

# Tailoring polyethylenes through constraining geometry of nickel complex: Synthesis, characterization and ethylene polymerization of 8-(2-benzhydrylnaphthylimino)-5,6,7-trihydroquinolynickel halides



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## ABSTRACT

The newly prepared 8-(2-benzhydrylnaphthylimino)-5,6,7-trihydroquinoline derivatives (**L1–L3**) individually reacted with (DME)NiBr<sub>2</sub> or NiCl<sub>2</sub> to form their corresponding nickel bromide complexes (**Ni1–Ni3**) and nickel chloride complexes (**Ni4–Ni6**). These nickel complexes were fully characterized by FT-IR spectroscopy and elemental analysis as well as single crystal X-ray analysis. The representative molecular structures of **Ni1** and **Ni4**, confirmed by single crystal X-ray diffraction, revealed a distorted octahedral geometry around nickel atom as the halo-bridged centro-symmetric dimers with formulae as L<sub>2</sub>Ni<sub>2</sub>X<sub>4</sub> (X = Br, **Ni1–Ni3**; X = Cl, **Ni4–Ni6**). All nickel complexes, activated with either modified methylaluminoxane (MMAO) or diethylaluminumchloride (Et<sub>2</sub>AlCl), exhibited high activities toward ethylene polymerization, producing branched polyethylene with low molecular weights. The obtained polyethylenes showed tail peaks in the high molecular weight portion according to the GPC curves due to the constrained geometry caused by the bulky 2-benzhydrylnaphthyl-substituted 8-arylimino-5,6,7-trihydroquinoline derivatives.

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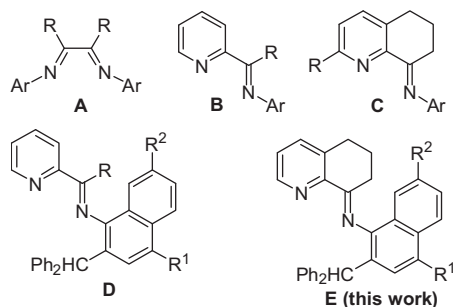
## 1. Introduction

The discovery of  $\alpha$ -diiminometal (Ni<sup>2+</sup> and Pd<sup>2+</sup>) complexes as highly active precatalysts toward ethylene polymerization has been recognized as a milestone of polyolefins [1,2], which resurrected the late-transition metal precatalysts in ethylene oligomerization and polymerization after the nickel-based SHOP process [3–7]. In the past two decades, the explosive investigations of late-transition metal precatalysts have been made and summarized in numerous review articles [8–13]. Targeting advanced polyethylenes, the branched polyethylenes were produced by either nickel or palladium precatalysts [8–15], meanwhile the highly linear polyethylenes were obtained from the catalytic systems on the base of either iron or cobalt precatalysts

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[8–13,16–18]. Focusing on nickel complexes, their ligands are commonly containing coordinative nitrogen atoms, either multi-nitrogen atoms or nitrogen along with other heteroatom. In general, the nickel precatalysts bearing nitrogen-other-heteroatom ligands often oligomerized ethylene [3–7,19–22], whilst the *N,N*-bidentate nickel complexes commonly polymerized ethylene [8–15] to produce branched polyethylenes in the “Chain Walking” mechanism [1,2,14,15,23–26]. The branched polyethylenes provide the advantage of easy processing, however, the better performance of polyethylenes still requires the tensile and compressive strengths, which could commonly be achieved by blending with a portion of higher molecular weight polyethylene. It would be an ideal catalytic system to tailor polyethylenes, in which the resultant polyethylenes contain major branched polyethylene along with small amount of higher molecular weight polyethylene. It is possible to create differently active species by using bulky-substituents for the constrained geometry of metal precatalysts. In past, the *N,N*-bidentate ligands have been extensively modified; two equivalents of reactant anilines were required for  $\alpha$ -diimine ligands (**A**, Scheme 1) [1,2], in contrast, one equivalent of reactant anilines was used for the model ligands of 2-iminopyridine (**B**, Scheme 1)



**Scheme 1.** The  $N^N$  bidentate ligand models for active nickel precatalysts.

[27–30] or aryliminocycloheptapyridines [31] as well as 8-(arylimino)-5,6,7-trihydroquinolines (**C**, Scheme 1) [32–35]. The latter model (**C**, Scheme 1) increased the tension by the ring-fused frame of 5,6,7-trihydroquinoline instead of the rotatable carbon–carbon bond bridging the two coordinating  $Sp^2$ -nitrogen groups [1,2]. Besides the high activities achieved, the **C**-model precatalysts showed unique properties depending on 2-substituents used or not: ethylene polymerization by using ligands without 2-substituent [32–35], and ethylene oligomerization by the ligands containing the additional 2-substituents [36,37]. Inspired by the higher active and better thermo-stable systems of the iron and cobalt complexes through using benzhydryl-substituted bis(imino)pyridine derivatives [38–45], the nickel complexes employing benzhydryl-derived  $N^N$  bidentate ligands of 2,3-bis(arylimino)butanes [46,47], 1,2-bis(arylimino)acenaphthylenes [48–51], 2-(aryliminomethyl)pyridines [29] as well as 8-(arylamino)-5,6,7-trihydroquinolines [52,53] have been investigated and showed better catalytic performances. Moreover, the conjugated frameworks have been also explored as new ligands; the ethylene oligomerization was achieved in moderate activity by the 4-arylimino-1,2,3-trihydroacridylnickel complexes [54,55], but the 8-arylimino-5,6,7-trihydroquinolylnickel complexes [52,53] showed high activities for ethylene polymerization. The ethylene polymerization of nickel complexes bearing 2-iminopyridines was enhanced by using 2-benzhydryl-1-aminonaphthalenes (**D**, Scheme 1) [56,57] instead of benzhydryl-substituted anilines [29], more importantly, 1-(2-benzhydrylnaphthylimino)-2-phenylimino-acenaphthylnickel complexes showed higher activity and better thermal-stability [58]. To extend the precatalyst model of 8-(arylimino)-5,6,7-trihydroquinolylnickel complexes [32–35,52,53], subsequently a series of 8-(2-benzhydrylnaphthylimino)-5,6,7-trihydroquinoline derivatives (**E**, Scheme 1) is prepared and further reacts with nickel halides to afford the title nickel complexes. These nickel complexes exhibit higher activities in ethylene polymerization than their nickel analogues bearing 8-(2-benzhydrylphenylimino)-5,6,7-trihydroquinolines [52,53] and 8-(arylimino)-5,6,7-trihydroquinolines [32–35]. The synthesis and characterization of 8-(2-benzhydrylnaphthylimino)-5,6,7-trihydroquinoline derivatives and their corresponding nickel halides are reported, and the catalytic performance of the title nickel complexes is investigated and discussed along with the properties of the resulting polyethylenes in terms of the molecular weights and polydispersity as well as branching.

## 2. Experimental

### 2.1. General considerations

All manipulations involving air- and moisture-sensitive compounds were performed using standard Schlenk techniques under a nitrogen atmosphere. Toluene was refluxed over sodium and

distilled under nitrogen prior to use. Methylaluminoxane (MAO, 1.46 M in toluene) and modified methylaluminoxane (MMAO, 1.93 M in heptane) were purchased from Akzo Nobel Corp. Diethylaluminum chloride ( $Et_2AlCl$ , 0.5 M in toluene) was purchased from Acros Chemicals. High-purity ethylene was purchased from Beijing Yansan Petrochemical Co. and used as received. Other reagents were purchased from Aldrich, Acros, or local suppliers. NMR spectra were recorded on a Bruker DMX 400 MHz instrument at ambient temperature using TMS as an internal standard; IR spectra were recorded on a Perkin–Elmer System 2000 FT-IR spectrometer. Elemental analysis was carried out using a Flash EA 1112 micro-analyzer. Molecular weights and molecular weight distribution (MWD) of polyethylene were determined by PL-GPC 220 at 150 °C, with 1,2,4-trichlorobenzene as the solvent. The melting points of polyethylene were measured on a Perkin–Elmer TA-Q2000 differential scanning calorimetry (DSC) analyzer under a nitrogen atmosphere; in the procedure, 4.0 mg sample was heated from 20 to 140 °C at a rate of 10 °C/min and kept for 5 min at 140 °C to remove the thermal history, and cooled at a rate of 10 °C/min to –40 °C, then the DSC trace and the melting points of the samples were obtained from the second scanning run.  $^{13}C$  NMR spectra of the polyethylenes were measured on a Bruker DMX 300 MHz instrument at 135 °C in deuterated 1,2-dichlorobenzene with TMS as an internal standard.

### 2.2. Synthesis and characterization of ligands and complexes

#### 2.2.1. Synthesis of 8-(2-benzhydrylnaphthylimino)-5,6,7-trihydroquinoline derivatives (**L1–L3**)

**2.2.1.1.** 8-(2-Benzhydrylnaphthylimino)-5,6,7-trihydroquinoline (**L1**). A 150 mL toluene solution of 5,6,7-trihydroquinolin-8-one (0.882 g, 5.99 mmol), 2-benzhydrylnaphthylamine (2.04 g, 6.59 mmol), and a catalytic amount of *p*-toluenesulfonic acid (0.228 g, 1.20 mmol) was refluxed for 8 h. The solvent was evaporated under reduced pressure, and then the mixture was purified by column chromatography on basic alumina with petroleum ether/ethyl acetate ( $v/v = 10:1$ ) as eluent to afford the product as a yellow powder in 37% yield. Mp: 165–166 °C.  $^1H$  NMR (400 MHz,  $CDCl_3$ , TMS):  $\delta$  8.80 (d, 1H,  $^3J_{HH} = 3.2$  Hz, Py–H), 7.79 (d, 1H,  $^3J_{HH} = 8.0$  Hz, Py–H), 7.57 (d, 1H,  $^3J_{HH} = 8.4$  Hz, Py–H), 7.50 (d, 2H,  $^3J_{HH} = 8.4$  Hz, Ar–H), 7.41–7.08 (m, 14H, Ar–H), 5.92 (s, 1H, –CHPh<sub>2</sub>), 2.72–2.64 (m, 1H, –CH<sub>2</sub>), 2.53–2.46 (m, 1H, –CH<sub>2</sub>), 1.90–1.83 (m, 1H, –CH<sub>2</sub>), 1.20–1.13 (m, 1H, –CH<sub>2</sub>), 0.88–0.77 (m, 2H, –CH<sub>2</sub>).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ , TMS): 167.8, 149.8, 148.9, 146.2, 144.5, 142.9, 137.5, 137.2, 132.8, 130.2, 129.7, 128.6, 128.3, 128.1, 127.6, 126.1, 125.5, 125.0, 123.5, 122.5, 51.8, 31.4, 29.2, 21.2. FT-IR (KBr, disk,  $cm^{-1}$ ): 3054, 3026, 1641 ( $\nu_{C=N}$ ), 1564, 1488, 1450, 1428, 1375, 1315, 1199, 1097, 1028, 790, 745, 701. Anal. Calc.d for  $C_{32}H_{26}N_2$  (438.21): C, 87.64; H, 5.98; N, 6.39%; Found: C, 87.48; H, 6.22; N, 6.27%.

**2.2.1.2.** 8-(2,4-Dibenzhydrylnaphthylimino)-5,6,7-trihydroquinoline (**L2**). In a manner similar to that described for **L1**, **L2** was prepared as a yellow powder in 36% yield. Mp: 118–119 °C.  $^1H$  NMR (400 MHz,  $CDCl_3$ , TMS):  $\delta$  8.80 (d, 1H,  $^3J_{HH} = 3.2$  Hz, Py–H), 7.94 (d, 1H,  $^3J_{HH} = 8.0$  Hz, Py–H), 7.60 (d, 1H,  $^3J_{HH} = 8.0$  Hz, Py–H), 7.52 (d, 1H,  $^3J_{HH} = 7.2$  Hz, Ar–H), 7.34–6.88 (m, 23H, Ar–H), 6.63 (s, 1H, Ar–H), 6.16 (s, 1H, –CHPh<sub>2</sub>), 5.80 (s, 1H, –CHPh<sub>2</sub>), 2.74–2.67 (m, 1H, –CH<sub>2</sub>), 2.56–2.49 (m, 1H, –CH<sub>2</sub>), 1.93–1.86 (m, 1H, –CH<sub>2</sub>), 1.27–1.20 (m, 2H, –CH<sub>2</sub>), 0.98–0.97 (m, 1H, –CH<sub>2</sub>).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ , TMS): 167.9, 149.8, 148.9, 145.0, 144.3, 137.5, 137.3, 134.0, 130.3, 130.1, 129.7, 129.4, 129.3, 128.4, 128.3, 127.9, 126.2, 126.0, 125.8, 125.7, 125.1, 125.0, 124.6, 124.5, 53.0, 51.8, 31.6, 29.3, 21.3. FT-IR (KBr, disk,  $cm^{-1}$ ): 3053, 3025, 1643 ( $\nu_{C=N}$ ), 1577, 1491, 1450, 1381, 1327, 1190, 1108, 1075, 1031,

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