



## Highly selective nickel catalysts for ethylene oligomerization based on tridentate pyrazolyl ligands

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### ABSTRACT

A series of new nickel complexes  $\text{NiCl}_2(\text{L})$  based on tridentate NZN ligands (**1**, L = bis[2-(3,5-dimethyl-pyrazolyl)methyl]benzylamine; **2**, L = bis[2-(3,5-dimethyl-1-pyrazolyl)methyl]butylamine; **3**, L = bis[2-(3,5-dimethyl-1-pyrazolyl)methyl]sulfide; **4**, L = bis[2-(3-phenyl-1-pyrazolyl)methyl]sulfide)) has been prepared and characterized by elemental analysis. Upon activation with methylaluminumoxane (MAO) or diethylaluminum chloride (DEAC), these new pre-catalysts show high activity in ethylene oligomerization (TOF =  $1.7\text{--}104.5 \times 10^3 \text{ mol(ethylene)(mol(Ni))}^{-1} \text{ h}^{-1}$ ), giving predominantly 1-butene (70–94% yield). The catalytic performance is substantially affected by the co-catalyst type and ligand environment, especially the bridge donor atom. Under optimized conditions ( $[\text{Ni}] = 10 \mu\text{mol}$ ,  $30^\circ\text{C}$ , 20 bar ethylene, MAO-to-Ni = 250), pre-catalyst **3** leads to TOF =  $104.5 \times 10^3 \text{ h}^{-1}$  and 70% selectivity for 1-butene.

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### 1. Introduction

Olefin oligomerization is a major industrial process [1]. The commercial oligomerization of ethylene is predominately carried out using transition-metal catalysts that produce a broad distribution of linear  $\alpha$ -olefins (LAOs) which are used as comonomers in the polymerization of ethylene to give linear low-density polyethylene (LLDPE), and in the preparation of a variety of economically important compounds, e.g. detergents, synthetic lubricants, and plasticiser alcohols. Many efforts are still devoted to the development of highly selective ethylene oligomerization catalysts, and among classes of catalysts used for production of  $\alpha$ -olefins, nickel complexes are the most frequently studied. While a number of selective ethylene dimerization catalysts based on tetracoordinated nickel complexes have been extensively studied [2], just a few examples of valuable pentacoordinated Ni(II) catalyst precursors have been disclosed in the literature [3]. We recently communicated first results in this regard, whereby a number of pentacoordinated Ni(II) complexes based on tridentate nitrogen- or oxygen-bridged bis(pyrazolyl) ligands (NZN) forming 6-membered chelate rings proved to be highly selective and efficient pre-catalysts for ethylene dimer-

ization in the presence of methylaluminumoxane (MAO) [4]. For instance, up to 92% selectivity for 1-butene, combined with a TOF of  $60.0 \times 10^3 \text{ mol(ethylene)(mol(Ni))}^{-1} \text{ h}^{-1}$ , has been obtained under moderate conditions ( $30^\circ\text{C}$ , 40 bar, MAO-to-Ni = 250) using  $\text{NiCl}_2\{\text{bis}[2-(5\text{-phenyl-pyrazolyl})\text{ethyl}]\text{ether}\}$  as the catalyst precursor.

Herein, we report the synthesis and characterization of a new series of Ni(II) complexes bearing 5-membered chelating NZN ligands (Z = N, S) which, in association with alkylaluminum (MAO or DEAC), afford active catalysts for selective dimerization of ethylene to 1-butene. The aim of this study was to investigate mainly the effect of the ligand chelate rings size (decrease from 6- to 5-membered) on activity and selectivity towards 1-butene. We also show the effect of the central donor atom, pyrazolyl substituents and alkylaluminum co-catalyst on turnover frequency (TOF), selectivity for  $\alpha$ -olefins, and product distributions.

### 2. Experimental

#### 2.1. General procedures

All manipulations were performed using standard vacuum line and Schlenk techniques under a purified argon atmosphere.  $\text{Et}_2\text{O}$ , THF, and toluene were distilled from sodium-benzophenone ketyl under argon and degassed by freeze-thaw-vacuum cycles prior to use.  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (Aldrich) was used as received. 1-(2-

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Chloromethyl)-3,5-dimethylpyrazole hydrochloride [5] and known ligands bis[2-(3,5-dimethyl-pyrazolyl)methyl]benzylamine (**L1**) and bis[2-(3,5-dimethyl-pyrazolyl)methyl]butylamine (**L2**) were prepared by following literature procedures [6]. 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) and diethylaluminum chloride (DEAC) (Aldrich, 1.8 M, 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.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded on a Varian Inova 300 spectrometer operating at 25 °C. Chemical shifts are reported in ppm vs.  $\text{SiMe}_4$  and were determined by reference to the residual solvent peaks. Infrared spectra were performed on a Bomem B-102 spectrometer in KBr pellets or neat. High-resolution mass spectra of Ni(II) complexes were obtained by ESI in the positive mode (6 keV) in  $\text{CH}_3\text{CN}$  or  $\text{CHCl}_3/\text{CH}_3\text{CN}$  (95:5) solutions using a Micromass Zab-Spec TOF 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  $\mu\text{m}$ ) operating at 36 °C for 15 min followed by heating at 5 °C  $\text{min}^{-1}$  until 250 °C; cyclohexane was used as internal standard.

## 2.2. Synthesis and characterization of tridentate pyrazolyl ligands

### 2.2.1. 1-(2-Hydroxymethyl)-3-phenylpyrazole

A solid mixture of 3-phenylpyrazole (6.34 g, 44.0 mmol) and paraformaldehyde (1.32 g, 44.0 mmol) was heated in a closed vessel to 120 °C for 48 h. The desired compound was collected as a white solid (0.54 g, 82%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 298 K, 300 MHz):  $\delta$  4.68 (1H, br), 5.61 (2H, s), 6.61 (1H, d,  $J=2.27$  Hz, 4-CH Pz), 7.40–7.81 (phenyl 5H, and 5-CH Pz, m).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 298 K, 75 MHz):  $\delta$  73.68 ( $\text{CH}_2$ ), 103.94 (Pz 4-C), 125.92 (phenyl 2-C), 128.09 (phenyl 4-C), 128.64 (phenyl 3-C), 131.35 (Pz 5-C), 132.58 (phenyl 1-C), 152.93 (Pz 3-C).

### 2.2.2. 1-(2-Chloromethyl)-5-phenylpyrazole hydrochloride

A solution of thionyl chloride (0.43 mL, 5.98 mmol) in  $\text{CHCl}_3$  (15 mL) was added dropwise to a solution of 1-(2-hydroxymethyl)-3-phenylpyrazole (0.51 g, 2.93 mmol) in  $\text{CHCl}_3$  (25 mL) at 0 °C and the resulting solution was refluxed for 4 h. The solution was evaporated under reduced pressure, and the solid residue was dissolved in ethanol (10 mL). After diethyl ether (50 mL) had been layered over the ethanol solution, the mixture was allowed to stand for 3 days. The resulting white crystals were filtered, washed with diethyl ether, and dried in air (0.54 g, 82%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 298 K, 300 MHz):  $\delta$  (ppm) 5.85 (2H, s), 6.59 (1H, d,  $J=2.24$  Hz, 4-CH Pz), 7.31–7.76 (phenyl 5H and 5-CH Pz, m).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 298 K, 75 MHz):  $\delta$  58.15 ( $\text{CH}_2$ ), 105.33 (Pz 4-C), 125.62 (phenyl 2-C), 128.12 (phenyl 4-C), 128.41 (phenyl 3-C), 131.74 (phenyl 1-C), 132.62 (Pz 5-C), 153.40 (Pz 3-C).

### 2.2.3. Bis[2-(3,5-dimethyl-pyrazolyl)methyl]sulfide (**L3**)

A solution of 1-(2-chloromethyl)-3,5-dimethylpyrazole (4.93 g, 34.1 mmol) and sodium hydroxide (1.36 g, 34.1 mmol) in 50% aqueous ethanol (100 mL) was treated with  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  (5.13 g, 21.4 mmol). The solution was refluxed for 3 h, cooled to room temperature, and evaporated at reduced pressure. Water was added to the residue, the product was extracted with dichloromethane, and the organic extracts were dried over  $\text{Na}_2\text{SO}_4$ . An analytically pure product was obtained as a colorless oil (1.61 g, 38%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 298 K, 300 MHz):  $\delta$  2.24 (6H, s), 2.26 (6H, s), 5.30 (4H, s), 5.85 (2H, d,  $J=2.25$  Hz, CH Pz).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 298 K, 75 MHz):  $\delta$  10.40

( $\text{CH}_3$ ), 13.50 ( $\text{CH}_3$ ), 44.50 ( $\text{SCH}_2$ ), 105.30 (Pz 4-C), 140.70 (Pz 5-C), 147.70 (Pz 3-C). IR data (neat,  $\text{cm}^{-1}$ ): 3233 (s), 2954 (m), 2917 (m), 2896 (w), 1612 (m), 1538 (m), 1477 (s), 1445 (w), 1378 (m), 1295 (m), 1257 (w), 1181 (m), 1101 (m), 1012 (s), 986 (m), 876 (m), 785 (m), 708 (m).

### 2.2.4. Bis[2-(3-phenylpyrazolyl)methyl]sulfide (**L4**)

This product was prepared by following a procedure similar to what was described above for **L3**, starting from 1-(2-chloromethyl)-5-phenylpyrazole (6.55 g, 34.1 mmol), sodium hydroxide (1.36 g, 34.1 mmol) in 50% aqueous ethanol (100 mL), and  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  (5.13 g, 21.4 mmol). After workup, ligand **L4** was recovered as a pale yellow solid (1.59 g, 27%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 298 K, 300 MHz):  $\delta$  5.26 (4H, s), 6.58 (2H, d,  $J=2.25$  Hz, Pz CH), 7.19–7.79 (12H, m), 7.75 (4H, m).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 298 K, 75 MHz):  $\delta$  47.00 ( $\text{SCH}_2$ ), 105.00 (Pz 4-C), 130.70 (Pz 5-C), 127.50 (phenyl 2-C), 128.70 (phenyl 4-C), 129.20 (phenyl 3-C), 133.00 (phenyl 1-C), 152.00 (Pz 3-C). IR (neat,  $\text{cm}^{-1}$ ) 3209 (s), 3139 (s), 3062 (s), 3035 (m), 2973 (m), 2889 (m), 1955 (w), 1893 (w), 1814 (w), 1760 (w), 1604 (m), 1581 (w), 1550 (w), 1529 (m), 1502 (s), 1458 (m), 1406 (m), 1352 (m), 1301 (m), 1228 (s), 1159 (s), 1076 (m), 1049 (m), 1027 (m), 1000 (m), 946 (m), 919 (m), 765 (s), 698 (s), 613 (m).

## 2.3. Synthesis and characterization of bis(pyrazolyl)-Ni(II) complexes

### 2.3.1. $\text{NiCl}_2\{\text{bis}[2-(3,5\text{-dimethylpyrazolyl})\text{methyl}]\text{benzylamine}\}$ (**1**)

To a solution of  $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$  (130 mg, 0.56 mmol) in THF (10 mL) was added a solution of bis[2-(3,5-dimethylpyrazolyl)methyl]benzylamine (200 mg, 0.62 mmol) in THF (10 mL), and the resulting solution was stirred for 24 h at room temperature. Volatiles were removed under reduced pressure, and the resulting green solid residue was washed with  $\text{Et}_2\text{O}$  ( $2 \times 10$  mL) to afford **1** as a green solid (189 mg, 75%). Anal. calcd. for  $\text{C}_{19}\text{H}_{25}\text{N}_5\text{Cl}_2\text{Ni}\cdot 2\text{H}_2\text{O}$ : C, 46.66; H, 5.98; N, 14.32. Found: C, 46.51; H, 5.90; N, 14.07. HRMS-ESI [ $\text{M}-\text{Cl}$ ] $^+$ , calcd. for  $\text{C}_{19}\text{H}_{25}\text{N}_5\text{Cl}^{58}\text{Ni}$ : 416.11520; found: 416.1144. IR data (KBr pellet,  $\text{cm}^{-1}$ ): 3462 (sbr), 3253 (s), 3207 (s), 3168 (s), 3026 (w), 2998 (w), 2971 (w), 2917 (w), 2972 (w), 2918 (w), 1628 (m), 1607 (m), 1557 (s), 1489 (m), 1464 (s), 1421 (m), 1394 (m), 1382 (w), 1365 (w), 1299 (m), 1284 (m), 1267 (m), 1051 (s), 979 (m), 746 (s), 707 (s), 624 (m).

### 2.3.2. $\text{NiCl}_2\{\text{bis}[2-(3,5\text{-dimethylpyrazolyl})\text{methyl}]\text{butylamine}\}$ (**2**)

This compound was prepared according to the method described for **1** using  $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$  (80 mg, 0.35 mmol) and bis[2-(3,5-dimethylpyrazolyl)methyl]butylamine (110 mg, 0.38 mmol). Complex **2** was obtained as a light green solid (122 mg, 91%). Anal. calcd. for  $\text{C}_{16}\text{H}_{27}\text{N}_5\text{Cl}_2\text{Ni}\cdot 2\text{H}_2\text{O}$ : C, 42.23; H, 6.87; N, 15.39. Found: C, 42.04; H, 6.64; N, 14.97. HRMS-ESI [ $\text{M}-\text{Cl}$ ] $^+$ , calcd. for  $\text{C}_{16}\text{H}_{27}\text{N}_5\text{Cl}^{58}\text{Ni}$ : 382.13085; found: 382.1309. IR data (KBr pellet,  $\text{cm}^{-1}$ ): 3338 (sh), 3220 (s), 2962 (m), 2935 (w), 2877 (w), 1639 (m), 1556 (m), 1467 (s), 1421 (w), 1394 (m), 1303 (m), 1263 (w), 1182 (m), 1118 (w), 1056 (s), 973 (m), 889 (w), 788 (m), 713 (w).

### 2.3.3. $\text{NiCl}_2\{\text{bis}[2-(3,5\text{-dimethylpyrazolyl})\text{methyl}]\text{sulfide}\}$ (**3**)

This compound was prepared according to the method described for **1** using  $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$  (50 mg, 0.21 mmol) and bis[2-(3,5-dimethylpyrazolyl)methyl]sulfide (55 mg, 0.22 mmol). Complex **3** was obtained as a light green solid (140 mg, 65%). Anal. calcd. for  $\text{C}_{12}\text{H}_{18}\text{N}_4\text{Cl}_2\text{NiS}\cdot 2\text{H}_2\text{O}$ : C, 34.65; H, 5.33; N, 13.47. Found: C, 34.51; H, 5.12; N, 13.22. HRMS-ESI [ $\text{M}-\text{Cl}$ ] $^+$ , calcd. for  $\text{C}_{12}\text{H}_{18}\text{N}_4\text{Cl}^{58}\text{Ni}^{32}\text{S}$ : 343.02942; found: 343.0291. IR data (KBr pellet,  $\text{cm}^{-1}$ ): 3461 (sh), 3278 (br), 3217 (m), 3109 (vw), 3033 (vw),

2975 (w), 2925 (w), 2871 (w), 1622 (w), 1577 (s), 1467 (m), 1417 (m), 1290 (m), 1043 (m), 784 (m), 698 (m).

### 2.3.4. $\text{NiCl}_2\{\text{bis}[2-(3\text{-phenylpyrazolyl})\text{methyl}]\text{sulfide}\}$ (**4**)

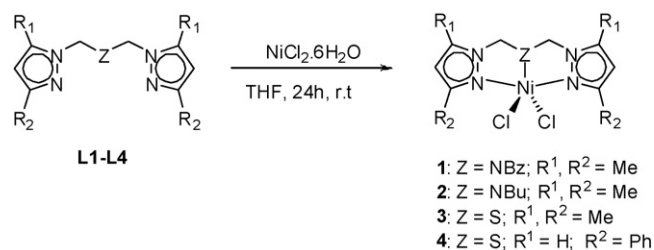
This compound was prepared according to the method described for **1** using  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (60 mg, 0.25 mmol), bis[2-(3-phenylpyrazolyl)methyl]sulfide (86 mg, 0.25 mmol). Workup afforded **4** as a yellow solid (78 mg, 70%). Anal. calcd. for  $\text{C}_{20}\text{H}_{18}\text{Cl}_2\text{N}_4\text{NiS} \cdot 2\text{H}_2\text{O}$ : C, 46.91; H, 4.33; N, 10.94. Found: C, 46.72; H, 4.21; N, 10.72. HRMS-ESI  $[\text{M}-\text{Cl}]^+$ , calcd. for  $\text{C}_{20}\text{H}_{18}\text{N}_4^{35}\text{Cl}^{58}\text{Ni}^{32}\text{S}$ : 439.02942; found: 439.0296. IR data (KBr pellet,  $\text{cm}^{-1}$ ): 3357 (s), 3269 (s), 3097 (w), 3066 (w), 3031 (w), 1623 (s), 1564 (m), 1498 (m), 1473 (m), 1454 (m), 1357 (m), 1319 (m), 1265 (m), 1224 (m), 1120 (m), 1097 (m), 1074 (m), 964 (m), 792 (m), 759 (s), 686 (m).

### 2.4. General oligomerization procedure

Ethylene oligomerization reactions were performed in a 100 mL double-walled stainless Parr reactor equipped with mechanical stirring, internal control of temperature, and continuous feed of ethylene was used. A Parr reactor was dried in an oven at  $120^\circ\text{C}$  for 5 h prior to each run, and then placed under vacuum for 30 min. A typical reaction was performed by introducing toluene (30 mL) and the proper amount of MAO or DEAC into the reactor under ethylene atmosphere. After 15 min, the toluene catalyst solution (10 mL,  $[\text{Ni}] = 10 \mu\text{mol}$ ) 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 20 bar. After 20 min, the reaction was stopped by cooling the system to  $-20^\circ\text{C}$ , 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.

## 3. Results and discussion

The tridentate nitrogen-, or sulfur-bridged bis(pyrazolyl) ligands (NZN) used in this study, which include two new derivatives (Scheme 1), were readily prepared in high yields via literature procedures [6] or through adaptation of these (see Section 2). The reaction of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  with 1.1 equiv. of the appropriate tridentate NZN ligand in THF at room temperature for 24 h affords the corresponding complexes  $\text{NiCl}_2(\text{NZN}) \cdot 2\text{H}_2\text{O}$  (**1–4**) (Scheme 2), which were isolated as green or light green-colored solids in high yields (typically 87–92%). These complexes show moderate solubility at room temperature in dichloromethane or methanol. Due to the paramagnetic

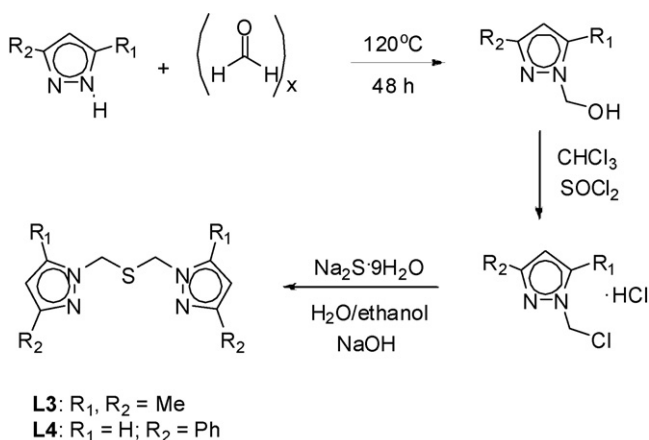


Scheme 2.

nature of these  $\text{NiCl}_2(\text{NZN})$  complexes,  $^1\text{H}$  NMR spectra featured very broad resonances and proved uninformative. The identity of complexes **1–4** was established by elemental analysis, IR spectroscopy, and high-resolution mass spectrometry (see Section 2).

The ethylene oligomerization behavior of nickel complexes **1–4** has been evaluated using optimized conditions recently established for related 6-membered chelate nickel catalysts [4], i.e., toluene as solvent at  $30^\circ\text{C}$  under 20 bar of ethylene and Al-to-Ni ratios of 250. Representative results are given in Table 1 and featured in Fig. 1. When activated with MAO, all systems proved to be active for dimerization of ethylene. Moderate turnover frequencies (TOFs) in the range of  $3900\text{--}18,900 \text{ mol}(\text{ethylene})(\text{mol}(\text{Ni}))^{-1} \text{ h}^{-1}$  were obtained with **1**, **2** and **4** (entries 1, 3 and 5); on the other hand, the catalyst system derived from **3** that contains a sulfur-bridged ligand bearing methyl substituents at the 3- and 5-positions of the pyrazolyl rings gave a very high TOF of  $104,500 \text{ mol}(\text{ethylene})(\text{mol}(\text{Ni}))^{-1} \text{ h}^{-1}$ . A similar activity trend has been observed in 6-membered ring nickel and chromium catalysts [4,7].

The catalytic performance in ethylene oligomerization is substantially affected by the ligand environment. Thus, pre-catalyst **1** that bears a *N*-benzyl substituted ligand is ca. 3 times more active than **2** that contains a *N*-butyl substituent; however, in the latter case, the 1-butene selectivity was largely improved to 93.7% with minimal production of 2-butenes and hexenes. The introduction of relatively bulky phenyl substituents (as compared to methyl groups) on the pyrazolyl groups led to a noticeable decrease in catalytic activity in (NSN)Ni(II) systems based on complexes **3** and **4** (compare entries 4 and 5). Furthermore, for systems containing sulfur-bridged bis(pyrazolyl) ligands, the nickel pre-catalyst  $\text{NiCl}_2\{\text{bis}[2-(3,5\text{-dimethyl-pyrazolyl})\text{methyl}]\text{sulfide}\}$  (**3**,  $\text{TOF} = 104,500 \text{ h}^{-1}$ ) led to an activity almost twice as high as that of  $\text{NiCl}_2\{\text{bis}[2-(3,5\text{-dimethyl-pyrazolyl})\text{ethyl}]\text{sulfide}\}$  ( $\text{TOF} = 57,200 \text{ h}^{-1}$ ) [4]. This observation suggests that the chelating



Scheme 1.

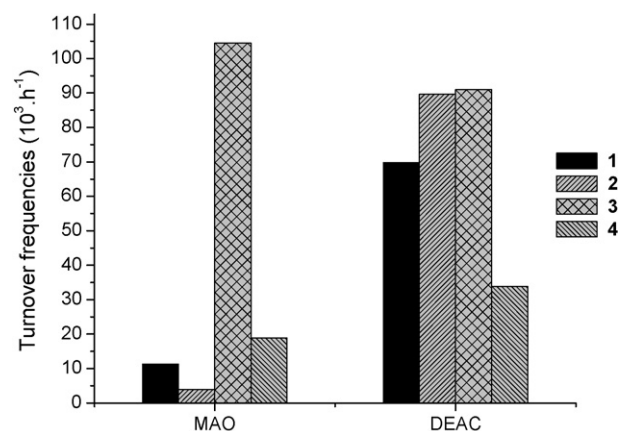


Fig. 1. Influence of alkylaluminum and nickel catalyst on TOF ( $30^\circ\text{C}$ , 20 bar,  $[\text{Al}]/[\text{Ni}] = 250$ ).

**Table 1**  
Ethylene oligomerization with complexes **1–4**<sup>a</sup>

Entry	Complex	T (°C)	Cocat.	Olig. (mg)	TOF <sup>b</sup> ( $\times 10^3$ h <sup>-1</sup> )	Selectivity (%) <sup>c</sup>				
						C <sub>4</sub>	$\alpha$ -C <sub>4</sub>	cis-C <sub>4</sub>	trans-C <sub>4</sub>	$\alpha$ -C <sub>6</sub>
1	<b>1</b>	30	MAO	1054	11.3	96.3	84.4	8.5	6.5	3.7
2	<b>1</b>	60	MAO	172	1.7	95.3	82.3	14.4	2.5	4.7
3	<b>2</b>	30	MAO	371	3.9	100	93.7	5.1	1.3	–
4	<b>3</b>	30	MAO	9761	104.5	97.8	71.9	16.9	9.0	2.2
5	<b>4</b>	30	MAO	1782	18.9	98.0	81.8	11.7	6.1	1.9
6	<b>1</b>	30	DEAC	6470	69.8	100	81.3	10.6	8.1	–
7	<b>2</b>	30	DEAC	8389	89.6	98.4	72.0	15.0	11.5	1.6
8	<b>3</b>	30	DEAC	8499	91.0	98.2	72.5	14.7	11.0	1.7
9 <sup>d</sup>	<b>3</b>	30	DEAC	7380	79.0	98.3	76.3	12.9	9.1	1.7
10	<b>4</b>	30	DEAC	3192	33.9	98.0	77.6	12.8	9.1	1.9

<sup>a</sup> Reaction conditions: toluene = 40 mL, [Ni] = 10.0  $\pm$  0.5  $\mu$ mol, P(ethylene) = 20 bar, oligomerization time = 20 min, [Al]/[Ni] = 250. The results shown 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;  $\alpha$ -C<sub>n</sub>, amount of terminal alkene in the C<sub>n</sub> fraction; as determined by quantitative GLC.

<sup>d</sup> [Al]/[Ni] = 50.

ring size of the former tridentate bis(pyrazolyl) ligand (leading to a 5-membered ring complex) determines the formation of a more active catalyst. In fact, we did not observe any significant impact of the chelating ring size on selectivity for 1-butene, which remains around 70–73% [8].

For all nickel complexes **1–4** activated with MAO, the selectivity for butenes and especially 1-butene was high, attaining 81.8–93.7% of the total amount of olefins formed in the oligomerization reactions (i.e. ca. 83–94% of the C<sub>4</sub> fraction). Larger amounts of 2-butenes (ca. 26%) were produced from **3**. In all cases, minimal amounts of hexenes [9] and no polymer were detected.

For the system **1**/MAO, increase in the temperature from 30 to 60 °C resulted in a noticeable decrease in TOF from 11.3 to 1.7 h<sup>-1</sup>. This effect can be likely associated with a partial deactivation of active species at higher temperatures; however, a decrease in the ethylene concentration in solution at this oligomerization temperature, which would induce indirect catalyst decay, cannot be ruled out.

Activation of nickel complexes **1–4** with diethylaluminumchloride (DEAC) instead of MAO produced in general much more active systems (TOFs varying from 33,900 to 91,000 h<sup>-1</sup>), along with lower selectivity for 1-butene (72.0–81.3%) and concomitant production of larger amounts of butenes (18.7–25.7%), as can be seen in Fig. 2. It is interesting to note that the TOFs of systems based on **1–3** under DEAC activation were quite similar, attaining 69,800, 89,600 and

91,000 h<sup>-1</sup>, respectively (entries 6–8). This observation, which is in striking contrast with the aforementioned marked difference with the corresponding MAO-activated systems, could reflect a better stabilization of active species with DEAC than with MAO, possibly thanks to the chlorine atom.

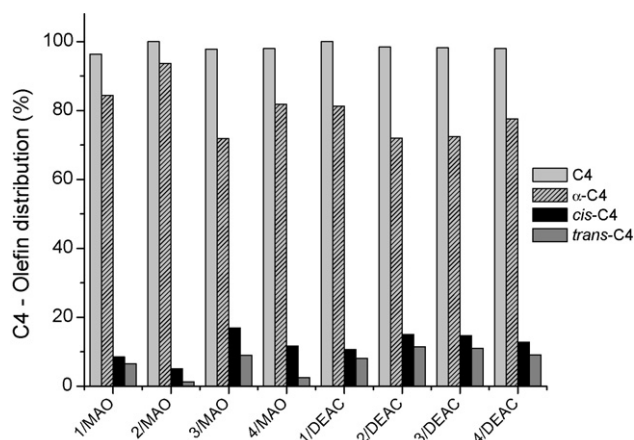
In fact, when activated with 50 equiv. of DEAC, complex **3** provided a high activity (TOF = 79,000 h<sup>-1</sup>, entry 9), which is very close to that one using higher DEAC loading (250 equiv., TOF = 91,000 h<sup>-1</sup>, entry 8). At the same time, decreasing the amount of DEAC from 250 to 50 equiv. led to slightly improved selectivity for 1-butene (72.5–76.3%) with production of lower amounts of 2-butenes (25.7–22.0%). The possibility to use small amounts of co-catalyst is obviously an interesting feature of these catalyst systems.

Our results for two sets of oligomerization reactions using MAO or DEAC as co-catalysts show that the selectivities for 1-butene afforded by pre-catalysts **1–4** are very similar. This indicates that the central donor atoms and also the pyrazolyl R<sup>1</sup>, R<sup>2</sup> substituents play 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 [4].

In summary, we have introduced a new class of Ni(II) complexes based on NZN ligands (Z = N, S) that form 5-membered chelate rings which, in association with alkylaluminum (MAO or DEAC), afford active catalysts for selective dimerization of ethylene to 1-butene. Our results show that decrease in the ligand chelate size from 6- to 5-membered rings provides more active catalysts, probably due to the formation of more stable active species. On the other hand, no significant impact of the chelating ring size on the selectivity for 1-butene is observed. Both turnover frequency and selectivity are mostly dependent on the nature of the alkylaluminum co-catalyst employed in the oligomerization reactions, suggesting that these activators act also as ligands for the nickel center of active species. The system based on complex **3** in the presence of a minimal amount of DEAC ([Al]/[Ni] = 50) shows high activity (TOF = 79,000 h<sup>-1</sup>) for ethylene oligomerization associated with good selectivity for 1-butene (76.3%).

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**Fig. 2.** Influence of alkylaluminum and catalyst type on selectivity for butenes (30 °C, 20 bar, [Al]/[Ni] = 250).



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