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New air stable cationic methallyl Ni complexes bearing imidoylindazole carboxylate ligand: Synthesis, characterization and their reactivity towards ethylene

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Graphical abstract



Highlights

- Design and synthesis of three neutral *N*,*N* imidoyl-indazole methoxycarbonyl ligands
- Synthesis and characterization of air-stable [(methallyl)Ni(*N*,*N*)]B(Ar')₄ complexes
- Study of ethylene polymerization with Ni-complexes and B(C₆F₅)₃
- Polymerization products strongly depended of the complex and reaction conditions

Abstract

Three new neutral *N*,*N* imidoyl-indazole ligands with a methoxycarbonyl functional group (**1**-**3**) and three new air-stable cationic methallyl nickel complexes (**4**-**6**) were prepared. These compounds were characterized by NMR, FT-IR and elemental analyses. In addition, compounds **1**, **2**, **3** and **4** were analyzed using X-ray diffraction. An evaluation of the reactivity of complexes **4**-**6** towards ethylene was conducted by using 5 equivalents of $B(C_6F_5)_3$. At 1 bar of ethylene and 20 °C, only complexes **4** and **6** were able to produce butene, showing unusual air stability and dimerizing ethylene even after exposure to air for 48 hours. By increasing the pressure to 12 bar at 20 °C, complex **6** showed a catalytic activity of 401 Kg product (mol Ni)⁻¹ h⁻¹, producing a low molecular weight polyethylene (26.6 Kg/mol) with almost exclusively methyl branches (2.3 mol%). By increasing the temperature to 60 °C at 12 bar of ethylene, the system **6** / B(C₆F₅)₃ increased its catalytic activity to 487 Kg product (mol Ni⁻¹) h⁻¹, but produced a significant decrease in the molecular weight of the polymer (1.8 Kg/mol) and a broad distribution of branches.

KEYWORDS: Nickel; Ethylene; Dimerization; Polymerization; Imidoyl-indazole.

1. Introduction

The development of post-metallocene catalysts based on late transition metals has allowed access to a variety of branched polyolefins, with different grades and sizes of these branches.[1–3]

Among these, methyl branches are of great interest because of the improvements in polymer properties, such as resistance to traction or break elongation.[4,5] There are several reports on catalytic systems that indicate that they are able to produce polyethylene with varying branching degrees.[6–8] To date it is not possible to have an absolute control of the branching size and degree using only ethylene as monomer. It is a challenge to have a catalyst that allows absolute control of the microstructure of the polyethylene produced having only methyl branches.

Furthermore, Ni-allyl or Ni-methallyl complexes are a post-metallocene catalyst class that have been synthesized to meet this challenge.[9] These complexes bear a P,O; N,O or N,N chelating ligand (see Fig. 1) and some of these contain in their structure a Lewis base group such as carboxylate or cyano. This group serves two purposes: Act as an electron-withdrawing group activating the metal center by a resonance effect and the ability to coordinate a Lewis acid, thereby increasing the electron deficiency of the metal center, making it more reactive towards olefins and avoiding by this way the use of a large amount of cocatalyst.[10–12]

Recently, it was published by our group an efficient Ni-methallyl complex employing a β -diketimine *N*,*N* chelating ligand (Fig. 1c).[13] This complex was remotely activated by using B(C₆F₅)₃ as Lewis acid, which formed a strong coordination adduct between the cyano group and the borane. This adduct was active towards the polymerization of ethylene with high activities for this kind of system. It produced polyethylene with isolated methyl branches that resemble the polymer structure of that obtained by the copolymerization of ethylene with propene.[14]

To the extent of our knowledge, in literature only have been reported Ni-allyl or Nimethallyl complexes that bear a N,N chelating ligand corresponding to α -diimine or β -diimine kind of.[15] Of interest is our research on Ni-methallyl complexes with a new type of N,N

ligand that exhibits high activities towards α -olefins and, in the case of ethylene, are highly selective to methyl branches.

Herein we report the synthesis and characterization of new air-stable cationic methallyl nickel complexes bearing an N,N imidoyl-indazole derivative ligand. These complexes have a methoxycarbonyl functional group at different positions in the indazole fragment. A study is detailed in this report on the reactivity of these new complexes towards ethylene, using B(C₆F₅)₃ as a cocatalyst. Also to the position of the methoxycarbonyl group in the ligand is expected to have a decisive effect on the reactivity of the complexes.

2. Experimental

2.1. Reagents and materials

All manipulations were performed under an inert atmosphere using standard glovebox and Schlenk-line techniques. All reagents were used as received from Aldrich, unless otherwise specified. Ethylene was purchased from *Matheson Tri-Gas* (research grade, 99.99 % pure). Toluene and pentane were distilled from benzophenone ketyl.

2.2. Synthesis and characterization of imidoyl-indazole carboxylate ligands (1-3) and cationic methallyl Ni complexes (4-6)

2.2.1. Imidoyl-indazole carboxylate 1

N-(2,6-diisopropylphenyl)acetimidoylchloride [16] (405 mg, 1.72 mmol) was added dropwise to a solution of methyl-1*H*-indazole-3-carboxylate (300 mg, 1.72 mmol) in anhydrous toluene (40 ml). The mixture was refluxed for 3 h with vigorous stirring. The yellow solution was evaporated in vacuum to dryness. Crude product was purified via silica gel chromatography (4:1 Petroleum ether / ethyl acetate). **1** was isolated as white solid in 85% yield (546 mg, 1.45 mmol). ¹H NMR (400 MHz, CD₃Cl, 298 K): δ /ppm = 8.87 (d, *J* = 8.4Hz, 1H), 8.32 (d, *J* = 8.4Hz, 1H), 7.55 (t, *J* = 8.4Hz, 1H), 7.41 (t, *J* = 8.4Hz, 1H), 7.19 (m, 3H), 4.07 (s, 3H), 2.95 (hept, *J* = 6.9Hz, 2H), 2.54 (s, 3H), 1.21 (d, *J* = 2.0 Hz, 6H), 1.18 (d, *J* = 2.0 Hz, 6H). ¹³C{¹H} NMR (100 MHz, CD₃Cl, 298 K): δ /ppm = 162.7, 155.6, 143.3, 140.4, 137.8, 137.0, 129.1, 125.2, 125.0, 124.2, 123.3, 122.0, 116.6, 52.4, 28.4, 23.6, 23.0, 17.3. Elemental analysis (%)

 $C_{23}H_{27}N_3O_2$ (M = 377.48 g/mol): calculated C 73.18, H 7.21, N 11.13; found C 72.86, H 7.57, N 10.92. HRMS-ESI ($C_{23}H_{28}N_3O_2$ [M + H]): Calc: 378.2182; Found: 378.2161. For additional 2D NMR spectrum and assignments data see *Supplementary data*.

2.2.2. Imidoyl-indazole carboxylate 2

N-(2,6-diisopropylphenyl)acetimidoylchloride [16] (405 mg, 1.72 mmol) was added dropwise to a solution of methyl-1*H*-indazole-5-carboxylate (300 mg, 1.72 mmol) in anhydrous toluene (40 ml). The mixture was refluxed for 3 h with vigorous stirring. The yellow solution was evaporated in vacuum to dryness. Crude product was purified via silica gel chromatography (4:1 Petroleum ether / ethyl acetate). **2** was isolated as white solid in 90% yield (578 mg, 1.53 mmol). ¹H NMR (400 MHz, CD₃Cl, 298 K): δ /ppm = 8.86 (d, *J* = 8.9Hz, 1H), 8.54 (s, 1H), 8.22 (s, 1H), 8.21 (m, 1H), 7.20 (d, *J* = 7.4Hz, 2H), 7.13 (t, *J* = 7.4Hz, 1H), 3.95 (s, 3H), 2.94 (hept, *J* = 6.8Hz, 2H), 2.45 (s, 3H), 1.19 (t, *J* = 7.4Hz, 12H). ¹³C{¹H} NMR (100 MHz, CD₃Cl, 298 K): δ /ppm = 166.8, 155.0, 143.4, 140.9, 137.6, 137.1, 129.3, 126.1, 125.4, 124.0, 123.6, 123.2, 116.0, 52.2, 28.4, 23.5, 22.9, 17.1. Elemental analysis (%) C₂₃H₂₇N₃O₂ (M = 377.48 g/mol): calculated C 73.18, H 7.21, N 11.13; found C 73.31, H 7.35, N 11.24. HRMS-ESI (C₂₃H₂₈N₃O₂ [M + H]): Calc: 378.2182; Found: 378.2162. For additional 2D NMR spectrum and assignments data see *Supplementary data*.

2.2.3. Imidoyl-indazole carboxylate 3

N-(2,6-diisopropylphenyl)acetimidoylchloride [16] (405 mg, 1.72 mmol) was added dropwise to a solution of methyl-1*H*-indazole-6-carboxylate (300 mg, 1.72 mmol) in anhydrous toluene (40 ml). The mixture was refluxed for 3 h with vigorous stirring. The yellow solution was evaporated in vacuum to dryness. Crude product was purified via silica gel chromatography (4:1 Petroleum ether / ethyl acetate). **3** was isolated as white solid in 87% yield (559 mg, 1.48 mmol). ¹H NMR (400 MHz, CD₃Cl, 298 K): δ /ppm = 9.45 (s, 1H, H14), 8.19 (s, 1H), 8.02 (d, *J* = 8.5Hz, 1H), 7.82 (d, *J* = 8.5Hz, 1H), 7.24 (d, *J* = 8.1Hz, 2H), 7.15 (m, 1H), 3.91 (s, 3H), 2.94 (hept, *J* = 6.8Hz, 2H), 2.43 (s, 3H), 1.20 (dd, *J* = 7.0, 2.9Hz, 12H). ¹³C{¹H} NMR (100 MHz, CD₃Cl, 298 K): δ /ppm = 167.3, 155.0, 143.7, 138.8, 137.4, 136.5, 130.4, 128.9, 124.2, 124.0, 123.4, 120.6, 118.4, 52.5, 28.5, 23.7, 23.0, 17.2. Elemental analysis (%) C₂₃H₂₇N₃O₂ (M = 377.48 g/mol): calculated C 73.18, H 7.21, N 11.13; found C 73.02, H 7.11, N 10.98.

HRMS-ESI ($C_{23}H_{28}N_3O_2$ [M + H]): Calc: 378.2182; Found: 378.2185. For additional 2D NMR spectrum and assignments data see *Supplementary data*.

2.2.4. Cationic methallyl Ni complex 4

Methyl-1-(1-((2,6-diisopropylphenyl)imino)ethyl)-1H-indazole-3-carboxylate (1) (40)mg, 0.105 mmol) and NaBAr'₄ (Sodium-tetrakis(3,5-bis(trifluoromethyl)phenyl)borate) (94 mg; 0.105 mmol) were mixed in dichloromethane (20ml). The suspension was stirred vigorously and a solution of $[(\eta^3-CH_3C(CH_2)_2)NiCl]_2$ [12] (16 mg, 0.053 mmol) in dichloromethane was added. The mixture was stirred for 2 hours at room temperature. The resulting solution was filtered through celite and the product was crystallized adding pentane and storing at -20 °C. 4 was obtained as dark orange crystalline solid in 70 % yield (100 mg; 0.074 mmol). ¹H NMR (400 MHz, CD₃Cl, 298 K): δ /ppm = 8.10 (d, J = 8.3 Hz, 1H), 7.69 (m, 1H), 7.67 (s, 8H), 7.49 (m, 2H), 7.46 (s, 4H), 7.38 (t, J = 7.7 Hz, 1H), 7.29 (m, 2H), 4.12 (s, 3H), 3.82 (s, 1H), 3.23 (hept, J = 6.8 Hz, 1H), 2.84 (hept, J = 6.8 Hz, 1H), 2.79 (s, 1H), 2.59 (s, 3H), 2.52 (s, 1H), 2.37 (s, 1H), 2.21 (s, 3H), 1.31 (d, J = 6.8 Hz, 6H), 1.17 (d, J = 6.8 Hz, 3H), 1.07 (d, J = 6.8 Hz, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃, 298 K,): δ /ppm = 161.4 (t, $J^{CF} = 49 H_{Z}$, 160.7, 159.6, 139.4, 138.8, 134.8, 133.1, 129.0, 127.5, 125.1, 124.8, 124.5, 124.5 (q, $J^{CF} = 270 H_z$), 117.4, 111.7, 63.2, 61.4, 54.1, 28.9, 28.8, 24.2, 24.0, 23.6, 23.2, 22.5, 17.3. ¹⁹F NMR (400 MHz, CDCl₃, 298 K): δ /ppm = -62.45. ¹¹B{1H} NMR (400 MHz, CDCl₃, 298 K): $\delta/\text{ppm} = -6.65$ (v_{1/2} ~ 11 Hz). Elemental analysis (%) C₅₉H₄₆BF₂₄N₃NiO₂ (M = 1354.48 g/mol): calculated C 52.32, H 3.42, N 3.10; found C 52.12, H 3.50, N 3.05. For additional 2D NMR spectrum and assignments data see Supplementary data.

2.2.5. Cationic methallyl Ni complex 5

Methyl-1-(1-((2,6-diisopropylphenyl)imino)ethyl)-1*H*-indazole-5-carboxylate (**2**) (40 mg, 0105 mmol) and NaBAr'₄ (Sodium-tetrakis(3,5-bis(trifluoromethyl)phenyl)borate) (94 mg; 0.105 mmol) were mixed in dichloromethane (20ml). The suspension was stirred vigorously and a solution of $[(\eta^3-CH_3C(CH_2)_2)NiCl]_2$ [12] (16 mg, 0.053 mmol) in dichloromethane was added. The mixture was stirred for 2 hours at room temperature. The resulting pale orange solution was filtered through celite and the product was crystallized adding pentane and storing at -20 °C. **5** was obtained as orange solid in 80 % yield (115 mg; 0.085 mmol). ¹H NMR (400 MHz, CD₃Cl, 298 K): $\delta/\text{ppm} = 8.60$ (s, 1H), 8.46 (s, 1H), 8.41

(d, J = 9 Hz, 1H), 7.77 (d, J = 9 Hz, 1H), 7.69 (s, 8H), 7.48 (s, 4H), 7.39 (t, J = 7.8 Hz, 1H), 7.31 (d, J = 9 Hz, 2H), 3.99 (s, 3H), 3.50 (s, 1H), 3.20 (hept, J = 6.8 Hz, 1H), 2.85 (hept, J = 6.8 Hz, 1H'), 2.65 (s, 1H), 2.60 (s, 3H), 2.57 (s, 1H), 2.38 (s, 1H), 2.17 (s, 3H), 1.30 (d, J = 6.8 Hz, 6H), 1.17 (d, J = 6.8 Hz, 3H), 1.08 (d, J = 6.8 Hz, 3H). $^{13}C{^{1}H}$ NMR (100 MHz, CDCl₃, 298 K,): δ /ppm = 164.6, 161.6 (t, $J^{CF} = 50 Hz$), 160.3, 146.3, 140.0, 139.9, 139.7, 134.8, 134.4, 133.6, 129.0, 128.7, 126.1, 125.0, 124.5 (q, $J^{CF} = 270 Hz$), 117.4, 111.4, 62.9, 56.8, 52.9, 28.9, 28.7, 24.1, 23.9, 23.5, 23.1, 23.0, 16.4. ^{19}F NMR (400 MHz, CDCl₃, 298 K): δ /ppm = -62.40. $^{11}B{1H}$ NMR (400 MHz, CDCl₃, 298 K): δ /ppm = -6.53 (v_{1/2} ~ 11 Hz). Elemental analysis (%) C₅₉H₄₆BF₂₄N₃NiO₂ (M = 1354.48 g/mol): calculated C 52.32, H 3.42, N 3.10; found C 52.39, H 3.53, N 3.15. For additional 2D NMR spectrum and assignments data see *Supplementary data*.

2.2.6. Cationic methallyl Ni complex 6

Methyl-1-(1-((2,6-diisopropylphenyl)imino)ethyl)-1H-indazole-6-carboxylate (3) (40 mg, 0105 mmol) and NaBAr'₄ (Sodium-tetrakis(3,5-bis(trifluoromethyl)phenyl)borate) (94 mg; 0.105 mmol) were mixed in dichloromethane (20ml). The suspension was stirred vigorously and a solution of $[(\eta^3-CH_3C(CH_2)_2)NiCl]_2$ [12] (16 mg, 0.053 mmol) in dichloromethane was added. The mixture was stirred for 2 hours at room temperature. The resulting orange solution was filtered through celite and the product was crystallized adding pentane and storing at -20 °C. 6 was obtained as brown orange solid in 75 % yield (108 mg; 0.079 mmol). ¹H NMR (400 MHz, CD₃Cl, 298 K): δ /ppm = 8.35 (s, 1H), 8.26 (s, 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.64 (d, J = 8.7 Hz, 1H), 7.60 (s, 8H), 7.38 (s, 4H), 7.29 (t, J = 7.8 Hz, 1H), 7.61 (s, 800), 7.38 (s, 400), 7.29 (t, J = 7.8 Hz, 100)1H), 7.20 (m, 2H), 3.83 (s, 3H), 3.40 (s, 1H), 3.11 (hept, J = 6.8 Hz, 1H), 2.76 (hept, J = 6.8*Hz*, 1H), 2.57 (s, 1H), 2.57 (s, 3H), 2.49 (s, 1H), 2.30 (s, 1H), 2.07 (s, 3H), 1.20 (d, J = 6.8*Hz*, 6H), 1.08 (d, J = 6.8 Hz, 3H), 0.99 (d, J = 6.8 Hz, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃, 298 K,): $\delta/\text{ppm} = 165.7$, 161.8 (t, $J^{CF} = 50 \text{ Hz}$), 160.5, 145.4, 140.2, 139.9, 139.5, 138.0, 134.9, 134.0, 129.2, 129.2, 127.0, 125.2, 124.7 (q, $J^{CF} = 270 H_Z$), 124.0, 117.6, 113.2, 63.2, 57.1, 53.4, 29.1, 28.9, 24.2, 24.0, 23.6, 23.2, 23.1, 16.6, C23 (n.o.). ¹⁹F NMR (400 MHz, CDCl₃, 298 K): $\delta/\text{ppm} = -62.37$. ¹¹B{1H} NMR (400 MHz, CDCl₃, 298 K): $\delta/\text{ppm} = -6.64$ $(v_{1/2} \sim 11 \text{ Hz})$. Elemental analysis (%) C₅₉H₄₆BF₂₄N₃NiO₂ (M = 1354.48 g/mol): calculated C 52.32, H 3.42, N 3.10; found C 52.25, H 3.36, N 3.01. For additional 2D NMR spectrum and assignments data see Supplementary data.

2.3. Characterization

NMR spectra were recorded on NMR Bruker AV 400. Chemical shifts are given in parts per million relatives to TMS [¹H and ¹³C, $\delta(SiMe_4) = 0$] or an external standard $[\delta(BF_3OEt_2) = 0 \text{ for } {}^{11}B \text{ NMR}, \delta(CFCl_3) = 0 \text{ for } {}^{19}F \text{ NMR}].$ Most NMR assignments were supported by additional 2D experiments. Elemental analysis data were recorded on a Foss-Heraeus CHNO-Rapid analyzer. HRMS-ESI-MS experiments were carried out using a Thermo Scientific Exactive Plus Orbitrap Spectrometer. FT-IR spectra were recorded on a Bruker Vector-22 Spectrophotometer using KBr pellets. GPC analysis was performed on a Polymer Laboratories high temperature GPC system (model PL 220) equipped with a refractive index detector. DSC analysis was performed on a Perkin-Elmer DSC7 calorimeter. GC(MS) of dimeric products was conducted on a GC Perkin Elmer Clarus 680 with Phenomenex column model Zebron ZB-5MS and MS detector Clarus SQ8T. Thin layer chromatography (TLC) was performed using Merck GF-254 type 60 silica gel. Column chromatography was carried out using Merck silica gel 60 (70-230 mesh). For X-ray crystal structure analysis, data sets were collected with a Nonius Kappa CCD diffractometer by Dr. Constantin G. Daniliuc; full details can be found in the independently deposited crystallography information files (cif), CCDC numbers: 1430776 for compound 1, 1430777 for compound **2**, 1430778 for compound **3** and 1430779 for compound **4**.

¹³C NMR spectra of the obtained polymers were measured at 120 °C, on a Varian 300, operating 75 MHz. Polymer samples were prepared in *o*-dichlorobenzene and benzene- d_6 (20% v/v) in a 5-mm sample tube.

2.4. Polymerization tests

2.4.1. Polymerization at 1 bar of ethylene in a NMR tube with J. Young valve

Polymerizations were carried out in a NMR tube with *J. Young* valve, loaded inside a glove-box with the appropriate amount of the precatalyst (**4**, **5** and **6**), the corresponding Lewis acid ($B(C_6F_5)_3$, BCl_3 or BF_3) and $CDCl_3$ as solvent. The tube was sealed with the valve inside the glove-box and was attached to a *Schlenk* line with ethylene. Ethylene was fed into the tube to a pressure of 1 bar and ¹H NMR was measured every 30 minutes. After the corresponding time, the reaction mixture was filtered and stored at -30 °C for GC(MS) measurements.

2.4.2. Polymerization at 12 bar of ethylene in a Parr autoclave reactor

Polymerizations were carried out in a *Parr* autoclave reactor (100 mL), loaded inside a glove-box with the appropriate amount of the precatalyst (**4** and **6**), 5 equivalents of $B(C_6F_5)_3$ and toluene, such that the final volume of the toluene solution was 30 mL. The reactor was sealed inside the glove-box and was attached to an ethylene line. Ethylene was fed continuously into the reactor to a pressure of 12 bar. The pressurized reaction mixture was stirred at the appropriate temperatures. After 10 min, the ethylene was vented and acetone was added to quench the polymerization. The precipitated polymer was collected by filtration and dried overnight.

3. Results and discussion

3.1. Synthesis and characterization of cationic methallyl Ni complexes

The reaction sequence to obtain the cationic Ni complexes started with the synthesis of the new indazole derivative ligands **1-3**, which was accomplished using an addition reaction between equimolar amounts of the respective imidoyl chloride [16] and the respective methyl-1*H*-indazole-carboxylate derivatives as is shown in Scheme 1. Each ligand was isolated as a pale orange solid in good yield and characterized by elemental analyses, FT-IR, NMR spectroscopy, mass spectrometry and X-ray crystallography.

¹H NMR spectra confirm the formation of one isomer for each ligand and show the chemical shifts of the CH_3^{iPr} fragment as a double doublet in the region of 1.20 ppm. In addition, a septet at 2.94 ppm was observed, that correspond to the HC^{iPr} protons of the aniline moiety. At ~ 4.00 ppm a singlet belonging to the $CH_3^{C=N}$ group of the imine is observed. Moreover, ligands 1-3 were characterized by X-ray crystallography and their structures are shown in Fig. 2. These ligands exhibit an *E* configuration in the imine, meanwhile the diisopropylphenyl groups are orthogonal to the indazole ring plane. *For further details of the characterization, see Supplementary data.*

These ligands are neutral and capable of coordinate to metal center in a N,N fivemembered ring manner and have a methoxycarbonyl functional group which can modify the electronic properties of the ligand. This promotes the oligomerization or polymerization catalysis. A diisopropylphenyl substituent was incorporated to provide steric hindrance around the nickel center as was reported by Brookhart et al. [3]

The methallyl nickel complexes formation proceeded smoothly upon the direct reaction of two equivalents of the respective ligands **1-3** with one equivalent of $[(\eta^3 - CH_3C(CH_2)_2)NiCl]_2$ [12] in the presence of one equivalent of NaBAr'₄ (Ar': 3,5-bis(trifluoromethyl)phenyl).[17] This reaction was carried out at room temperature, and to this way forming compounds **4-6** as orange solids in 70%, 80% and 86% yield respectively (see Scheme 1 and *Supplementary data*).

The selected NMR characterization data of complexes **4-6** are summarized in Table 1 and are consistent with the formation of a single isomer containing a nickel center coordinated to the respective ligand in a *N*,*N* fashion and to a η^3 -(CH₂)₂CCH₃ as a secondary ligand. Complexes **4-6** exhibit similar ¹H NMR spectra, having distinctive chemical shifts for $CH_3^{OC=O}$, HC^{iPr} and CH_3^{iPr} . The methyl group in methoxy carbonyl substituent is shown as a singlet at δ 4.12, 3.99 and 3.83 ppm for complex **4**, **5** and **6**, respectively, confirming the presence of the functional group. The methine proton of diisopropyl groups substituent are distinct between each other, giving rise to a pair of septets HC^{iPr} shifts (3.23; 2.84 ppm for **4**, 3.20 ; 2.85 ppm for **5**, 3.11 ; 2.76 ppm for **6**). A total of three doublets in the ¹H NMR are observed, which correspond to the CH_3^{iPr} shifts (1.31; 1.17; 1.07 ppm for **4**, 1.30; 1.17; 1.08 ppm for **5**, 1.20; 1.08; 0.99 ppm for **6**).

Regarding to the secondary ligand, in all three complexes **4-6**, the signals of the allylic hydrogen protons are well defined and sharp. Each of these signals, exhibit a highly restricted movement on the NMR time scale (δ 3.82, 2.79, 2.52 and 2.37 ppm for **4**; 3.50, 2.65, 2.57 and 2.38 ppm for **5**; 3.40, 2.49 and 2.30 ppm for **6**).¹³C NMR characterization display the presence of the ^{MeO}*C*=O, ^{N-C}*C*^{C=N} and *C*H₃^{OC=O} carbon atom. For ^{MeO}*C*=O group, the ¹³C NMR shifts are 159.6 ppm (**4**), 164.6 ppm (**5**) and 165.7 ppm (**6**). For ^{N-C}*C*^{C=N} carbon atom, the shifts are 160.7 ppm (**4**), 160.3 ppm (**5**) and 160.5 ppm (**6**). Finally, for *C*H₃^{OC=O} carbon atom, the ¹³C NMR shifts are 54.1ppm (**4**), 52.9 ppm (**5**) and 53.4 ppm (**6**).

The ¹¹B and ¹⁹F NMR spectra of complexes **4-6** show characteristic singlets for the $B(Ar')_4$ counterion in CDCl₃, indicating that these counterions are "free" ions and are not or to a very small extent only ion-pairing with the cationic complex parts (¹¹B: -6.5 ppm ($v_{1/2} = 11 \text{ Hz}$); ¹⁹F: -62.4 ppm) (*For further information, see Supplementary data*).

The molecular structure of complex **4** was determined by an X-ray diffraction study and is shown in Fig. 3. The crystal structures of the complex confirm a four coordinated nickel metal center, which adopts an almost ideal square-planar geometry. The dihedral angle corresponding to *N*,*N* chelate section is -0.4° (N1-C43-C41-N3) and the Ni-N1 ; Ni-N3 bond lengths are 1.932(5) and 1.934(5) Å, respectively. These distances are in agreement with similar Ni complexes reported on literature.[13] All Ni-C_{methallyl} bond lengths are within the range of 1.986(5) - 2.070(5) Å, typically for η^3 -methallyl ligated nickel complex. The methoxycarbonyl group (CH₃^{OC=O}) group is rotated out of indazole plane with a dihedral angle of -35.0(1)° (N1-C1-C31-O1). In regard to 2,6-diisopropylphenyl substituent, this lies rotated out of the central ligand frame, staying orthogonal to the indazole plane (dihedral angle: -83.0(8)° (C8-N3-C11-C16)).

3.2. Reactivity of complexes toward ethylene

In order to study the reactivity of complexes 4-6, ethylene oligomerization reactions were conducted at NMR scale using chloroform-d as solvent and the obtained products were analyzed by mass spectrometry. Likewise, the reaction conditions were optimized, as well as the co-activator used, the temperature, and the ethylene pressure. The selected results are summarized in Table 2.

¹H NMR spectroscopy analysis showed that complexes **4-6** do not act as single component. The complexes reactivity was then tested with five equivalents of $B(C_6F_5)_3$ as a reference coactivator, 1 atm of ethylene pressure and 20 °C as reaction temperature. Complexes **4** and **6** were active to ethylene dimerization; meanwhile complex **5** does not exhibit reactivity. This is due to the position of the electron withdrawing methoxycarbonyl functional group in the indazole ring. The positions activated by electronic delocalization are the 3 and 6 (complex **4** and **6**, respectively) as is shown in Fig. 4, while position 5 is not activated by conjugation, having only an inductive electron withdrawing effect (complex **5**). It

failed to generate a sufficiently deficient electron density metal center as to be reactive towards ethylene. Remarkable is the fact that the complexes proved to be stable in the air, showing the same activity in the case of complex **4** and **6** even after being exposed for 48 hours.

Coactivator was then evaluated, studying the complex **4** and **6** at 20 °C, 1 atm of ethylene pressure and five equivalents of three different Lewis acids as coactivators (BF₃, BCl₃ and B(C₆F₅)₃), exhibiting the activation of the complexes only by using B(C₆F₅)₃.

The analysis of the ¹H NMR of the ethylene dimerization reactions (Scheme 2) showed that complex **4** exhibit a series of new chemical shifts in the olefinic region at δ 5.87 and 4.95 ppm and in the aliphatic region at δ 1.62 and 1.00 ppm, that suggest the formation of a terminal olefin (see Fig. 5a). Additionally, it was observed a new shift at δ 5.45 ppm, which was assigned to the protons of an internal double bond because of an isomerization of the terminal olefin. Obtaining an isomer distribution of 50% of 1-butene and 50% of 2-butene with a catalytic activity of 0.5 Kg pol mol⁻¹ h⁻¹ (Entry 1, Table 2).

By contrast, complex **6** only shows the shifts at δ 5.45 ppm, which are assigned to the protons of an internal double bond as a result of the isomerization of the terminal olefin (see Fig. 5b), producing 100% of 2-butene with a catalytic activity of 1.2 Kg pol mol⁻¹ h⁻¹ (Entry 2, Table 2). These results are consistent with the fact that the complex **4** has a higher steric hindrance around the metal center than the complex **6**, caused by the presence of the methoxycarbonyl group in the insertion area, decreasing the catalytic activity and preventing the reinsertion of the terminal olefin, favoring the formation of 1-butene.

As system $6/B(C_6F_5)_3$ was two times more active toward ethylene dimerization, the effect of the reaction pressure over this system at 20 °C was evaluated, using 12 bar of ethylene pressure in chloroform as solvent. Amazingly, the formation of a wax was observed, with an activity 330 times higher than the reaction at 1 bar of ethylene (401 Kg pol mol⁻¹ h⁻¹, Entry 3, Table 2). This is considered a high catalytic activity and is twice active than similar Ni complexes previously reported by our group.[13] The reaction product was characterized by DSC and GPC, showing a melting point of 119 °C and a molecular weight of 26.6x10³ g/mol, respectively. Microstructural analysis of this polymer was performed using ¹³C NMR

spectroscopy, where the assignation of their respective spectra and the nomenclature used were done according to literature.[6] As shown in Fig. 6a, the polymer obtained at 20 °C and 12 bar of ethylene, is composed mainly by methyl branches (2.3 mol%) and by a small amount (0.4 mol%) of long branches (n \geq 6). It was thus possible to obtain a highly active catalyst capable to produce low molecular weight polyethylene, where the 85% of the total branches are methyl kind.

Finally, the activity of $6/B(C_6F_5)_3$ at 12 bar of ethylene and 60 °C was evaluated, seeking to determine the influence of temperature on the catalytic activity and the morphology of the obtained product. It was found that by increasing the reaction temperature, the catalytic activity increased by 20% (487 Kg pol mol⁻¹ h⁻¹, Entry 4, Table 2). The molecular weight of the obtained product was 1.8×10^3 g/mol (M_n) and is completely amorphous, as was observed from the DSC where it was not possible to measure any thermal transition.

Microestructural analysis of the polymer by ¹³C NMR showed that the product morphology changes dramatically with the reaction temperature (see Fig. 6b), increasing nine times the total branches in the wax and exhibiting a broad distribution of chain lengths in the branches. This highly branched polymer shown the presence of methyl branches (8.7 mol%) at 19.90 ppm (1B₁), 27.42 ppm (β B₁), 30.36 ppm (γ B₁), 33.14 ppm (brB₁) and 37.47 ppm (α B₁). Ethyl branches (2.3 mol%) are confirmed by the presence of resonances at 11.10 ppm (1B₂), 26.51 ppm (2B₂) and 39.44 ppm (brB₂). Propyl branches (3.2 mol%) are mainly represented by resonances at 14.65 ppm (1B₃) and 36.72 ppm (3B₃), butyl branches (1.4 mol%) by resonance at 23.37 ppm (2B₄), amyl branches (0.6 mol%) by resonance at 32.65 ppm (3B₅) and long branches (6.9 mol%) by resonances at 29.59 ppm (4B_n) and 32.16 ppm (3B_n). Note that the methyl branches are only the 38% of the total. This catalytic behavior is consistent with higher reaction temperature, where increasing the rate of chain termination is due to the raise of the β -elimination.[18]

4. Conclusions

Three new neutral N,N chelate ligands derived from methyl-1H-indazole-carboxylate **1-3** were successfully synthesized and characterized. The X-ray single crystal characterization shown an E configuration in the imine and the diisopropylphenyl groups were orthogonal to the indazole ring plane. From these ligands, cationic Ni complexes **4-6** bearing also a

methallyl ligand were prepared in high yields and characterized by NMR, FT-IR and elemental analyses. The X-ray diffraction study was performed for complex **4** and confirms an almost ideal square-planar geometry with a four coordinated nickel metal center.

Complexes 4-6 were activated for ethylene dimerization by 5 equivalents of $B(C_6F_5)_3$. These compounds bear an electron withdrawing functional group in different ring positions, which influenced dramatically in their reactivity. At 1 bar of ethylene and 20 °C, complex 4 was able to produce a mixture of butenes, with a distribution of 50% of 1-butene and 50% of 2-butene. By other hand, complex 5 was not active and complex 6 was the most active, producing 100% of 2-butene. In addition, it was found that complexes 4 and 6 showed an unusual stability in air, and were reactive towards ethylene even after exposure to air for 48 hours.

By increasing the pressure to 12 bar at 20 °C, complex **6** showed a catalytic activity of 401 Kg product (mol Ni)⁻¹ h⁻¹, being 330 times higher than the reaction at 1 bar of ethylene. At the same time, this increase in pressure caused that the catalyst was able to produce polyethylene with a molecular weight of 26.6×10^3 g/mol and almost exclusively methyl branches (2.3 mol%). In addition, by increasing the temperature to 60 °C at 12 bar of ethylene the system **6** / B(C₆F₅)₃ it increased its catalytic activity to 487 Kg product (mol Ni⁻¹) h⁻¹ and was capable of generating a wax with a molecular weight of 1.8×10^3 g/mol and with a broad distribution of branches, being the methyl only the 38% of total.

It is remarkable that complex 6 is able to generate several products only by changing the reaction conditions as well as the location of the substituent in the indazole derivative ring allows us to modulate the catalytic activity of the complexes. These catalytic results encourage us to continue our research toward the optimization of these types of Ni complexes, aiming to control of the molecular weight and the branching degree of the polymer obtained.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, including spectroscopic and crystallographic details: CCDC-1430776 for **1**, CCDC-1430777 for **2**, CCDC-1430778 for **3** and CCDC-1430779 for **4**.

References

- [1] (a) H. Mu, L. Pan, D. Song, Y. Li, Chem. Rev. (2015) DOI:10.1021/cr500370f .(b) M.
 Poyatos, J.A. Mata, E. Peris, Chem. Rev. 109 (2009) 3677-3707. (c) G.J. Domski, J.M.
 Rose, G.W. Coates, A.D. Bolig, M. Brookhart, Prog. Polym. Sci. 32 (2007) 30-92.
- [2] (a) A. Nakamura, S. Ito, K. Nozaki, Chem. Rev. 109 (2009) 5215-5244. (b) D. Takeuchi, Dalton Trans. 39 (2010) 311-328. (c) Z. Guan, Chem. Asian J. 5 (2010) 1058-1070.
- [3] (a) S.D. Ittel, L.K. Johnson, M. Brookhart, Chem. Rev. 100 (2000) 1169-1204. (b) W.-H. Sun, W. Kaminsky (Eds.), Polyolefins: 50 Years after Ziegler and Natta II. Polyolefins by Metallocenes and Other Single-Site Catalysts, Springer, New York, 2013, pp. 163-178. (c) H. Makio, H. Terao, A. Iwashita, T. Fujita, Chem. Rev. 111 (2011) 2363-2449. (d) M.C. Baier, M.A. Zuideveld, S. Mecking, Angew. Chem., Int. Ed. 53 (2014) 9722-9744.
- [4] A.W. Qiu, M. Pyda, E. Nowak-Pyda, B.W. Habenschuss, K.B. Wagener, J. Polym. Sci. Part B Polym. Phys. 44 (2006) 3461-3474.
- [5] G.J.A. Smith, K.B.W. Lieser, G. Wegner, Polym. Prepr. 42 (2001) 454-457.
- [6] G.B. Galland, R.F. de Souza, R.S. Mauler, F.F. Nunes, Macromolecules 32 (1999) 1620-1625.
- [7] X. Wang, Y.L.Y. Wang, X. Shi, Y. Liu, C. Chen, Macromolecules 47 (2014) 552-559.
- [8] R.C. Klet, C.N. Theriault, J. Klosin, J.A. Labinger, J.E. Bercaw, Macromolecules 47 (2014) 3317-3324.
- [9] (a) J. Heinicke, M. Kohler, N. Peulecke, M.K. Kindermann, W.Keim, M. Kockerling, Organometallics 24 (2005) 344-352. (b) M. Chen, W. Zou, Z. Cai, C. Chen, Polym. Chem. 6 (2015) 2669-2676. (c) C.B. Shim, Y.H. Kim, B.Y. Lee, Y. Dong, H. Yun, Organometallics 22 (2003) 4272-4280. (d) W. Liu, J.M. Malinoski, M. Brookhart, Organometallics 21 (2002) 2836-2838. (e) B. Lee, Y. Kim, H. Shin, C. Lee, Organometallics 21 (2002) 3481-3484. (f) M.C. Bonnet, F. Dahan, A. Ecke, W. Keim, R.P. Schulz, I.J.Tkatchenko, Chem. Soc., Chem. Commun. 5 (1994) 615-616. (g) B.Y. Lee, X. Bu, G.C. Bazan, Organometallics 20 (2001) 5425-5431.
- [10] W. Liu, J.M. Malinoski, M. Brookhart, Organometallics 21 (2002) 2836-2838.
- [11] (a) Z.J.A. Komon, X. Bu, G.C. Bazan, J. Am. Chem. Soc. 122 (2000) 12379-12380. (b)

J.D. Azoulay, Z. Koretz, G. Wu, G.C. Bazan, Angew. Chem. 122 (2010) 8062-8066.(c) J.D. Azoulay, R.S. Rojas, A.V. Serrano, H. Ohtaki, G.B. Galland, G. Wu, G.C. Bazan, Angew. Chem., Int. Ed. 48 (2009) 1089-1092.

- [12] C.B. Shim, Y.H. Kim, B.Y. Lee, Y. Dong, H. Yun, Organometallics 22 (2003) 4272-4280.
- [13] (a) O.S. Trofymchuk, D.V. Gutsulyak, C. Quintero, M. Parvez, C.G. Daniliuc, W.E. Piers, Organometallics 32 (2013) 7323-7333. (b) M. Escobar, O.S. Trofymchuk, B.E. Rodriguez, C. Lopez-Lira, R. Tapia, C. Daniliuc, H. Berke, F.M. Nachtigall, L.S. Santos, R.S. Rojas, ACS Catal. 5 (2015) 7338-7342.
- [14] O.S. Trofymchuk, G.B. Galland, M.A. Milani, R.S. Rojas, J. Polym. Sci. Part A Polym. Chem. 53 (2015) 452-458.
- [15] R.F. de Souza, R.S. Mauler, L.C. Simon, A. Nunes, D.V. Vescia, F.F. Cavagnolli, Macromol. Rapid Commun. 18 (1997) 795-800.
- [16] C. Quintero, M. Valderrama, A. Becerra, C.G. Daniliuc, R.S. Rojas, Org. Biomol. Chem. 13 (2015) 6183-6193.
- [17] N.A Yakelis, R.G. Bergman, Organometallics 24 (2005) 3579-3581.
- [18] S.D. Ittel, L.K. Johnson, M. Brookhart, Chem. Rev. 100 (2000) 1169-1203.



Fig. 1. Nickel methallyl complexes previously reported.



Fig. 2. X-ray crystal structure of the ligand **1** (a), ligand **2** (b) and ligand **3** (c) with thermal ellipsoids drawn at the 30% probability level.



Fig. 3. X-ray crystal structure of **4** with thermal ellipsoids drawn at the 30% probability level. $B(ArF)_4^-$ counterion was omitted for clarity.



Activated positions: **3** and **6** Unactivated position: **5**

Ar: 2,6-diisopropylphenyl





Fig. 5. ¹H NMR spectra of: (a) $4/B(C_6F_5)_3/ethylene$; (b) $6/B(C_6F_5)_3/ethylene$.



Fig. 6. ¹³C NMR spectra of the polymers obtained at: (a) $6/B(C_6F_5)_3/12$ bar/20 °C; (b) $6/B(C_6F_5)_3/12$ bar/60 °C.



(i) (2,6-diisopropylphenyl)acetimidoyl chloride, toluene, \triangle , 12h. (ii) $\frac{1}{2} [(\eta^3-CH_3C(CH_2)_2)NiCl]_2$, NaB(Ar`)₄, CH₂Cl₂, R.T., 2h.

Ar`: 3,5-bis(trifluoromethyl)phenyl

Scheme 1. Synthetic route for ligands 1-3 and cationic methallyl Ni complexes 4-6.



Scheme 2. Dimerization of ethylene using $4-6/B(C_6F_5)_3$ at 1 bar of C_2H_4 .

	4	5	6				
¹³ C NMR (ppm)							
Indazole-N C^{N-Ar}	160.7	160.3	160.5				
<i>C</i> H ^{Indazole}	127.5	146.3					
$CH_2^{Methallyl}$	63.2, 61.4	62.9, 56.8	63.2, 57.1				
$\mathbf{H}C^{i\mathrm{Pr}}$	28.9, 28.7	28.9, 28.7	29.1, 28.9				
$CH_3^{Methallyl}$	22.5	23.0	23.1				
<i>C</i> H ₃ ^{C-N}	17.2	16.4	16.6				
¹ H NMR(ppm)							
C H ^{Indazole}	-	8.46	8.26				
$CH_3^{OC=O}$	4.12	3.99	3.83				
$CH_2^{Methallyl}$	3.82, 2.79	3.50, 2.65	3.40, 2.49				
	2.52, 2.37	2.57, 2.38	2.30				
HC^{iPr}	3.23, 2.84	3.20, 2.85	3.11, 2.76				
CH_3^{C-N}	2.59	2.60	2.57				
$CH_3^{Methallyl}$	2.21	2.17	2.07				
¹¹ B NMR / ¹⁹ F NMR (ppm)							
	-6.7 / -62.5	-6.5 / -62.4	-6.6 / -62.4				
a		-					

Table 1: Selected NMR parameters of complexes 4-6.^a

^a NMR spectra in chloroform-*d* solution.

Entry	Complex	Pb	Tc	Ad	Mne	PDI	T _m f	Isomer distribution ^g / ramification ^h
1	4	1	20	0.5	-	-	-	50% 1-butene ; 50% 2-butene
2	6	1	20	1.2	-	-	-	100% 2-butene
3	6	12	20	401	26.6	1.8	119	2.3 mol% methyl ; 0.4 mol% larger
4	6	12	60	487	1.8	2.3	n.o.	8.7 mol% methyl ; 14.4 mol% larger

Table 2: Selected ethylene oligomerization reactions.^a

^a Oligomerization were carried out with 3.7 µmol of Ni, CHCl₃ as solvent and the cocatalyst

was 5 equivalents of B(C₆F₅)₃. Duration of reaction was 1 hour. ^b Ethylene pressure (in bar). ^c Temperature of reaction (in °C). ^d Catalytic activity (in Kg pol mol⁻¹ h⁻¹). ^e in x10³ g/mol. ^f Melting point in °C as determined by DSC. ^g Determined by GC-MS(ESI). ^h Determined by ¹³C NMR spectroscopy at 120 °C, in *o*-dichlorobenzene and benzene- d_6 (20% v/v) solution. n.o.: not observed.