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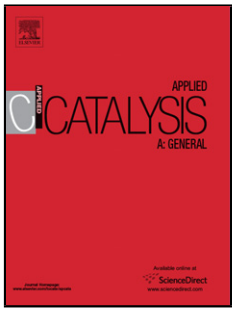

Title: Nickel Catalysts Based on Phenyl Ether-Pyrazol Ligands: Synthesis, XPS study, and use in Ethylene Oligomerization

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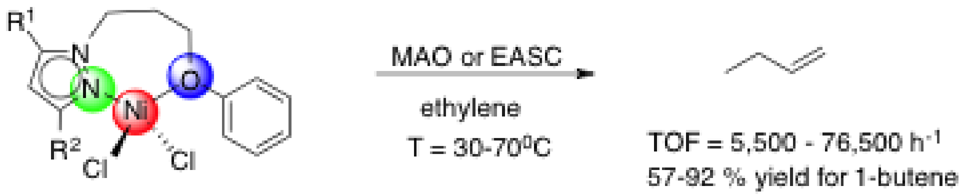
R1
N
N
Ni
O
R2
Cl
Cl
MAO or EASC
ethylene
T = 30-70°C
TOF = 5,500 - 76,500 h-1
57-92 % yield for 1-butene

Research highlights

> Nickel complexes supported by pheny ether-pyrazol ligands

> The probability of (co)existing dimeric species increases in the following order: Ni4 < Ni1 < Ni2 < Ni3.

> Nickel precatalysts exhibit high activities in ethylene oligomerization

> Selectivities for 1-butene produced varying from 57 to 92.5 %

Nickel Catalysts Based on Phenyl Ether-Pyrazol Ligands: Synthesis, XPS study, and use in Ethylene Oligomerization

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ABSTRACT

A series of nickel(II) complexes bearing phenyl ether-pyrazol ligands [$NiCl_2L$] (**Ni1**: L= 3,5-dimethyl-1-(3-phenoxypropyl)-1H-pyrazole; **Ni2**: L= 1-(3-phenoxypropyl)-3-phenyl-1H-pyrazole; **Ni3**: L = 3,5-di-tert-butyl-1-(3-phenoxypropyl)-1H-pyrazole; **Ni4**: L = 1-(3-phenoxypropyl)-1H-pyrazole) were synthesized and fully characterized by elemental analysis, high-resolution mass spectrometry (HRMS) and X-ray photoelectron spectroscopy (XPS). X-ray photoelectron data illustrates that the probability of (co)existing dimeric species increases in the following order: **Ni4** < **Ni1** < **Ni2** < **Ni3**. All nickel precatalysts, activated with methylaluminoxane (MAO), exhibited moderate to high activities for ethylene oligomerization [TOF = 18.4-45.7 x 10^3 mol(ethylene)$(mol(Ni))^{-1}$ h^{-1})] with good selectivities for 1-butene produced (62.6 – 80.7%). The ligand environment regarding the substituents on the pyrazolyl unit as well as the reaction parameters influence the catalytic performance and selectivity toward production of 1-butene. When activated with ethylaluminum sesquichloride ($Et_3Al_2Cl_3$, EASC), **Ni1** displayed low catalytic activity (TOF = 9,300 (mol C_2H_4)·(mol Ni^{-1} h^{-1}); however, the 1-butene selectivity was increased, attaining 92.5%. The use of triphenylphosphine (PPh_3) as auxiliary ligand afforded highly active catalyst system [TOF = 118.3 x 10^3 mol(ethylene)$(mol(Ni))^{-1}$ h^{-1})] with poor selectivity for production of 1-butene (13.7%).

Keywords: Nickel(II) complexes; Phenyl ether-pyrazol ligands; Ethylene oligomerization; 1-butene; XPS studies

1. Introduction

The oligomerization of ethylene is one of the most important industrial processes to obtain linear α-olefins (LAOs).[1-5] These substrates have been extensively used for preparing detergents, lubricants, plasticizers, and oil field chemicals or as monomers for copolymers, etc.[6-7] Among classes of catalysts used for the production of α-olefins, nickel complexes containing P,P-,[8-12] P,N-,[13-31] P,O-,[32-44] N,N-,[45-61] or N,O-[62-68] as bidentate chelating ligands are the most frequently studied. Specially, anionic bidentate N,O ligands such as the imidazole-alcoholate, [69] iminocarboxamide,[70] and 2-(alkylideamino)benzoate ligands[71] have been successfully applied in the synthesis of nickel(II) oligomerization catalysts. On the other hand, just a few examples of Ni(II) complexes based on neutral N,O-type ligands have been reported in the literature.[72-73] For instance, Braunstein et al. have recently reported a nickel complexes bearing oxazoline alcohols/pyridine alcohols bidentate ligands that show high activities in ethylene oligomerization [TOF up to 187,000 (mol C_2H_4)·(mol Ni^{-1} h^{-1})] giving mostly C_4 olefins and 1-butene. Over the past few years, pyrazolyl-based ligand metal complexes have attracted attention as efficient catalysts for oligo- and polymerization of ethylene.[74-78] Our group has also been interested in exploring the potential applications of pyrazolyl-based ligands in the oligomerization catalysis field. We have thus previously communicated new classes of Ni^{II}[79-83] and Cr^{III}[84] complexes based on tridentate pyrazolyl ligands, which act as highly selective and highly active precatalysts for ethylene oligomerization when activated with alkylaluminum (MAO or $AlEt_2Cl$). Herein, we wish to report the synthesis and characterization of several new nickel(II) complexes bearing bidentate phenoxi-pyrazoyl ligands, as well as their catalytic behavior for ethylene oligomerization. We also discuss the effect of substituents and reaction conditions on their activity and selectivity towards the production of 1-butene.

2. Experimental

2.1. General Procedures

All manipulations involving air- and/or water-sensitive compounds were carried out in an MBraun glovebox or under dry nitrogen using standard Schlenk techniques. Solvents were dried from the appropriate drying agents under argon before use. 3-bromopropyl phenyl ether (Aldrich) and $NiCl_2 \cdot 6H_2O$ (Aldrich) were used as received. $(DME)NiCl_2$ (DME = 1,2-dimethoxyethane),[85] 3,5-di-tert-butyl-1H-pyrazole and 3-phenyl-1H-pyrazole were prepared by following literature procedure.[86] Ethylene (White Martins Co.) and argon were deoxygenated and dried through BTS columns (BASF) and activated molecular sieves prior to use. PMAO-IP (Akzo Nobel, 12.9 wt.% Al solution in toluene) was used as received. EASC (Akzo Nobel) was used with the previous dilution (2.1 wt.% Al solution in toluene). Infrared spectra were performed on a FT-IR Bruker Alpha Spectrometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian Inova 300 spectrometer operating at 25°C. Chemical shifts are reported in ppm vs. $SiMe_4$ and were determined by reference to the residual solvent peaks. High-resolution mass spectra of bidentate ligands (**L1-L4**) and Ni(II) complexes (**Ni1-Ni4**) were obtained by ESI in the positive mode in CH_3CN or CH_3OH solutions using a Micromass Waters® Q-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, 100m length, 0.25 mm i.d. and film thickness of 0.5 μm) operating at 36°C for 15 min followed by heating at $5°C \cdot min^{-1}$ until 250°C; cyclohexane was used as the internal standard.

2.2. Synthesis of the Phenyl Ether-Pyrazolyl ligands

3,5-dimethyl-1-(3-phenoxypropyl)-1H-pyrazole (**L1**): A solution of 3,5-dimethyl-1H-pyrazole (0.30 g, 3.2 mmol) in DMF/THF (v/v = 1:1, 12 mL) was added to a suspension of NaH (0.15 g, 6.4 mmol) in DMF/THF (v/v = 2:1, 15 mL) and stirred at 60°C for 2 h. Then, the resulting solution was added under stirring to a solution of 3-bromopropyl phenyl ether (0.70 g, 3.2 mmol) in DMF (7 mL). The mixture was allowed to stir for 24 h at 60 °C, cooled, and treated cautiously with H_2O (5 mL) to decompose excess NaH. The solvents were then evaporated under reduced pressure. The residue was extracted with ethyl acetate (3 x 15 mL), washed with H_2O (2 x 15 mL). The organic phase was dried over $MgSO_4$ and filtered, before the solvent was evaporated under reduced pressure. After workup and purification by chromatographic column on silica gel (hexane/ethyl acetate, 90:10), **L1** was obtained as a colorless oil (0.47 g, 64%). ^{1}H NMR ($CDCl_3$, 298K, 300 MHz): δ 2.18 (3H, s), 2.26 (3H, s), 2.30 (2H, m, $^3J_{HH}$ = 6.2 Hz), 3.88 (2H, t, $^3J_{HH}$ = 5.8 Hz), 4.18 (2H, t, $^3J_{HH}$ = 6.6 Hz), 5.77 (1H, s), 6.88 (2H, d, $^3J_{HH}$ = 7.6 Hz), 6.95 (1H, t, $^3J_{HH}$ = 7.3 Hz), 7.29 (2H, t, $^3J_{HH}$ = 7.4 Hz). ^{13}C NMR ($CDCl_3$, 298K, 300MHz): 10.54, 13.29, 29.62, 44.44, 63.76, 104.39, 114.11, 120.51, 129.20, 138.91, 147.23, 158.33. IV (ATR): 3062 (w), 3042 (w), 2946 (m), 2930 (m), 2874 (m), 1600 (s), 1586 (s), 1552 (s), 1496 (s), 1470 (s), 1423 (m), 1387 (m), 1355 (f), 1298 (m), 1241 (s), 1172 (s), 1152 (w), 1130 (w), 1079 (m), 1054 (s), 1037 (m), 1021 (m), 997 (w), 978 (w), 908 (s), 882 (w), 778 (m), 752 (s), 728 (s), 690 (s), 643 (m), 597 (m), 510 (m). Anal. calcd. for $C_{14}H_{18}N_2O$: C, 73.01; H, 7.88; N, 12.16. Found: C, 72.54; H, 8.58; N, 12.09.

1-(3-phenoxypropyl)-3-phenyl-1H-pyrazole (**L2**): This product was prepared by following a procedure similar to what was described above for **L1**, starting from 3-phenyl-1H-pyrazole (0.70 g, 4.5 mmol), NaH (0.22 g, 9.0 mmol) and 3-bromopropyl phenyl ether (0.96 g, 4.5 mmol). After workup and purification by chromatographic column on silica gel (hexane/ethyl acetate, 90:10), **L2** was obtained as a colorless oil (0.75 g, 60%). ^{1}H NMR ($CDCl_3$, 298K, 300 MHz): δ 2.32 (2H, m, $^3J_{HH}$ = 6.3 Hz), 3.87 (2H, t, $^3J_{HH}$ = 5.8 Hz), 4.32 (2H, t, $^3J_{HH}$ = 6.7 Hz), 6.48 (1H, d, $^3J_{HH}$ = 2.2 Hz), 6.88 (2H, d, $^3J_{HH}$ = 7.8 Hz), 6.93 (1H, t, $^3J_{HH}$ = 7.4 Hz), 7.34 (6H, m), 7.81 (2H, d, $^3J_{HH}$ = 7.0 Hz). ^{13}C NMR ($CDCl_3$, 298K, 300MHz): 29.56, 48.63, 63.95, 102.35, 114.29, 120.71, 125.40, 127.39, 128.45, 129.35, 130.99, 133.45, 151.53, 158.51. Anal. calcd. for $C_{18}H_{18}N_2O$: C, 77.67; H, 6.52; N, 10.06. Found: C, 77.01; H, 6.35; N, 10.01.

3,5-di-tert-butyl-1-(3-phenoxypropyl)-1H-pyrazole (**L3**): This product was prepared by following a procedure similar to what was described above for **L1**, starting from 3,5-di-tert-butyl-1H-pyrazole (0.81

g, 4.5 mmol), NaH (0.22 g, 9.0 mmol) and 3-bromopropyl phenyl ether (0.96 g, 4.5 mmol). After workup and purification by chromatographic column on silica gel (hexane/ethyl acetate, 90:10), **L3** was obtained as a colorless oil (1.10 g, 75%). ^{1}H NMR ($CDCl_3$, 298K, 300 MHz): δ 1.28 (9H, s), 1.35 (9H, s), 2.37 (2H, m, $^3J_{HH}$ = 6.3 Hz), 4.03 (2H, t, $^3J_{HH}$ = 5.9 Hz), 4.32 (2H, t, $^3J_{HH}$ = 7.2 Hz), 5.78 (1H, s), 6.87-6.94 (3H, m), 7.09 (2H, t, $^3J_{HH}$ = 7.9 Hz). ^{13}C NMR ($CDCl_3$, 298K, 300MHz): 30.19, 30.45, 30.92, 31.16, 31.88, 47.36, 64.90, 99.04, 114.32, 120.58, 129.36, 150.95, 158.70, 158.78. IR data (neat, cm^{-1}): 3104 (w), 3061 (w), 3039 (w), 2945 (m), 2876 (m), 1703 (w), 1599 (s), 1586 (s), 1494 (s), 1470 (s), 1454 (m), 1395 (s), 1358 (w), 1338 (w), 1289 (s), 1239 (s), 1172 (s), 1153 (w), 1080 (s), 1039 (s), 996 (w), 965 (s), 918 (m), 882 (m), 831 (m), 816 (m), 791 (w), 752 (s), 690 (s), 653 (m), 617 (s), 596 (m), 510 (s). Anal. calcd. for $C_{20}H_{30}N_2O$: C, 76.39; H, 9.62; N, 8.91. Found: C, 76.80; H, 10.43; N, 8.72.

1-(3-phenoxypropyl)-1H-pyrazole (**L4**): This product was prepared by following a procedure similar to what was described above for **L1**, starting from 1H-pyrazole (1.01 g, 14.7 mmol), NaH (0.70 g, 29.4 mmol) and 3-bromopropyl phenyl ether (3.46 g, 16.1 mmol). After workup and purification by chromatographic column on silica gel (hexane/ethyl acetate, 90:10), **L4** was obtained as a colorless oil (2.23 g, 75%). ^{1}H NMR ($CDCl_3$, 298K, 300 MHz): δ 2.31 (2H, q, $^3J_{HH}$ = 6.3 Hz), 3.87 (2H, t, $^3J_{HH}$ = 5.8 Hz), 4.33 (2H, t, $^3J_{HH}$ = 6.6 Hz), 6.20 (1H, t, $^3J_{HH}$ = 2.0 Hz), 6.85 (1H, d, $^3J_{HH}$ = 7.8 Hz), 6.93 (1H, t, $^3J_{HH}$ = 6.9 Hz) 7.27 (2H, t, $^3J_{HH}$ = 7.7 Hz), 7.34 (1H, d, $^3J_{HH}$ = 2.2 Hz), 7.51 (1H, d, $^3J_{HH}$ = 1.5 Hz). ^{13}C NMR ($CDCl_3$, 298K, 300MHz): 29.77, 48.29, 63.85, 105.00, 114.19, 120.63, 129.25, 129.35, 139.25, 158.42. Anal. calcd. for $C_{12}H_{14}N_2O$: C, 71.26; H, 6.98; N, 13.85. Found: C, 70.90; H, 6.42; N, 13.97.

2.3. Synthesis of the Ni(II) Complexes

$NiCl_2$\{3,5-dimethyl-1-(3-phenoxypropyl)-1H-pyrazole\} (**Ni1**): To a solution of (DME)$NiCl_2$ (0.22 g, 0.99 mmol) in dichloromethane (10 mL) was added a solution of 3,5-dimethyl-1-(3-phenoxypropyl)-1H-pyrazole (0.20 g, 1.1 mmol) in dichloromethane (10 mL) and the resulting solution was stirred for 24 h at room temperature. The solvent was removed, and the resulting yellow solid residue was washed with

Et_2O (3 x 10 mL). Complex **Ni1** was obtained as a yellow solid (0.27 g, 76%). Anal. calcd. for $C_{28}H_{36}N_4Cl_4Ni_2O_2$: C, 46.72; H, 5.04; N, 7.78. Found: C, 46.13; H, 4.87; N, 7.44. ESI-HRMS (CH_3OH, m/z): 323.0468 $[M-Cl]^+$ (Calc. for $C_{14}H_{18}ClN_2NiO$, 323.0461).

$NiCl_2$\{1-(3-phenoxypropyl)-3-phenyl-1H-pyrazole\}(**Ni2**): This compound was prepared according to the method described for **Ni1** using (DME)$NiCl_2$ (0.18 g, 0.83 mmol) and 1-(3-phenoxypropyl)-3-phenyl-1H-pyrazole (0.25 g, 0.92 mmol). Complex **Ni2** was obtained as a yellow solid (0.27 g, 81%). Anal. calcd. for $C_{18}H_{18}N_2Cl_2NiO$: C, 53.00; H, 4.45; N, 6.87. Found: C, 52.87; H, 4.21; N, 6.61. ESI-HRMS (CH_3OH, m/z): 371.0473 $[M-Cl]^+$ (Calc. for $C_{18}H_{18}ClN_2NiO$, 371.0461).

$NiCl_2$\{3,5-di-tert-butyl-1-(3-phenoxypropyl)-1H-pyrazole \}(**Ni3**): This compound was prepared according to the method described for **Ni1** using (DME)$NiCl_2$ (0.19 g, 0.89 mmol) and 3,5-di-tert-butyl-1-(3-phenoxypropyl)-1H-pyrazole (0.31 g, 0.98 mmol). Complex **Ni3** was obtained as a yellow solid (0.31 g, 79%). Anal. calcd. for $C_{16}H_{22}N_2Cl_2NiO$: C, 49.53; H, 5.72; N, 7.22. Found: C, 49.16; H, 5.13; N, 6.81. ESI-HRMS (CH_3OH, m/z): 407.1415 $[M-Cl]^+$ (Calc. for $C_{20}H_{30}ClN_2NiO$, 407.1400).

$NiCl_2$\{1-(3-phenoxypropyl)-1H-pyrazole\} (**Ni4**): This compound was prepared according to the method described for **1** using (DME)$NiCl_2$ (0.53 g, 2.40 mmol) 1-(3-phenoxypropyl)-1H-pyrazole (0.53 g, 2.65 mmol). Complex **Ni4** was obtained as a yellow solid (0.59 g, 74%). Anal. calcd. for $C_{24}H_{28}N_4Cl_4Ni_2O_2$: C, 43.43; H, 4.25; N, 8.44. Found: C, 42.92; H, 3.87; N, 7.88. ESI-HRMS (CH_3OH, m/z): 295.0152 $[M-Cl]^+$ (Calc. for $C_{12}H_{14}ClN_2NiO$, 295.0148 g).

2.4 General oligomerization procedure

Ethylene oligomerization reactions were performed in a 100 mL double-walled stainless Parr reactor equipped with mechanical stirring, internal temperature control and continuous feed of ethylene. The Parr reactor was dried in an oven at 120°C for 5 h prior to each run, and then placed under vacuum for 30 min. A typical reaction was performed by introducing toluene (30 mL) and the proper amount of co-catalyst (MAO or EASC) into the reactor under an ethylene atmosphere. After 20 min, the toluene catalyst solution (10 mL, [Ni] = 10 μmol) was injected into the reactor under a stream of ethylene and then the reactor was immediately pressurized. Ethylene was continuously fed in order to maintain the desired ethylene pressure. After 20 min, the reaction was stopped by cooling the system to −60°C and depressurizing. An exact amount of cyclohexane was introduced (as an internal standard) and the mixture was analyzed by quantitative GLC.

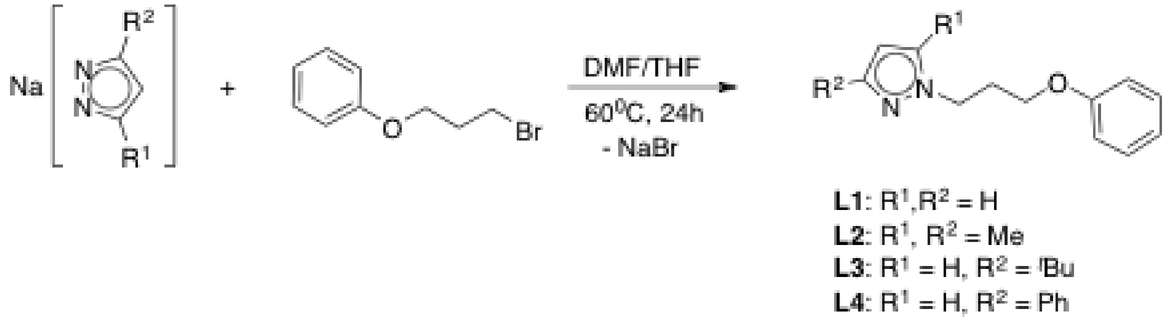
2.5. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy was performed in an Omicron-SPHERA station using Al $K\alpha$ radiation (1486.6 eV). The anode was operated at 225W (15 kV, 15 mA). Survey spectra were recorded with a 50 eV pass energy. O 1s, Cl 2p, and Ni 2p regions were recorded with a higher resolution (pass energy of 20 eV). The detection angle of the photoelectrons with respect to the sample surface (take-off angle) was fixed at 53° for all measurements. The C 1s signal from adventitious carbon at 285 eV was used as an internal energy reference. All spectra were fitted assuming a Shirley background. Lines were fitted by 70% Gaussian + 30% Lorentzian functions with set values of full width at half maximum for each line

3. Results and Discussion

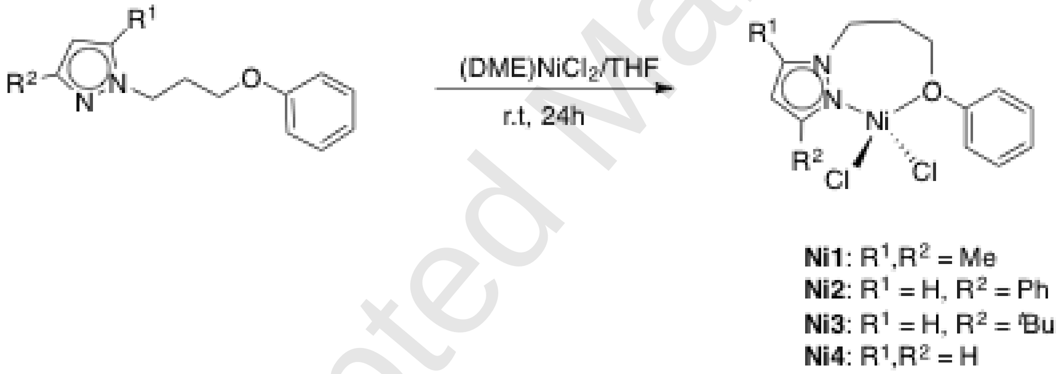
3.1 Synthesis and Characterization of the Phenyl Ether-Pyrazol ligands and Nickel Complexes

The phenyl ether-pyrazol ligands (**L1-L4**) were prepared by reaction of 3-bromopropyl phenyl ether with sodium pyrazolate in DMF/THF in moderate to good yields (60-75%) as shown in Scheme 1. The identity of this class of ligand was established by IR, elemental analysis, and NMR spectroscopy.



Scheme 1

Reacting (DME)NiCl$_2$ (DME = 1,2-dimethoxyethane) with 1.1 equiv of the appropriate phenyl ether-pyrazolyl ligand (**L1-L4**) in THF at room temperature leads to the corresponding nickel complexes (**Ni1–Ni4**), which were isolated as yellow solids in high yields (typically 74–81%)(Scheme 2).



Scheme 2

These nickel complexes were initially characterized by elemental analysis, and mass spectrometry. High-resolution mass spectrometry (HRMS) with the electrospray ionization method afforded spectra where the main peak corresponds to $[Ni(L)Cl]^+$ ions (L = **L1-L4**). The informative NMR data were not obtained due to the paramagnetic nature of these nickel complexes. In addition, no good-quality single crystals were obtained in order to obtain the structural characterization of these nickel complexes. Thus, these results prompted us to explore the structural nature of these nickel species using X-ray photoelectron spectroscopy (XPS). Table 1 shows the binding energies (BE) extracted from the high-resolution spectra from the following regions: Ni 2p, O 1s, and Cl 2p

Table 1.

BE of investigated nickel complexes in the Ni 2p, O 1s and Cl 2p regions.

Complex	**Binding Energy (eV)**		
	Ni (2p)	**O (1s)**	**Cl (2p)**
Ni1	857.53	533.43	201.63
Ni2	856.63	532.73	200.63
Ni3	855.16	531.16	199.36
Ni4	856.00	532.00	199.90

The lowest BE energy value found for **Ni3** indicates highest electron density in its coordination sphere compared to the others nickel compounds (**Ni1-Ni2, Ni4**). It seems that the Ni metal center is affected by the presence of the *tert*-Bu group, which its donor character drives electron density up to Ni atom. In the high resolution Cl 2p region, the relative low BE (in comparison to the other nickel complexes) suggests that such Cl ligand may be terminal. Furthermore, the potential steric effect played by the groups may suggest that such complex is monomeric. In addition, the narrow full width at half maximum (FHWM) of Cl 2p peak (1.63 eV) may also suggest homogeneity in the nature of such species, i.e., mostly in a monomeric form.

In the case of complex **Ni2**, the donor character of the phenyl group is not enough to guarantee an electron rich coordination sphere in comparison to that exhibited by **Ni3**. The BE of Ni (856.63 eV) is close to that reported to $NiCl_2$ (856.7 eV). [87-89] In such systems, the electron density seems to be driven by the chloride ligands, which Cl 2p XPS peaks indicates a decrease in electron density (200.63 eV). The comparison to Cl (2p) binding energy reported for $NiCl_2$ (199.4 eV) grounds this supposition.[87-89] The same rationale can be applied for **Ni1**, which the Ni metal center seems less affected by the presence of methyl groups at 3- and 5-positions of the pyrazolyl rings (857.53 eV). In this case, the electron density is also driven from chloride ligands, which the biding energy is relatively much higher (201.63 eV) indicating an electron deficiency on the chloride ligands. Furthermore, such values may determine a bridge chloride configuration, which in turn be possible due to the lower steric effect played by these methyl groups. The broader FHWM of Cl peaks (1.74 and 1.76 eV) may indicate a mixture of Cl species.

Finally, in the case of complex **Ni4**, the lower steric hindrance of the bidentate ligand may affords the proximity between the Ni metal centers, resulting in the formation of a dimeric species. The proximity of the nickel metal centers may render easier the electron flux of electrons, which guarantee a lower cationic character of Ni (856.0 eV) in comparison for that on species **Ni1** and **Ni2**, which in turn drives lower electron density from the chloride ligands (199.9 eV).

In sum, based on the XPS results, taking into account the BE of Ni (2p) and Cl (2p), and considering the steric effects played by the ligands coordinated to the Ni center, one can suggest that the probability of (co)existing dimeric species increases in the following order: **Ni4** < **Ni1** <**Ni2** < **Ni3**.

3.2 Ethylene Oligomerization Studies

Complexes **Ni1-Ni4** have been evaluated in the ethylene oligomerization at 20 bar of ethylene pressure, and using methylaluminoxane (MAO) (250 equiv) as co-catalyst. Table 2 summarizes the results of reactions carried out using 10 μmol of precatalyst in 40 mL of a toluene. All nickel complexes investigated have been found to generate active systems for the production of short-chain olefins in the C_4-C_6 range.

The ligand environment regarding the substituents on the pyrazolyl unit influenced the catalytic performance of the nickel precatalysts on ethylene oligomerization, as can be better visualized in Fig. 1. Thus, the catalytic system **Ni1/MAO** was found to give reasonable activity [TOF = 45,700 (mol C_2H_4)·(mol Ni^{-1} h^{-1})] along with good selectivity towards 1-butene (62.6%). The presence of bulkier ligands in **Ni2/Ni3** caused a decrease in activity as compared to the catalytic performance displayed by **Ni1**. The abovementioned observations can be associated to the effect of the R substituents size toward the insertion of monomers; usually bulkier substituents offer maximum resistance to monomers coming into the active metal center. The lower activity of **Ni4** can be associated to the poorer electron-donating ability of pyrazolyl unit as compared to the substituted ones with alkyls groups (methyl, *tert*-Butyl). [90]

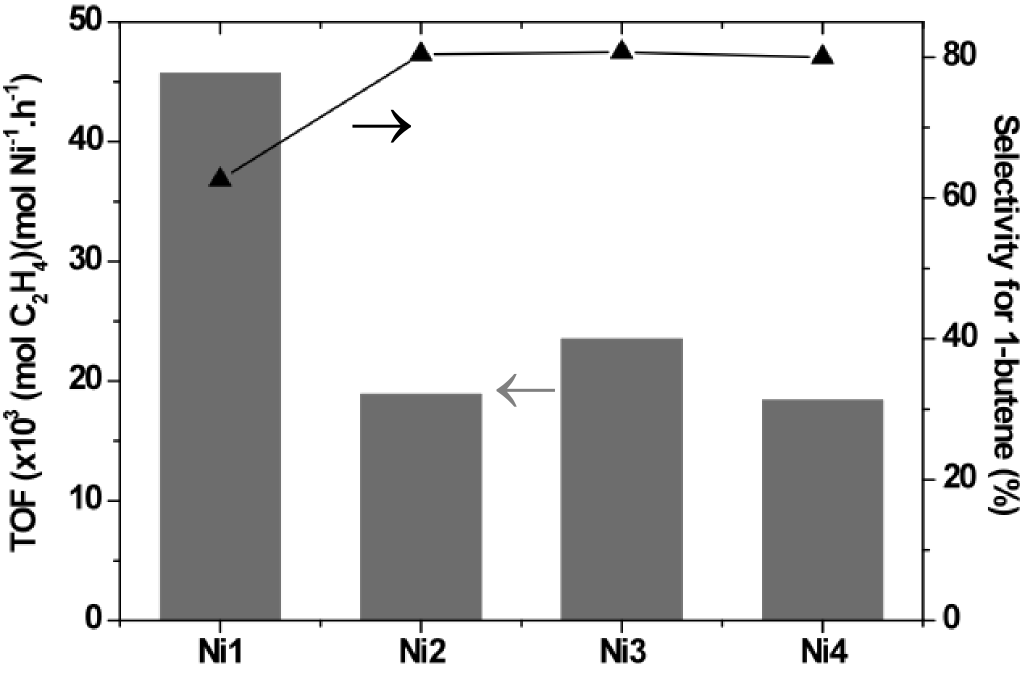


Fig. 1. Influence of nickel precatalyst on TOF and selectivity for 1-butene (30°C, 20 bar, [Al]/[Ni] = 250).

For all nickel complexes (**Ni1-Ni4**), the selectivity for butenes and especially 1-butene varied from 62.6 to 80.7% of the total amount of olefins produced in the oligomerization reactions. As shown in Table 2, the selectivities for 1-butene afforded by **Ni2-Ni4** were similar, indicating that the introduction of steric hindrance on the pyrazolyl group had little influence on the product distribution. This observation is in agreement with the previous ethylene oligomerization results using MAO-activated nickel complexes bearing pyrazolyl ligands.[79-80] In all cases, minimal amounts of hexenes (4.7-9.2%) were detected with poor selectivity for 1-hexene (1.4-1.7%).

The preliminary study was extended to investigate the effect of temperature, oligomerization time, [Al]/[Ni] molar ratio, and co-catalyst type on TOF and oligomers distributions. The precatalyst **Ni1** showed slightly lower oligomerization activity at lower temperature [10°C, TOF = 38,800 (mol

C_2H_4)·(mol Ni^{-1} h^{-1}] as compared to the result obtained at 30°C. This effect can be associated to a reduced solubility of **Ni1** in toluene at 10°C generating lower amounts of active species. Elevating the temperature from 30°C to 70°C led to a huge reduction in activity [TOF = 10,500 (mol C_2H_4)·(mol Ni^{-1} h^{-1})], suggesting that a partial decomposition of the active catalytic sites took place. However, it should be pointed out that even at a higher temperature (50°C), the **Ni1**/MAO system was much more active than nickel precatalysts based on pyrazoly ligands such as $NiCl_2${bis[2-(3,5-dimethylpyrazolyl)ethyl)]ether} [TOF = 7,100 (mol C_2H_4)·(mol Ni^{-1} h^{-1})][82], and $NiCl_2${1-(2-(2-(2,6-diisopropylphenoxy)ethoxy)ethyl)-3,5-dimethyl-1H-pyrazole}[TOF = 17,100 (mol C_2H_4)·(mol Ni^{-1} h^{-1})][83] under identical reaction conditions (30°C, toluene, [Al]/[Ni] = 250, 20 bar of ethylene, MAO as co-catalyst). As expected at 10°C, the **Ni1**/MAO catalytic system displayed the best selectivity for 1-butene (84.2%). On elevating the temperature from 10 to 30 °C, led to reduced 1-butene selectivity (62.6%) which remained at the same level at 70°C (66.1%).

The selectivities and catalyst activity were monitored versus time in the ethylene oligomerization reaction promoted by the **Ni1**/MAO catalytic system. The oligomerization activity progressively decreased when the reaction was prolonged from 10 to 20 min and finally to 40 min, which indicates that the catalyst lifetime is relatively short. On the other hand, the reaction time did not significantly affect the selectivity for 1-butene, varying from 65.0% (10 min) to 57.0% (40 min). These results thus indicate that isomerization of butenes is a minor pathway in these reactions and that the observed selectivities directly reflect the dimerization abilities of the catalyst.

The influence of the MAO loading on the catalyst behavior was also studied. When activated with 100 equiv of MAO, precatalyst **Ni1** gave a lower activity [TOF = 30,300 (mol C_2H_4)·(mol Ni^{-1} h^{-1}), entry 9], which was increased upon using 250 equiv [TOF = 45,700 (mol C_2H_4)·(mol Ni^{-1} h^{-1}), entry 1] and even further with 500 equiv (TOF = 65,100 (mol C_2H_4)·(mol Ni^{-1} h^{-1}), entry10). At the same time, increasing the amount of MAO from 100 to 500 equiv led to slightly reduced selectivity for the α-C_4 (72.4 to 62.6 wt%). Thus, the use of lower MAO loading (100 equiv) seems to be more reasonable to get a moderate active system associated to a more selectivity towards production of 1-butene.

Table 2.

Ethylene Oligomerization with **Ni1-Ni4** catalytic systems.[a]

Entry	Cat.	T (°C)	Time (min)	Cocat. (equiv)	Olig. (g)	TOF[b] (x 10^3)	selectivity (%)[c]				2-C_4[d]
							C_4 (α-C_4)	C_4 (*cis*)	C_4 (*trans*)	C_6 (α-C_6)	
1	**Ni1**	30	20	MAO (250)	4.3	45.7	90.8 (69)	18.1	9.8	9.2 (19)	1.8
2	**Ni2**	30	20	MAO (250)	1.6	18.9	94.6 (85)	9.0	5.0	5.4 (27)	1.8
3	**Ni3**	30	20	MAO (250)	2.1	23.5	94.9 (85)	9.0	5.0	5.1 (30)	1.8
4	**Ni4**	30	20	MAO (250)	1.6	18.4	95.3 (84)	9.5	5.1	4.7 (30)	1.9
5	**Ni1**	10	20	MAO (250)	3.6	38.8	96.7 (87)	8.4	4.1	3.3 (34)	2.0
6	**Ni1**	50	20	MAO (250)	3.1	34.5	90.0 (73)	16.8	9.4	10.0 (21)	1.8
7	**Ni1**	70	20	MAO (250)	1.0	10.5	89.4 (74)	15.3	8.7	10.6 (26)	1.8
8	**Ni1**	30	10	MAO (250)	3.5	76.5	91.6 (71)	17.0	9.1	8.4 (21)	1.9
9	**Ni1**	30	40	MAO (250)	7.0	38.4	89.2 (64)	20.5	11.2	10.8 (17)	1.8
10	**Ni1**	30	20	MAO (100)	2.8	30.3	92.8 (78)	13.5	7.2	7.2 (24)	1.9
11	**Ni1**	30	20	MAO (500)	5.9	65.1	90.7 (69)	18.2	9.8	9.3 (19)	1.8
12	**Ni1**	30	20	EASC (100)	0.5	5.5	96.8 (94)	3.2	2.4	3.2 (37)	1.3
13	**Ni1**	30	20	EASC (250)	0.8	9.3	97.4 (95)	2.9	2.1	2.6 (49)	1.4
14[e]	**Ni1**	30	20	MAO (250)	10.7	118.3	91.4 (15)	28.7	48.8	8.6 (16)	0.6

[a] Reaction Conditions: toluene = 40 mL, P_{C2H4} = 20 bar, MAO as co-catalyst (250 equiv). The results shown are representative of at least duplicated experiments. [b] Mol of ethylene converted (mol of Ni)$^{-1}$·h^{-1} as determined by quantitative GLC. [c] C_n, amount of olefin with *n* carbon atoms in oligomers; α-C_n, amount of terminal alkene in the C_n fraction, as determined by quantitative GLC. [d] [*cis*-C_4]/[*trans*-C_4-*trans*] molar ratio. [e] triphenylphosphine (PPh_3) as auxiliary ligand (1 equiv).

Activation of nickel precatalyst **Ni1** with 100 equiv of ethylaluminum sesquichloride ($Et_3Al_2Cl_3$, EASC) instead of MAO gave a significantly lesser catalyst system than **Ni1/MAO** [TOF = 5,500 vs. 45,700 (mol C_2H_4)·(mol Ni^{-1} h^{-1}]. However, although the catalyst activity was reduced by approximately eight-fold, the 1-butene selectivity was substantially increased attaining 91.0% (compare entries 10 and 12). Higher EASC loading (250 equiv) generated a better catalyst system (TOF = 9,300 (mol C_2H_4)·(mol Ni^{-1} h^{-1}), entry 12) with slightly improvement on selectivity for 1-butene (91.0 to 92.5%), and production of lower amounts of 2-butenes (5.6 to 5.0%) and hexenes (3.2 to 2.6%).

It is noteworthy to observe that the molar ratio between 2-*cis*- and 2-*trans*-butene isomers remains constant ([cis-C_4]/[trans-C_4] = 1.9 ± 0.1) for all oligomerization reactions carried out in presence of MAO (entries 1-11). By replacing MAO with EASC this ratio decreases to 1.3 ± 0.1 which suggests that the nature of the active species are strictly dependent on the co-catalyst type used in the oligomerization reaction.

Previous studies on nickel-based catalysts have demonstrated that incorporating PPh_3 into catalytic systems leads to higher activity and longer catalyst lifetime.[82][91-94] With this in mind we decided to investigate the influence of PPh_3 in our nickel catalyst system. Using 1 equiv of Ph_3P, the activity of **Ni1/MAO** increased dramatically, reaching a TOF of 118,300 (mol C_2H_4)·(mol Ni^{-1} h^{-1}) (entry 14], which is 3 times higher than the catalytic system **Ni1/MAO** in the absence of PPh_3 (TOF = 45,700 (mol C_2H_4)·(mol Ni^{-1} h^{-1}), entry 1). The presence of this auxiliary ligand in the oligomerization medium plays no significant impact on the total C_4 production with selectivity of 91.4% (compare entries 1 and 14). On the other hand, the PPh_3 ligand has a strong impact in the selectivity towards the production of α-olefins, decreasing substantially the amount of 1-butene (13.7%) with a concomitant increase of internal olefins fractions (*cis*-C_4: 28.7%; *trans*-C_4 fractions: 48.8%). This is consistent with previous reports [95-98], and could be attributed to a higher isomerization rate. In addition, it was verified that the molar ratio between 2-*cis*- and 2-*trans*-butene changed significantly from 1.8 to 0.6 (compare entry 1 and 14), which strongly suggest that PPh_3 is acting as a ligand. Similar trend has been observed for ethylene oligomerization with MAO-activated nickel complexes bearing pyrazolyl ligands. [82]

4. Conclusions

In summary, we have synthesized and characterized a series of new nickel(II) complexes supported by phenyl ether-pyrazolyl ligands. The XPS results suggest that the probability of (co)existing dimeric nickel complexes increases in the following order: **Ni4** < **Ni1** <**Ni2** < **Ni3**. On treatment with MAO as the co-catalyst, the Ni(II) complexes showed good activities for ethylene oligomerization and high selectivity for 1-butene. The presence of bulkier ligands in **Ni2/Ni3** caused a decrease in activity as compared to the catalytic performance displayed by **Ni1**. The use of different co-catalyst (MAO, EASC) influences the nature of the catalytic species. Thus, the activation of **Ni1** with EASC promoted the formation of very low active catalytic system with higher selectivity for 1-butene. In parallel, the use of EASC instead of MAO caused a decrease of the molar ratio between 2-*cis*- and 2-*trans*-butene isomers varying from 1.9 to 1.3.

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