

New octahedral bis- α -diimine nickel(II) complexes containing chloro-substituted aryl groups: Synthesis, characterization and testing as ethylene polymerisation catalysts

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ABSTRACT

Three new 20-electron bis- α -diimine nickel (II) complexes containing chloro-substituted ligands, bis{bis[*N,N'*-(3-chloro-2-methylphenyl)imino]-1,2-dimethylethane}dibromonickel **2a**, bis{bis[*N,N'*-(3-chloro-2,6-dimethylphenyl)imino]-1,2-dimethylethane}dibromonickel **2b** and bis{bis[*N,N'*-(4-chloro-2,6-dimethylphenyl)imino]-1,2-dimethylethane}dibromonickel **2c**, were synthesized and characterized. The molecular structure of complex **2a** was determined by X-ray crystallography. In the solid state, complex **2a** has a pseudo-octahedral geometry about the nickel center, containing two α -diimine ligands in the pseudo-equatorial plane and two *trans* bromide ligands occupying the axial positions. These complexes, activated by diethylaluminum chloride (DEAC) were tested in the polymerization of ethylene under mild conditions. NMR analysis shows that highly branched polyethylenes are obtained using these bis- α -diimine nickel(II) complexes containing electron-withdrawing Cl groups in the aryl groups (e.g. 84 branches/1000 C, at 20 °C). The catalytic activity, polymer molecular weight and polymer degree of branching were significantly affected by the number of methyl substituents in the *ortho*-aryl position and the chlorine substituent position in the aryl rings of the coordinated α -diimine ligands.

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1. Introduction

The discovery of Ni(II) and Pd(II) α -olefin polymerisation catalysts containing a bulky α -diimine ligand, [MX₂(α -diimine)] (M = Ni, Pd; X = halide), by Brookhart and co-workers [1–8], has stimulated renewed interest in the chemistry of 1,4-diazadiene ligands and their complexes. The coordination chemistry of α -diimine ligands of the type *N,N'*-diaryl-1,4-diaza-1,3-butadiene (Ar-DAB) or bis(arylimino)acenaphthene (Ar-BIAN) to late transition metals has attracted much interest due to their unusual electron donor and acceptor properties [9,10]. Organometallic compounds containing Ar-DAB or Ar-BIAN ligands have been extensively studied in recent years as catalysts for the oligomerisation and polymerisation of α -olefins [11–17].

The ligand structure has a dramatic effect on the reactivity of organometallic complexes. This has been especially evident in the

recent development of late transition metal olefin polymerization catalysts. A variety of α -diimine ligands containing substituted *N*-aryl rings, including those with steric bulk and *ortho* and *para* substituted position modifications in the aryl rings [18–24], backbone effects on the α -diimine ligand structure [25–29], chiral α -diimine ligand systems [30,31], teraryl substituted- α -diimine ligands [32–35], cyclophane-based α -diimine ligands [36–39], were employed to study their influence on the catalytic activity of the 16-electron Ni(II) and Pd(II) [MX₂(α -diimine)] precatalysts. However, the effect of electron-withdrawing *N*-aryl rings substituents, especially of Cl atoms, on the catalytic behavior of α -diimine-Ni(II) complexes and the properties of the resulting polymers has only been reported in limited cases.

Conversely, the report of 20-electron complexes of NiX₂ bearing four coordinated nitrogen atoms that exhibit catalytic activity in the oligomerization or polymerization of olefins has also been scarce, being limited to the cases where the NiX₂ fragment is coordinated to two α -diimine ligands of the aryl-BIAN type ([NiBr₂(Ar-BIAN)₂]) [21] or to a tetradentate *N,N,N,N*-chelating α -diimine ligand ([NiBr₂(*N,N,N,N*- α -diimine)]) [40,41].

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In this paper, we report the synthesis and characterization of three new 20-electron octahedral bis- α -diimine Ni(II) complexes of the type $[\text{NiBr}_2(\text{Ar-DAB})_2]$ bearing electron-withdrawing substituents Cl in the *para*- or *meta*-aryl positions of the Ar-DAB ligand and their catalytic behaviors in the polymerization of ethylene when activated by diethylaluminum chloride (DEAC).

2. Results and discussion

2.1. Synthesis and characterization of ligands **1a–c** and complexes **2a–c**

The general synthetic route to three nickel(II) complexes **2a–c** is shown in Scheme 1. The free Ar-DAB ligands **1a–c** were prepared by the condensation of two equivalents of the appropriate aniline with one equivalent of 2,3-butanedione, usually in the presence of an acid catalyst. The compounds (**1a–c**) were characterized by ^1H NMR and ^{13}C NMR and were found elementally pure.

The reaction of 1 equivalent of $[\text{NiBr}_2(\text{DME})]$ and 2 equivalents of the α -diimine ligands **1a–c**, in CH_2Cl_2 , led to the displacement of 1,2-dimethoxyethane and afforded the catalyst precursors **2a–c** as moderately air-stable light red microcrystalline solids in good yields. Due to the geometry around the nickel atom, these bis- α -diimine Ni(II) complexes are paramagnetic and their ^1H NMR is not assignable. The elemental analyses of complexes **2a–c** fit the stoichiometry Ni: α -diimine of 1:2 ($[\text{NiBr}_2(\text{Ar-DAB})_2]$), which is further corroborated by the molecular structure obtained by X-ray structural studies. In fact, suitable crystals of **2a** for X-ray diffraction were obtained by double layering a solution of the complex in CH_2Cl_2 with *n*-hexane. The molecular structure of complex **2a** was determined and the corresponding ORTEP diagram is shown in Fig. 1, while selected bond distances and angles are summarized in Table 1.

In the solid state, the structure of complex **2a** shows two Ar-DAB and two bromide ligands featuring a six-coordinate distorted octahedral geometry around the nickel center, having a C_2 molecular symmetry. The nickel atom occupies a crystallographic inversion centre and only a half of the molecule is symmetry independent. The two α -diimine ligands coordinate the nickel atom in the equatorial plane, their corresponding DAB planes making a dihedral angle of 11.25° , whereas the two bromide ligands lie in the axial positions, their bonds to the nickel atom being perpendicular (89.98°) to the average plane defined by the nitrogens and the nickel atoms. Its structure is quite similar to that reported in the literature for the other $[\text{NiX}_2(\text{N,N}'\text{-diaryl-}\alpha\text{-diimine})_2]$ compound characterized by X-ray, the bis[bis(*N,N'*-2,3-dichlorophenylimino)

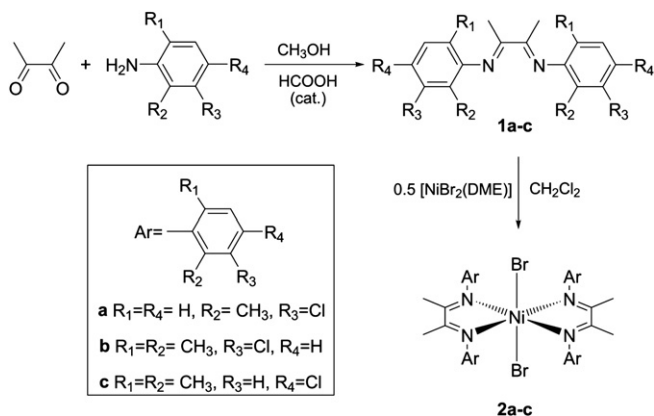
acenaphthene]dibromonickel [21], which contains two α -diimine ligands of the aryl-BIAN type. In fact, the Ni–N bond distances in complex **2a** (2.112–2.116 Å) are similar to that determined for that compound (2.144 Å), as well as the Ni–Br bond distances (2.5797–2.6128 Å for complex **2a** vs. 2.5354 Å) and the two bromine atoms are situated in the *trans*-position (Br–Ni–Br angle, 179° for complex **2a** vs. 180°), whereas the halide ligands display a *cis* geometry in the majority of the other nickel complexes containing two DAB-type ligands with non-aryl and non-bulky *N*-imine substituents [42–46]. The two imino C=N bonds have typical double bond character with C=N bond lengths of 1.272 Å. The aryl rings of each of the α -diimines lie nearly perpendicular to the plane formed by the nickel and coordinated nitrogen atoms, and face each others in a staggered conformation.

2.2. Polymerization of ethylene with nickel complexes **2a–c**

The three complexes **2a**, **2b** and **2c**, activated by diethylaluminum chloride (DEAC), were tested as catalyst precursors for the polymerization of ethylene, under the same reaction conditions. The results of the polymerization experiments are shown in Table 2. Noteworthy is the fact that blank experiments carried out with DEAC alone, under similar conditions, showed its inability to polymerize ethylene on its own.

For a ratio $[\text{Al}]/[\text{Ni}] = 600$, an increase in the reaction temperature in the range $0\text{--}40^\circ\text{C}$ increases the activity of precatalysts **2b** and **2c** (containing two methyl substituents in both *ortho* aryl positions) activated by DEAC, (**2b**: entries 6–8; **2c**: entries 11–13), while precatalyst **2a** (containing a single methyl substituent in one of the *ortho* aryl positions) revealed to be inactive (entries 1–3). An increase of the $[\text{Al}]/[\text{Ni}]$ ratio in the range 600–1500 increases the activity of all the precatalysts, at 20°C , which seem to go through a maximum around $[\text{Al}]/[\text{Ni}] = 1000$ (**2a**: entries 2, 4 and 5; **2b**: entries 7, 9 and 10; **2c**: entries 12, 14 and 15). The molecular weight of the polyethylenes (PE) produced under these conditions were found to slightly increase, in the case of **2b**, or decrease, in the cases of **2a** and **2c**, with an increasing $[\text{Al}]/[\text{Ni}]$ ratio.

The performances of the nickel precatalysts are significantly affected by the position of the chlorine substituent on the aryl rings of the bis- α -diimine Ni(II) complexes **2a–c** (Table 2). Complex **2b**, bearing a Cl substituent in the *meta*-aryl position of the ligand (two methyl groups in the *ortho*-aryl positions), displays the highest catalytic activity, of 7.08×10^5 g PE/(mol Ni·h·bar), and produces one of the highest molecular weights ($M_n = 53600$, entry 9, 20°C , $[\text{Al}]/[\text{Ni}] = 1000$) among our three complexes. Complex **2c**, bearing a Cl substituent in the *para*-aryl position of the ligand (also with two methyl groups in the *ortho*-aryl positions), exhibits a slightly lower catalytic activity of 6.81×10^5 g PE/(mol Ni·h·bar) and yields polyethylene with substantially lower molecular weight ($M_n = 39800$, entry 14, 20°C , $[\text{Al}]/[\text{Ni}] = 1000$). This shows that a Cl substituent in the *meta*-aryl position (**2b**) increases the rate of chain propagation (migratory insertion of coordinated ethylene into the Ni-chain alkyl bond) and decreases the rate of chain transfer (β -hydrogen transfer to the metal or to the monomer) in comparison with that in the *para*-aryl position (**2c**). For the same ratio $[\text{Al}]/[\text{Ni}] = 1000$, complex **2a**, bearing Cl substituent in the *meta*-aryl position in the ligand (only one methyl group in the *ortho*-aryl position), shows the lowest catalytic activity (1.90×10^5 g PE/(mol Ni·h·bar)) and produces the lowest molecular weight ($M_n = 15200$, Entry 4, 20°C) of the three precatalysts. These results indicate that the rate of chain propagation is greatly promoted by the bulkiness of the ligand's aryl rings. As a result, the following activity trend can be summarized for our Cl substituted precatalysts under low ethylene pressure (1.2 bar), in the range $0\text{--}40^\circ\text{C}$: **2b** > **2c** > **2a**.



Scheme 1. Syntheses of α -diimine ligands **1a–c** and their corresponding bis- α -diimine nickel(II) dibromide complexes **2a–c**.

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