



# New air stable cationic methallyl Ni complexes bearing imidoyl-indazole carboxylate ligand: Synthesis, characterization and their reactivity towards ethylene

Alan R. Cabrera<sup>a,d,\*</sup>, Ivan Martinez<sup>a</sup>, Constantin G. Daniliuc<sup>b</sup>, Griselda B. Galland<sup>c</sup>, Cristian O. Salas<sup>a</sup>, Rene S. Rojas<sup>a,\*</sup>

<sup>a</sup> Nucleus Millennium of Chemical Processes and Catalysis, Faculty of Chemistry, Pontificia Universidad Católica de Chile, Casilla 306, Santiago, Chile

<sup>b</sup> Chemisches Institut der Universität Münster, Corrensstrasse 40, 48149 Münster, Germany

<sup>c</sup> Instituto de Química, Universidade Federal do Rio Grande do Sul, Porto Alegre, Brazil

<sup>d</sup> Universidad Bernardo O Higgins, Departamento de Ciencias Químicas y Biológicas, Laboratorio de Bionanotecnología, General Gana 1702, Santiago, Chile

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## 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** toward 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 h. By increasing the pressure to 12 bar at 20 °C, complex **6** showed a catalytic activity of 401 Kg product (mol Ni)<sup>-1</sup> h<sup>-1</sup>, 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**/ $B(C_6F_5)_3$  increased its catalytic activity to 487 Kg product (mol Ni)<sup>-1</sup> h<sup>-1</sup>, but produced a significant decrease in the molecular weight of the polymer (1.8 Kg/mol) and a broad distribution of branches.

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## 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 toward 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  $\beta$ -diketimine *N,N* chelating ligand (Fig. 1c) [13]. This complex was remotely activated by using  $B(C_6F_5)_3$  as Lewis acid, which formed a strong coordination adduct between the cyano group and the borane. This adduct was active toward 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 Ni-methallyl complexes that bear a *N,N* chelating ligand corresponding to  $\alpha$ -diimine or  $\beta$ -diimine kind of [15]. Of interest is our research on Ni-methallyl complexes with a new type

\* Corresponding authors at: Nucleus Millennium of Chemical Processes and Catalysis, Faculty of Chemistry, Pontificia Universidad Católica de Chile, Casilla 306, Santiago, Chile.

E-mail address: [arcabrer@uc.cl](mailto:arcabrer@uc.cl) (A.R. Cabrera).

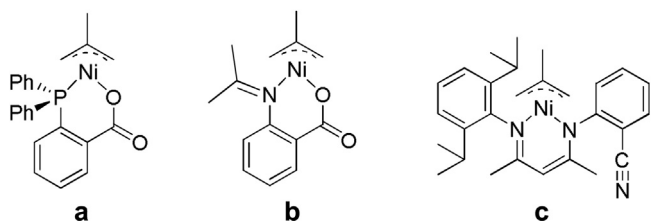


Fig. 1. Nickel methallyl complexes previously reported.

of *N,N* ligand that exhibits high activities toward  $\alpha$ -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 toward ethylene, using  $B(C_6F_5)_3$  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,  $CD_3Cl$ , 298 K):  $\delta/ppm$  = 8.87 (d,  $J$  = 8.4 Hz, 1H), 8.32 (d,  $J$  = 8.4 Hz, 1H), 7.55 (t,  $J$  = 8.4 Hz, 1H), 7.41 (t,  $J$  = 8.4 Hz, 1H), 7.19 (m, 3H), 4.07 (s, 3H), 2.95 (hept,  $J$  = 6.9 Hz, 2H), 2.54 (s, 3H), 1.21 (d,  $J$  = 2.0 Hz, 6H), 1.18 (d,  $J$  = 2.0 Hz, 6H).  $^{13}C\{^1H\}$  NMR (100 MHz,  $CD_3Cl$ , 298 K):  $\delta/ppm$  = 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,  $CD_3Cl$ , 298 K):  $\delta/ppm$  = 8.86 (d,  $J$  = 8.9 Hz, 1H), 8.54 (s, 1H), 8.22 (s, 1H), 8.21 (m, 1H), 7.20 (d,  $J$  = 7.4 Hz, 2H), 7.13 (t,  $J$  = 7.4 Hz, 1H), 3.95 (s, 3H), 2.94 (hept,  $J$  = 6.8 Hz, 2H), 2.45 (s, 3H), 1.19 (t,  $J$  = 7.4 Hz, 12H).  $^{13}C\{^1H\}$  NMR (100 MHz,  $CD_3Cl$ , 298 K):  $\delta/ppm$  = 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 (%)  $C_{23}H_{27}N_3O_2$  ( $M$  = 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 ( $C_{23}H_{28}N_3O_2$  [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,  $CD_3Cl$ , 298 K):  $\delta/ppm$  = 9.45 (s, 1H, H14), 8.19 (s, 1H), 8.02 (d,  $J$  = 8.5 Hz, 1H), 7.82 (d,  $J$  = 8.5 Hz, 1H), 7.24 (d,  $J$  = 8.1 Hz, 2H), 7.15 (m, 1H), 3.91 (s, 3H), 2.94 (hept,  $J$  = 6.8 Hz, 2H), 2.43 (s, 3H), 1.20 (dd,  $J$  = 7.0, 2.9 Hz, 12H).  $^{13}C\{^1H\}$  NMR (100 MHz,  $CD_3Cl$ , 298 K):  $\delta/ppm$  = 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 (%)  $C_{23}H_{27}N_3O_2$  ( $M$  = 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)-1*H*-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 (20 ml). 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 h at room temperature. The resulting solution was filtered through celite and the product was crystallized adding pentane and storing at  $-20^\circ C$ . **4** was obtained as dark orange crystalline solid in 70% yield (100 mg; 0.074 mmol).  $^1H$  NMR (400 MHz,  $CD_3Cl$ , 298 K):  $\delta/ppm$  = 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).  $^{13}C\{^1H\}$  NMR (100 MHz,  $CDCl_3$ , 298 K):  $\delta/ppm$  = 161.4 (t,  $J^{CF}$  = 49 Hz), 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 Hz), 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.  $^{19}F$  NMR (400 MHz,  $CDCl_3$ , 298 K):  $\delta/ppm$  =  $-62.45$ .  $^{11}B\{^1H\}$  NMR (400 MHz,  $CDCl_3$ , 298 K):  $\delta/ppm$  =  $-6.65$  ( $\nu_{1/2}$   $\sim$  11 Hz). Elemental analysis (%)  $C_{59}H_{46}BF_{24}N_3NiO_2$  ( $M$  = 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, 0.105 mmol) and  $NaBAR_4$  (Sodium-tetrakis(3,5-bis(trifluoromethyl) phenyl) borate) (94 mg; 0.105 mmol) were mixed in dichloromethane (20 ml). The suspension was stirred vigorously and a solution of  $[(\eta^3-$

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