



Ethylene polymerization by 2,3-diiminobutylnickel bromide pre-catalysts bearing remote benzhydryl substituents



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ABSTRACT

A series of remote benzhydryl-substituted 2,3-diiminobutane derivatives (**L1–L5**) was synthesized and used to react with (DME)NiBr₂ to form the corresponding 2,3-diiminobutylnickel bromide complexes (**Ni1–Ni5**). All compounds were characterized by FT-IR spectroscopy and elemental analysis as well as additional NMR measurements for organic compounds and single crystal X-ray diffraction study for a representative complex **Ni1**. Upon activation with cocatalyst Et₂AlCl, all nickel complexes exhibited high activity toward ethylene polymerization, producing polyethylenes with high molecular weights and narrow polydispersity. The existence of remote *para*-benzhydryl substituent probably retarded chain migration, which led to polyethylenes with high molecular weights and high linearity.

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Introduction

The discovery of α -diiminometal (Ni or Pd) complexes as highly active pre-catalysts in olefin polymerization was recognized as a milestone of polyolefin science [1]. Subsequently, various late-transition-metal complexes have extensively been developed as pre-catalysts toward ethylene oligomerization and polymerization [2–5]. Recently, the amount of funding devoted to the relative researches has been limited because late-transition-metal pre-catalysts have not yet met the expectations of the industry; still interestingly, novel polyethylenes obtained with nickel pre-catalysts draw great attention and show the potential to commercialization [2–4]. Though the bis(arylimino)acenaphthylnickel and 2,3-bis(arylimino)butylnickel pre-catalysts were found highly active toward ethylene polymerization [1], the low thermal stability was considered as the critical problem in the industrial application. In targeting systems of practical importance, many efforts have been undertaken to modify nickel complexes through using various substituents in bis(arylimino)acenaphthylnickel [6–15] and 2,3-bis(arylimino)butylnickel pre-catalysts [16–22]; meanwhile unique nickel pre-catalysts were also been developed through the application of newly designed *N*-coordinated bidentate ligands [23–36]. The substituents within the ligands made

significant influence on the catalytic activities of the complex pre-catalysts [2–5]; benzhydryl-substituted nickel complex pre-catalysts [9–15,20–22,29,30] drew more attention because of enhanced catalytic activities together with thermal stability. However, there are a few papers dealing with the remote substituents [37–39], in which fluoro-influence was studied due to its weak hydrogen bonds. Moreover, the remote benzhydryl substituent probably provides some interesting phenomena and affects the catalytic activity of the complex pre-catalysts. Therefore, *para*-benzhydrylphenylamine derivatives are prepared according to the literature method [40], and reacted with 2,3-butadione to form 2,3-bis(imino)butane derivatives, which further react with (DME)NiBr₂ resulting in nickel bromide complexes. Upon activation with Et₂AlCl, all title nickel complexes exhibited high activity toward ethylene polymerization and produced polyethylenes with high molecular weights and low branches. Herein we report the synthesis and characterization of the title nickel complexes as well as their catalytic behavior towards ethylene polymerization.

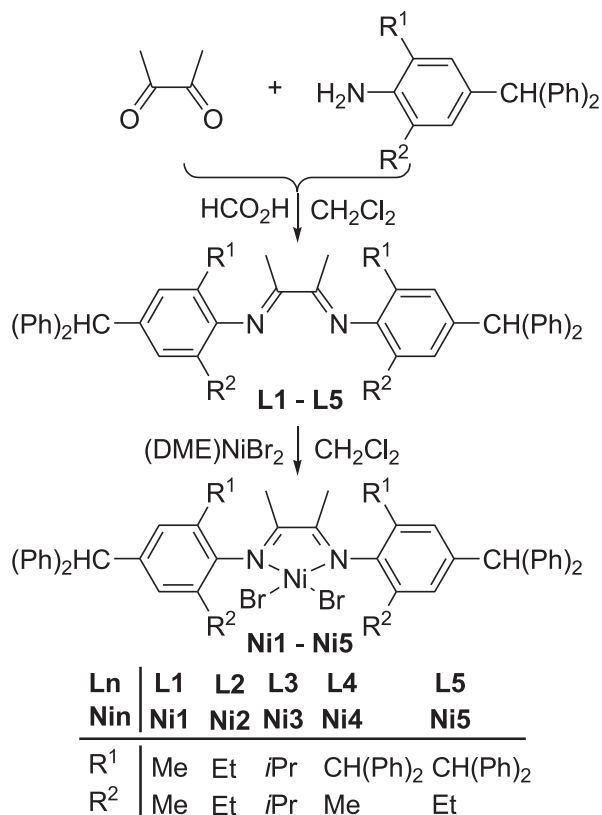
Results and discussion

Synthesis and characterization of ligands and complexes

The routine condensation reactions of 2,3-butanedione and two equivalents of 4-benzhydrylphenylamine derivatives were individually conducted to form the corresponding 2,3-diiminobutane

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Scheme 1. Synthesis of compounds L1–L5 and their nickel complexes Ni1–Ni5.

derivatives (L1–L5) according to the literature procedure [21]. The organic compounds were characterized by FT-IR, NMR measurements as well as elemental analysis. All these compounds reacted stoichiometrically with (DME)NiBr₂ in dichloromethane; the corresponding nickel (II) complexes (Ni1–Ni5) were afforded in reasonable yields (Scheme 1) and measured with FT-IR spectroscopy and elemental analysis. Comparing with the FT-IR spectra of the organic compounds, the C=N stretching frequencies in the nickel complexes were shifted into lower values (1620–1630 cm⁻¹) with weaker intensity, indicating the effective coordination between the imino-nitrogen and nickel. The unambiguous molecular structure of complex Ni1 was further confirmed by single crystal X-ray diffraction.

X-ray crystallographic study

Single crystals of complex Ni1 suitable for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into its dichloromethane solution. The molecular structure of Ni1 is shown in Fig. 1, and the selected bond lengths and angles are listed in Table 1. Like similar compounds reported in the literature [9–14,20–22], the Ni1 reveals a distorted tetrahedral geometry at the nickel center, and the apical position is occupied by the Br2 atom. The N(1)–Ni(1)–N(2) angle is 81.36(19)° and the Br(1)–Ni(1)–Br(2) angle is 117.74(3)°. These values are slightly larger than those of the previous unsymmetrical 2,3-diiminobutylnickel complexes [20,22]. Coordination plane is formed by the N1, Ni1, N2 atoms, and it is nearly perpendicular to the phenyl rings of the *N*-aryl. The dihedral angle between the coordination plane and the plane formed by C26, C27, C32 is 88.90°, whilst, another dihedral angle of 78.68° is observed between the coordination plane and the plane formed by C5, C6, C8. The bonds N(1)–C(1) and N(2)–C(2) are shorter than the bonds N(1)–C(26) and N(2)–C(5), which is consistent with the characteristics of the double and single bond.

Ethylene polymerization

Various alkyl aluminum reagents, such as methylaluminoxane (MAO), modified methylaluminoxane (MMAO) and dimethylaluminum chloride (Me₂AlCl) and diethylaluminum chloride (Et₂AlCl), were investigated with the complex Ni1 to find the suitable co-catalysts in ethylene polymerization (see Table 2). Though polyethylenes were obtained in all cases, the high activity was only achieved when Et₂AlCl was employed. Subsequently, diethylaluminum chloride (Et₂AlCl) was further used in the detailed investigation.

To optimize the polymerization conditions, different Al/Ni molar ratios, reaction temperatures and times were explored, and the results are showed as entries 1–17 in Table 3, indicating high activities of the order of 10⁶ gPE mol⁻¹(Ni) h⁻¹ in most cases. Ethylene polymerization was conducted at 30 °C and 10 atm of ethylene, with the Al/Ni ratios from 400 to 800 within 30 min (entries 1–5, Table 3). The optimum Al/Ni ratio was 600 and the corresponding activity achieved was 2.87 × 10⁶ gPE mol⁻¹(Ni) h⁻¹ (entry 3, Table 3). The GPC results show slight decrease in the molecular weights of the resultant polyethylenes for the higher Al/Ni ratios.

Changing reaction temperature from 20 °C to 100 °C (entries 3 and 6–11, Table 3), the best activity was observed at 30 °C; the observed activities decreased along with increasing reaction temperature, which is consistent with the observations made for the

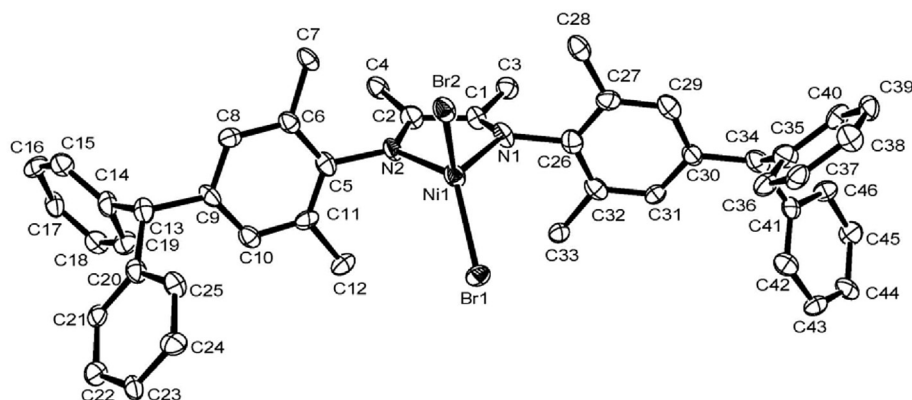


Fig. 1. ORTEP drawing of Ni1. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity.

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