at room temperature affords the corresponding  $[\text{CrCl}_3(\text{NZN})]$  complexes **1a** and **2a** (Scheme 2), which were isolated, respectively, as green or red wine-colored solids in high yields (typically 90-92%). These complexes show moderate solubility at room temperature in dichloromethane, thf and ethyl acetate, and are readily soluble in acetonitrile. Due to the paramagnetic nature of these  $[\text{CrCl}_3(\text{NZN})]$  complexes,  $^1\text{H}$  NMR spectra featured very broad resonances and proved to be uninformative. The identity of **1a** and **2a** was established on the basis of elemental analysis.

The ethylene oligomerization behavior of chromium complexes **1a** and **2a** has been evaluated using optimized conditions recently established for related 6-membered chelate chromium catalysts,<sup>7</sup> *i.e.*, toluene as solvent at 80 °C under 20 bar of ethylene and Al:Cr ratios of 300. Representative results are summarized in Table 1.

When activated with MAO, all catalytic systems proved to be active for oligomerization of ethylene. A moderate turnover frequency (TOF) of 22,900 mol(ethylene) mol(Cr)<sup>-1</sup> h<sup>-1</sup> was obtained with **1a** while the catalyst system derived from **2a**, which contains a sulfur-bridged ligand bearing methyl and phenyl substituents at the 3- and 5-positions of the pyrazolyl rings, gave a high TOF of 36,400 mol(ethylene) mol(Cr)<sup>-1</sup> h<sup>-1</sup>. These results are consistent with those observed in 6-membered ring nickel and chromium catalysts bearing an analogous tridentate sulfur-bridged ligand.<sup>4,6</sup>

The chromium complexes **1a** and **2a** produce oligomers ranging from C<sub>4</sub> to C<sub>14+</sub> with a high selectivity for  $\alpha$ -olefins attaining 67.71 and 73.47%, respectively. Both catalyst

systems show similar behaviour for production of  $\alpha$ -olefins as shown in Figure 1. This indicates that the central donor atoms and also the pyrazolyl R<sup>1</sup> and R<sup>2</sup> substituents play no significant influence in this series on product distribution. However, enriched fractions in  $\alpha$ -C<sub>4</sub> (16.2 wt.%),  $\alpha$ -C<sub>6</sub> (18.1 wt.%) and  $\alpha$ -C<sub>12</sub> (9.7 wt.%) are obtained using the catalyst system derived from **2a**. This result is consistent with those ones found for MAO-activated nickel and chromium complexes bearing analogous tridentate ligands.<sup>4,6</sup>

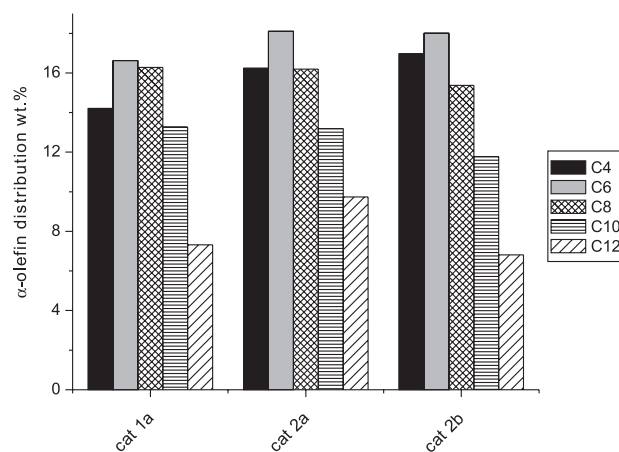


Figure 1. Selectivity of **1a**, **2a** and **2b**/MAO oligomerization systems for  $\alpha$ -olefins (80 °C, 20 bar, MAO-to-Cr = 300).

It is interesting to note that the presence of phenyl groups at 3-position of the pyrazolyl rings in  $\text{CrCl}_3\{\text{bis}[2-(3\text{-diphenyl-1-pyrazolyl)ethyl}]\text{amine}\}$  (**1a**) determines a dramatic effect on activity and selectivity as compared to the similar complex  $\text{CrCl}_3\{\text{bis}[2-(3,5\text{-dimethyl-1-pyrazolyl)ethyl}]\text{amine}\}$  (**1b**)<sup>6</sup> (compare entries 1 and 3, Table 1). For instance, catalyst **1a** (22,900 mol(ethylene) mol(Cr)<sup>-1</sup> h<sup>-1</sup>) is 2.2 times more active than **1b** (10,400 mol(ethylene) mol(Cr)<sup>-1</sup> h<sup>-1</sup>). Furthermore, the amount of PE produced by **1a** represents only 3.2% of the total amount of products (oligomers + PE), while the use of **1b** leads exclusively the formation of polyethylene (PE).

On the other hand, the introduction of relatively bulky phenyl substituents at 5-position of the pyrazolyl rings in **2a**



**Table 1.** Ethylene oligomerization with complexes **1a-b** and **2a-b**<sup>a</sup>

Entry	Cat.	TOF <sup>b</sup> (10 <sup>3</sup> )	Oligomer distribution (wt.%) <sup>c</sup>					C <sub>14+</sub>	Oligomers (wt.%)	PE (wt.%)	Total product (mg)
			C <sub>4</sub> (α-C <sub>4</sub> )	C <sub>6</sub> (α-C <sub>6</sub> )	C <sub>8</sub> (α-C <sub>8</sub> )	C <sub>10</sub> (α-C <sub>10</sub> )	C <sub>12</sub> (α-C <sub>12</sub> )				
1	<b>1a</b>	22.9	15.2 (93.5)	17.9 (92.9)	18.5 (88.0)	14.9 (89.1)	8.2 (89.3)	19.3	94.0	6.0	1600
2	<b>2a</b>	36.4	16.9 (96.1)	19.2 (94.3)	17.6 (92.0)	14.3 (92.3)	11.7 (83.3)	18.4	98.1	1.9	2600
3 <sup>d</sup>	<b>1b</b>	10.4	-	-	-	-	-	-	-	100	2200
4 <sup>d</sup>	<b>2b</b>	66.2	18.0 (94.3)	18.8 (95.8)	16.4 (93.7)	12.8 (92.0)	10.4 (65.5)	8.9	85.3	14.7	5400

<sup>a</sup> Reaction conditions: toluene = 40 mL, oligomerization time = 15 min, p(ethylene) = 20 bar, T = 80 °C, [Cr] = 10 μmol, [Al]/[Cr] = 300. The results shown are representative of at least duplicated experiments. <sup>b</sup> mol of ethylene converted (mol of Cr)<sup>-1</sup> h<sup>-1</sup> as determined by quantitative GLC. <sup>c</sup> C<sub>n</sub>, percentage of olefin with *n* carbon atoms in oligomers; α-C<sub>n</sub>, percentage of terminal alkene in the C<sub>n</sub> fraction, as determined by quantitative GLC. <sup>d</sup> reference 6.

as compared to methyl groups in CrCl<sub>3</sub>{bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]sulfide} (**2b**)<sup>6</sup> leads to a noticeable decrease in catalytic activity in (NSN)Cr<sup>III</sup> systems (compare entries 2 and 4, Table 1) which can be associated to the electronic effects of these phenyl groups to the chromium metal center. The selectivity for C<sub>4</sub>-C<sub>12</sub> fractions remains almost unchanged (compare entries 2 and 4).

*Synthesis and structural characterization of the tetrametallic nickel complex 4 derived from NiCl<sub>2</sub>{bis[2-(3,5-dimethyl-1-pyrazolyl)methyl]benzylamine} (1)*

The 5-membered-ring nickel catalyst NiCl<sub>2</sub>{bis[2-(3,5-dimethyl-1-pyrazolyl)methyl]benzylamine} (**3**) was readily prepared in high yield *via* literature procedures.<sup>8</sup> Recrystallization of **3** in methylene chloride at room temperature afforded a few green crystals of an unexpected tetrametallic nickel complex [(L)(μ<sub>3</sub>-Cl)NiCl]<sub>4</sub> (**4**, L = 1-anilinomethyl-3,5-dimethylpyrazole) (*ca.* 8% yield) (Scheme 3), and a large amount of unidentified products. The formation of tetranuclear nickel complex **4** can be rationalized in terms of a ligand redistribution/disproportionation reaction.

Crystal data and structure refinement for **4** are summarized in Table 2, and selected bond distances and angles are listed in Table 3. The molecular geometry and atom-labeling scheme are shown in Figure 2. Complex **4** has a cubane-type {Ni<sub>4</sub>(μ<sub>3</sub>-Cl)<sub>4</sub>} core with four Ni<sup>II</sup> and four chloro ligands occupying alternate vertices. Each

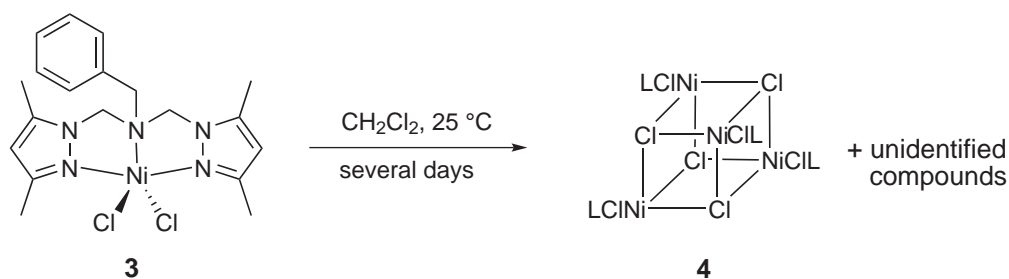
nickel center is crystallographically distinct and presents a slightly different distorted octahedral environment. The Ni<sup>II</sup> atoms are bound to three μ<sub>3</sub>-chloro ligands, a chelating anilinomethyl-3,5-dimethylpyrazole and one terminal chloride.

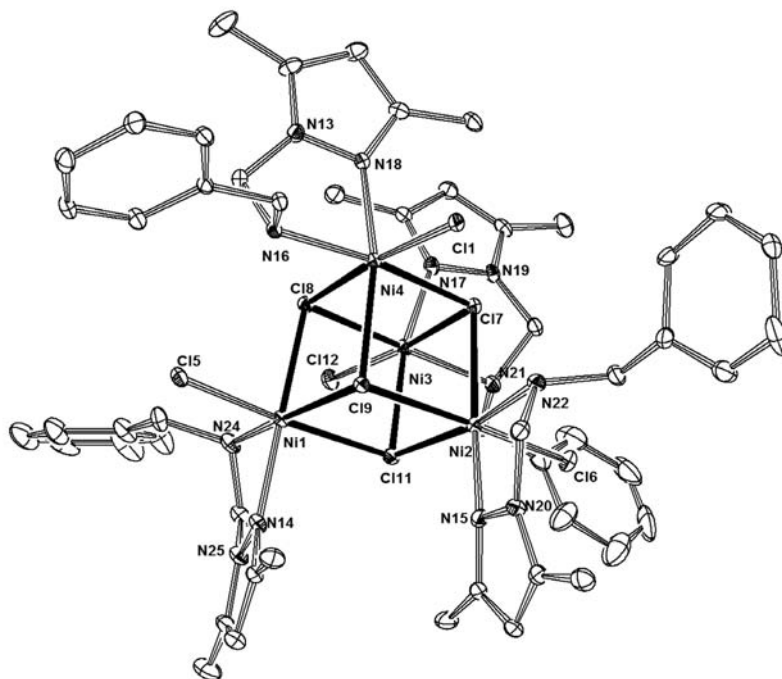
The Ni-N<sub>pyrazolyl</sub> distances lie in the range of 2.033-2.045 Å, while Ni-N<sub>anilino</sub> bonds are 2.105-2.124 Å. The μ<sub>3</sub>-chloro ligand in the coordination sphere of each nickel atom yields a Ni-Cl bonding distance lying in the range of 2.447-2.506 Å, while the Ni-Cl<sub>terminal</sub> bonds fall in the range of 2.3449(8)-2.3799(8) Å. All these values are in agreement with those disclosed in the literature.<sup>15</sup>

The Cl-Ni-Cl angles involving the bridging chlorine ligands are systematically lower than 90°, ranging from 82.73(2) to 86.4(2)°. On the other hand, Ni-Cl-Ni angles are significantly higher, typically in the range of 93.17-97.40°. Geometric constraints imposed by the cubane core reduce Ni-Cl-Ni angles from the ideal tetrahedral value of 109.5°, a reduction often associated with ferromagnetic coupling of nickel centers.<sup>16</sup> The distances varying from 3.588 to 3.726 Å between the nickel atoms in the cluster are beyond significant interactions.

*Effect of the auxiliary ligand on catalyst activity and selectivity using nickel(II) complexes bearing chelating NZN ligands*

Previous studies on nickel-based catalysts have demonstrated that the incorporation of PPh<sub>3</sub> into catalytic

**Scheme 3.**



**Figure 2.** Molecular structure of  $[(L)(\mu_3\text{-Cl})\text{NiCl}]_4$  (**4**). Thermal ellipsoids are drawn at the 30% probability level; hydrogen atoms are omitted for clarity.

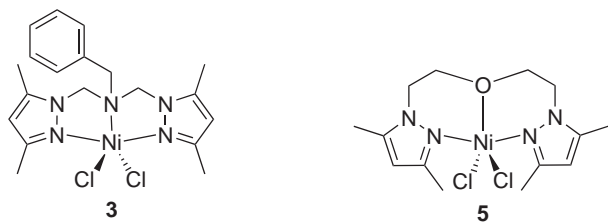
**Table 2.** Crystal data and structure refinement for **4**

Empirical formula	$\text{C}_{52}\text{H}_{68}\text{Cl}_8\text{N}_{12}\text{Ni}_4$
Formula weight / $\text{g mol}^{-1}$	1379.62
Temperature / K	100 (2)
Wavelength / $\text{\AA}$	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
$a$ / $\text{\AA}$	13.5355 (18)
$b$ / $\text{\AA}$	13.9534 (19)
$c$ / $\text{\AA}$	19.208 (2)
$\alpha$ / $^\circ$	82.961(6)
$\beta$ / $^\circ$	82.944(7)
$\gamma$ / $^\circ$	77.142(6)
Volume / $\text{\AA}^3$	3493.0(8)
$Z$	2
calculated density / $\text{g cm}^{-3}$	1.312
Absorption coefficient / $\text{mm}^{-1}$	1.407
$F(000)$	1424
Crystal size / mm	0.37×0.21×0.08
Theta range for data collection / $^\circ$	3.01 to 27.48
Index ranges	$-17 \leq h \leq 17$ , $-18 \leq k \leq 18$ , $-24 \leq l \leq 24$
Reflections collected / unique	50765 / 15824 [R(int) = 0.0461]
Completeness to $\theta$ max	0.988
Data / restraints / parameters	15824 / 0 / 733
Goodness-of-fit on $F^2$	1.038
Final R indices [ $I > 2 \sigma(I)$ ]	$R_1 = 0.0427$ , $wR_2 = 0.0944$
R indices (all data)	$R_1 = 0.0685$ , $wR_2 = 0.1021$
Largest diff. peak and hole / $e \text{\AA}^{-3}$	0.856 and $-0.431$

systems leads to higher activity and longer catalyst lifetime.<sup>17</sup> We were curious whether such effects would apply to our nickel catalyst systems. For verifying that, we have chosen the 5- and 6-membered ring nickel complexes  $\text{NiCl}_2\{\text{bis}[2\text{-}(3,5\text{-dimethyl-1-pyrazolyl)methyl]benzylamine}\}$  (**3**)<sup>8</sup> and  $\text{NiCl}_2\{\text{bis}[2\text{-}(3,5\text{-dimethyl-1-pyrazolyl)ethyl}]ether\}$  (**5**)<sup>7</sup> (Figure 3).

**Table 3.** Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for **4**

Ni(1)-N(14)	2.033(2)	Ni(3)-N(17)	2.037(2)
Ni(1)-N(24)	2.114(2)	Ni(3)-N(21)	2.105(2)
Ni(1)-Cl(5)	2.3799(8)	Ni(3)-Cl(12)	2.3449(8)
Ni(1)-Cl(8)	2.4471(7)	Ni(3)-Cl(11)	2.4508(7)
Ni(1)-Cl(9)	2.4683(7)	Ni(3)-Cl(8)	2.4897(8)
Ni(1)-Cl(11)	2.4950(8)	Ni(3)-Cl(7)	2.4926(8)
Ni(2)-N(15)	2.045(2)	Ni(4)-N(18)	2.034(2)
Ni(2)-N(22)	2.124(2)	Ni(4)-N(16)	2.123(2)
Ni(2)-Cl(6)	2.3530(8)	Ni(4)-Cl(1)	2.3457(8)
Ni(2)-Cl(11)	2.4640(8)	Ni(4)-Cl(9)	2.4636(7)
Ni(2)-Cl(7)	2.4676(7)	Ni(4)-Cl(7)	2.4661(8)
Ni(2)-Cl(9)	2.5057(8)		
Ni(4)-Cl(7)-Ni(2)	94.05(3)	Ni(4)-Cl(9)-Ni(1)	93.98(2)
Ni(4)-Cl(7)-Ni(3)	97.41(3)	Ni(4)-Cl(9)-Ni(2)	93.17(3)
Ni(2)-Cl(7)-Ni(3)	92.67(3)	Ni(1)-Cl(9)-Ni(2)	97.01(3)
Ni(1)-Cl(8)-Ni(4)	93.88(2)	Ni(3)-Cl(11)-Ni(2)	93.78(3)
Ni(1)-Cl(8)-Ni(3)	93.44(2)	Ni(3)-Cl(11)-Ni(1)	93.21(2)
Ni(4)-Cl(8)-Ni(3)	96.89(3)	Ni(2)-Cl(11)-Ni(1)	97.40(3)



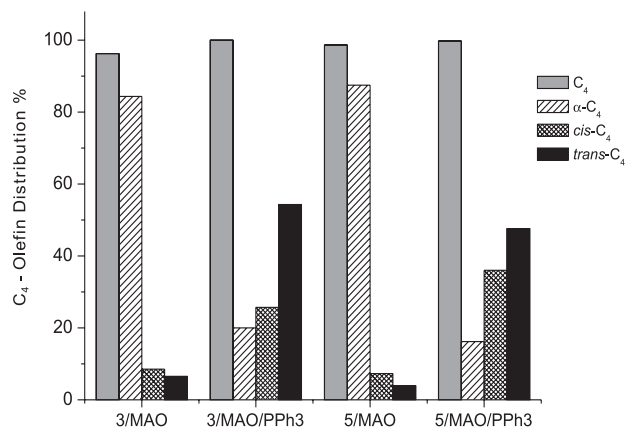
**Figure 3.** Nickel complexes  $\text{NiCl}_2\{\text{bis}[2-(3,5\text{-dimethyl-1-pyrazolyl)methyl]benzylamine}\}$  (**3**), and  $\text{NiCl}_2\{\text{bis}[2-(3,5\text{-dimethyl-1-pyrazolyl)ethyl]ether}\}$  (**5**) used in ethylene dimerization reactions in presence of  $\text{PPh}_3$ .

The ethylene oligomerization behavior of complexes **3** and **5** was investigated in toluene with MAO activation. Representative results are summarized in Table 4. Under optimized conditions (toluene as solvent at 30 °C under 20 bar of ethylene, Al:Ni ratios of 250) the nickel catalysts **3** and **5** are active for dimerization of ethylene in the absence of  $\text{PPh}_3$  (**3**, TOF = 11,300 mol(ethylene) mol(Ni)<sup>-1</sup> h<sup>-1</sup>; **5**, TOF = 7,100 mol(ethylene) mol(Ni)<sup>-1</sup> h<sup>-1</sup>) with selectivity for 1-butene attaining 84.4 and 87.5%, respectively (Table 4, entries 1 and 4).

The oligomerization reactions performed in the presence of 1 equiv of  $\text{PPh}_3$  resulted in much higher TOFs mainly in the case of catalyst system **5**/MAO (compare entries 4 and 6). One reasonable explanation for this phenomenon can be associated to the partial substitution of the tridentate NZN ligand by  $\text{PPh}_3$  to afford a bidentate NZ/N-Ni- $\text{PPh}_3$  complex. On the other hand, the fact that the active nickel species are coordinated with auxiliary  $\text{PPh}_3$  on the vacant coordination sites when lacking ethylene monomers should

be also considered. However, in both cases, the presence of  $\text{PPh}_3$  promotes the formation of more stable catalytic species and at the same time prevents deactivation by impurities of active reactants in the catalytic species.<sup>18</sup>

The presence of this auxiliary ligand in the oligomerization medium plays no significant influence on the total  $\text{C}_4$  production with selectivities varying from 99.8 to 100% (compare entries 1/2, and 4/6). On the other hand, the  $\text{PPh}_3$  ligand has a strong impact in the selectivity towards the production of  $\alpha$ -olefins, decreasing substantially the amount of 1-butene (16.2-20.0%) with a concomitant increase of internal olefins fractions (*cis*- $\text{C}_4$ : 25.7-36.0%; *trans*- $\text{C}_4$  fractions: 54.3-47.6%) as can be better visualized in Figure 4. We may reasonably assume that the favored formation of butenes-2 rather than butene-1



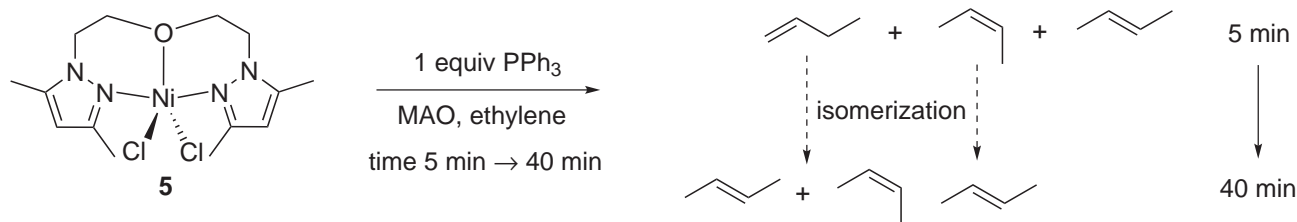
**Figure 4.** Influence of auxiliary ligand ( $\text{PPh}_3$ ) on selectivity for butenes (30 °C, 20 bar,  $[\text{Al}]/[\text{Ni}] = 250$ ,  $[\text{Ni}]/[\text{PPh}_3] = 1$ ).

**Table 4.** Ethylene oligomerization with nickel complexes **3** and **5**<sup>a</sup>

Entry	Cat. (μmol)	$\text{PPh}_3$ (equiv.)	Oligomers (mg)	TOF <sup>b</sup> (10 <sup>3</sup> )	Selectivity (%) <sup>c</sup>				
					C <sub>4</sub>	C <sub>4</sub> (α-C <sub>4</sub> )	C <sub>4</sub> ( <i>cis</i> -C <sub>4</sub> )	C <sub>4</sub> ( <i>trans</i> -C <sub>4</sub> )	C <sub>6</sub> (α-C <sub>6</sub> )
1	3 (10.0)	-	1054	11.3	96.3	84.4	8.5	6.5	3.7
2	3 (10.0)	1.0	3379	36.4	100	20.0	25.7	54.3	-
3	3 (3.0)	1.0	1301	45.1	100	61.0	16.2	22.8	-
4	5 (10.0)	-	680	7.1	98.7	87.5	7.3	3.9	1.3
5	5 (10.0)	0.5	7770	81.4	99.3	24.1	23.7	51.6	0.7
6	5 (10.0)	1.0	12420	113.4	99.8	16.2	36.0	47.6	0.2
7	5 (3.0)	1.0	4410	154.2	100.0	24.4	27.1	48.5	-
8	5 (10.0)	10.0	7950	83.5	99.7	31.5	27.9	40.5	0.3
9 <sup>d</sup>	5 (10.0)	1.0	1860	77.9	99.7	41.6	20.4	37.7	0.3
10 <sup>e</sup>	5 (10.0)	1.0	8280	43.3	99.7	20.4	26.5	52.8	0.3
11 <sup>f</sup>	5 (10.0)	1.0	11940	125.4	100.0	32.1	43.1	24.8	-

<sup>a</sup> Reaction conditions: toluene = 40 mL, p(ethylene) = 20 bar, oligomerization time = 20 min, MAO  $[\text{Al}]/[\text{Ni}] = 250$ . The results are representative of at least duplicated experiments. <sup>b</sup> mol of ethylene converted (mol of Ni)<sup>-1</sup> h<sup>-1</sup>, as determined by quantitative GLC. <sup>c</sup> C<sub>n</sub>, amount of olefin with *n* carbon atoms in the oligomers; α-C<sub>n</sub>, amount of terminal alkene in the C<sub>n</sub> fraction, as determined by quantitative GLC. <sup>d</sup> Oligomerization time = 5 min. <sup>e</sup> Oligomerization time = 40 min. <sup>f</sup> Oligomerization reaction using DEAC  $[\text{Al}]/[\text{Ni}] = 250$ .





Scheme 4.

is a consequence of the presence of PPh<sub>3</sub> in the milieu, which would block coordination of incoming ethylene and lead to isomerisation rather than  $\beta$ -H elimination of R.

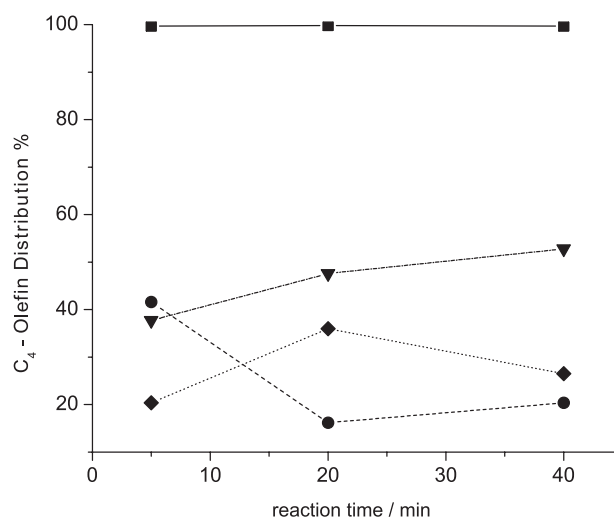
When the quantity of precatalysts **3** and **5** was decreased, very high activities were observed. For instance, with 3.0  $\mu$ mol of nickel complexes **3** and **5**, high TOFs of 45,100 mol(ethylene) mol(Ni)<sup>-1</sup> h<sup>-1</sup> and 154,200 mol(ethylene) mol(Ni)<sup>-1</sup> h<sup>-1</sup> were obtained, respectively (entries 3 and 7). This effect can be primarily associated to (i) an easier solubilization of the precatalyst in toluene solution<sup>and</sup> (ii) increase of molar ratio [ethylene]/[Ni]; however, a decrease of excessive exotherms during the oligomerization reactions, which would induce catalyst decay, cannot be ruled out.

Based on these preliminary results, complex **5** was selected for further optimization, investigating the [Ni]/[PPh<sub>3</sub>] ratio, oligomerization reaction time, and cocatalyst type. As demonstrated in Table 4, when a minor quantity of PPh<sub>3</sub> was used ([Ni]/[PPh<sub>3</sub>] = 0.5), complex **5** gave a high activity (TOF = 81,400 mol(ethylene) mol(Ni)<sup>-1</sup> h<sup>-1</sup>, entry 5), which was increased upon using 1.0 equivalent of PPh<sub>3</sub> (TOF = 113,400 mol(ethylene) mol(Ni)<sup>-1</sup> h<sup>-1</sup>, entry 6). A greater loading of PPh<sub>3</sub> (10 equivalents) led to lower activity (TOF = 83,500 mol(ethylene) mol(Ni)<sup>-1</sup> h<sup>-1</sup>, entry 8). At the same time, increasing the amount of PPh<sub>3</sub> from 0.5 to 10.0 equivalents led to slightly improved selectivities for 1-butene (24.1 to 31.5%).

The reaction time can have a significant effect on TOFs, and the selectivity. It was found that the activity at 5 min of reaction (Table 4, entry 9) was about 1.5 times lower than at 20 min (Table 4, entry 6), suggesting that this type of catalyst needs a long pre-activation time (up to 5 min) to promote the formation of a higher amount of catalytic species. Increasing the reaction time to 40 min led to a lower TOF value (43,300 mol(ethylene) mol(Ni)<sup>-1</sup> h<sup>-1</sup>, entry 10), indicating that a partial catalyst deactivation took place.

The reaction time affects significantly the selectivity for 1-butene. As can be seen in Figure 5, the selectivity for C<sub>4</sub> olefins remains high and constant over time (99.7-99.8%). However, varying the reaction time from 5 to 40 min, a larger amount of 2-butenes (from 58.1 to 79.3%) is produced in consequence of the isomerization process

(i.e., chain isomerization transfer is favored relative to chain propagation). It should be pointed out that the ability of Ni<sup>II</sup> complexes to isomerize  $\alpha$ -olefins is a well-known process.<sup>19</sup> In particular, it was found that increasing the reaction time results in higher quantity of *trans*-C<sub>4</sub> owing to the isomerization process involving 1-butene and *cis*-C<sub>4</sub> (Scheme 4).



**Figure 5.** Monitoring of selectivities in the ethylene oligomerization reaction promoted by the **5**/MAO/PPh<sub>3</sub> system ([Ni]/[PPh<sub>3</sub>] = 1.0, [MAO]/[Ni] = 250; T = 30 °C; 20 atm ethylene): ■ C<sub>4</sub> products, ● 1-butene, ◆ *cis*-2-butene, ▼ *trans*-2-butene. Hexenes, mostly 1-hexene, were also produced in 0.2-0.3% selectivity and are not shown in this figure.

Activation of nickel complex **5** with diethylaluminum-chloride (DEAC) instead of MAO resulted in a more active system (TOF 125,400 mol(ethylene) mol(Ni)<sup>-1</sup> h<sup>-1</sup>). This observation could reflect a better stabilization of active species with DEAC than with MAO, possibly thanks to the chlorine atom. At the same time, the use of DEAC led to slightly improved selectivity for 1-butene (32.1 %), with production of lower amounts of 2-butenes (67.9%).

## Conclusions

A new set of chromium(III) complexes based on tridentate ligands has been prepared and evaluated for ethylene oligomerization under MAO activation. Replacement of the

central bridging nitrogen with a sulfur donor atom affords a catalyst that exhibits higher TOF and higher selectivity for  $\alpha$ -C<sub>4</sub>,  $\alpha$ -C<sub>6</sub>, and  $\alpha$ -C<sub>8</sub>. The presence of phenyl groups at 3- or 5-position of the pyrazolyl rings determines a pronounced effect on activity and selectivity owing to the steric/electronic effects of these phenyl groups on the chromium metal center.

In parallel, the use of triphenylphosphine (PPh<sub>3</sub>) in the oligomerization reactions using nickel catalysts (**3** and **5**) resulted in much higher TOFs. However, the presence of this auxiliary ligand has a strong impact in the selectivity towards the production of  $\alpha$ -olefins, decreasing substantially the amount of 1-butene with a concomitant increase of the 2-butene fractions. Under optimized conditions ([Ni]/[PPh<sub>3</sub>] = 1.0, [Ni] = 3.0  $\mu$ mol, 30 °C, 20 bar ethylene, MAO-to-Ni = 250, oligomerization time = 20 min), pre-catalyst **5** leads to TOF = 154.2  $\times 10^3$  mol(ethylene) mol(Ni)<sup>-1</sup> h<sup>-1</sup> and selectivities for C<sub>4</sub> and  $\alpha$ -C<sub>4</sub> are 100.0 and 24.4%, respectively.

## Supplementary Information

CCDC 746569 contains the supplementary crystallographic data for **4**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk). Heteronuclear multiple bond correlation (HMBC) data for 1-(2-hydroxyethyl)-3-methyl-5-phenylpyrazole (isomer A) are available free of charge at <http://jbc.sbj.org.br>, as PDF file.

## Acknowledgments

This research was financially supported by CNPq, Petrobrás and INCT-Catálise. L. L. de Oliveira, R. Campadelli, A. L. Bergamo and A. H. D. P. dos Santos gratefully acknowledge CAPES, CNPq and FAPERGS for fellowships. The X-ray diffraction analysis of **4** was performed by Thierry Roisnel at the Laboratoire de Chimie du Solide et Inorganique Moléculaire, Institut de Chimie, Université de Rennes.

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Received: September 24, 2009

Web Release Date: April 22, 2010

## Substituted Tridentate Pyrazolyl Ligands for Chromium and Nickel-Catalyzed Ethylene Oligomerization Reactions. Effect of Auxiliary Ligand on Activity and Selectivity

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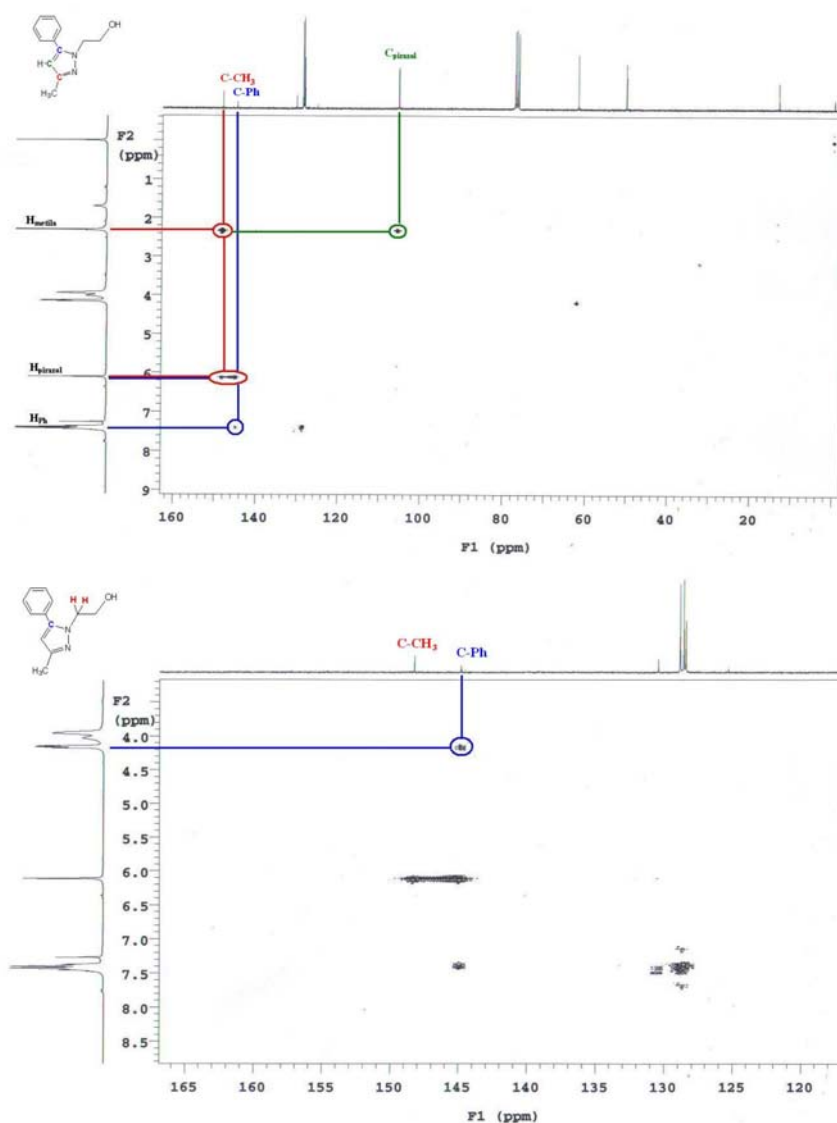


Figura S1. HMBC spectra of 1-(2-hydroxyethyl)-3-methyl-5-phenylpyrazole (isomer A).

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