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Highly active *ortho*-phenyl substituted α -diimine Nickel(II) catalysts for "chain walking polymerization" of ethylene: Synthesis of the nanosized dendritic polyethylene

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ABSTRACT

Three new α -diimine Ni(II) complexes {bis[N,N'-(4-fluoro-2,6-diphenylphenyl)imino]acenaphthene} dibromonickel **4a**, {bis[N,N'-(4-chloro-2,6-diphenylphenyl)imino]acenaphthene}dibromonickel **4b**, and {bis[N,N'-(4-methyl-2,6-diphenylphenyl)imino]acenaphthene}dibromonickel **4c**, were synthesized and characterized. The crystal structure of the complex **4a** was determined by X-ray crystallography. Complex **4a** has pseudo-tetrahedral geometry about the nickel center, showing $C_{2\nu}$ molecular symmetry. These complexes, activated by diethylaluminum chloride (DEAC) were tested in the polymerization of ethylene under mild conditions. Complex **4a** bearing 2,6-diphenyl and strong electron-withdrawing 4-fluorine groups, activated by diethylaluminum chloride (DEAC) shows highly catalytic activity for the polymerization of ethylene [4.95 × 10⁶ g PE/(mol Ni h bar)] and produced dendritic polyethylene (153.3 branches/1000 C). The dendritic polyethylene particle size obtained by **4a**/DEAC can be controlled in the 1–20 nm under 0.2 bar ethylene pressure, and could be expected to become a nano-targeted drug carrier after modified with water-soluble oligo(ethylene glycol) (OEG).

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1. Introduction

Late transition metal olefin polymerization catalysis has attracted increasing attention due to their high functional group tolerance and their ability to produce branched or dendritic polymer [1-24]. Nanosized dendrimers are artificial macromolecules with tree-like structures and synthesized from branched monomer units in a stepwise manner [25]. Due to their surface functional groups and highly branched architectures, nanosized dendrimers have an enormous capacity for solubilization of hydrophobic drugs and can be modified or conjugated with various interesting guest molecules [25,26]. Based on the "Enhanced Permeability and Retention (EPR) effect" [27-30], the nanosized dendrimers have shown great promise in the development of anticancer drug delivery systems [31]. However, it is very difficult to prepare dendrimers through stepwise synthesis. Recently, Guan and his coworker reported a simple method, chain walking polymerization (CWP) followed by atom transfer radical polymerization (ATRP), to efficiently synthesize water-soluble core-shell [core: polyethylene, PE; shell: oligo(ethylene glycol), OEG] dendritic nanoparticles with tunable sizes and reactive surface functionalities [32], which could

play a very important role in tumor targeted anti-cancer drugs. The key part of this method is to be the synthesis of highly active late transition metal catalysts, which could generate dendritic polyethylene and control the polyethylene particle diameter in the nanometer range. The dendritic polyethylene could be expected to become a nano-targeted drug carrier after modified with watersoluble oligo(ethylene glycol) (OEG).

In this work, we report the synthesis and characterization of three new α -diimine Ni(II) complexes of the type [NiBr₂(Ar-BIAN)] (Ar-BIAN = bis(arylimino)acenaphthene) bearing two bulky phenyl groups in the *ortho*-aryl position and different groups (strong electron-withdrawing group F, electron-withdrawing group Cl and electron-donating group methyl) in the *para*-aryl position of the arylimino group, in order to study the influence of different steric effects and electron densities at the metal center on the catalyst activity and, in particular, on the microstructure and size of polyethylene, and find new α -diimine Ni(II) complexes, which could produce nanosized dendritic polyethylene.

2. Experimental

2.1. General procedures and materials

All manipulations involving air and/or moisture-sensitive compounds were carried out with standard Schlenk techniques

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under nitrogen. Methylene chloride and *o*-dichlorobenzene were pre-dried with 4Å molecular sieves and distilled from CaH₂ under dry nitrogen. Toluene, diethyl ether, and 1,2-dimethoxyethane (DME) were distilled from sodium/benzophenone under N₂ atmosphere. Anhydrous NiBr₂ (99%), phenylboronic acid, Pd(OAc)₂ and diethylaluminum chloride (DEAC, 0.9 M solution in toluene) were obtained from Acros. Acenaphthoquinone (98%), 2,6-dibromo-4-fluorobenzenamine (98%) (**1a**), 4methylbenzenamine (98%), and 4-chlorobenzenamine (98%), were purchased from Alfa Aesar, and used without further purification. [NiBr₂(DME)] was synthesized according to the literature [33].

NMR spectra were recorded at 400 MHz on a Varian Mercury Plus-400 instrument, using TMS as internal standard. FTIR spectra were recorded on a Digilab Merlin FTS 3000 FTIR spectrophotometer on KBr pellets. The molecular weights and molecular weight distributions (M_w/M_n) of the polymers were determined by gel permeation chromatography/size-exclusion chromatography (GPC/SEC) via a Waters Alliance GPCV2000 chromatograph, using 1,2,4-trichlorobenzene as eluent, at a flow rate of 1.0 ml/min and operated at 140 °C. Effective hydrodynamic diameters of the dendritic polyethylenes were measured by particle size analyzer at 20 °C using a dynamic light scattering photometer (Nano ZS ZEN3600, Malvern Instruments Ltd., United Kingdom) equipped with laser at a wavelength of 633 nm.

2.2. Synthesis of 2,6-dibromo-4-chlorobenzenamine 1b

Acetic acid (2ml) was added to a stirred solution of 4chlorobenzenamine (0.64 g, 5 mmol) in CH₂Cl₂. The solution was stirred for 30 min. After the solution cooled to 5 °C with ice bath, Br₂ (2.00 g, 12.5 mmol) in 5 ml CH₂Cl₂ was slowly added to the stirred solution. The mixture was stirred for 5 h and neutralized by 10% saturated aqueous sodium hydroxide solution. The mixture was extracted three times with 50 ml petroleum ether. The combined organic phase was dried over MgSO₄, filtered, and the solvent was removed. The residue was purified by chromatography on silica gel with petroleum ether/ethyl ester (v/v = 15:1) to give 2,6-dibromo-4-chlorobenzenamine (0.94 g, 66% yield). ¹H NMR (400 MHz, CDCl₃): δ 4.55 (s, 2H, -NH₂), 7.38 (s, 2H, C₆H₂Br₂ClNH₂). ¹³C NMR (400 MHz, $CDCl_3$): δ 108.43 (benzenamine carbon connected with Br), 130.48 (benzenamine carbon connected with Cl), 131.46 (benzenamine carbon), 141.25 (benzenamine carbon connected with NH_2).

2.3. Synthesis of 2,6-dibromo-4-methylbenzenamine 1c

Acetic acid (2ml) was added to a stirred solution of 4methylbenzenamine (0.54 g, 5 mmol) in CH₂Cl₂. The solution was stirred for 30 min. After the solution cooled to 5 °C with ice bath, Br₂ (2.00 g, 12.5 mmol) in 5 ml CH₂Cl₂ was slowly added to the stirred solution. The mixture was stirred for 5 h and neutralized by 10% saturated aqueous sodium hydroxide solution. The mixture was extracted three times with 50 ml petroleum ether. The combined organic phase was dried over MgSO₄, filtered, and the solvent was removed. The residue was purified by chromatography on silica gel with petroleum ether/ethyl ester (v/v = 15:1)to give 2,6-dibromo-4-methylbenzenamine (0.97 g, 73% yield). ¹H NMR (400 MHz, CDCl₃): δ 2.20 (s, 3H, -CH₃), 4.38 (s, 2H, -NH₂), 7.19 (s, 2H, C₆H₂Br₂CH₃NH₂). ¹³C NMR (400 MHz, CDCl₃): δ 19.75 (–*CH*₃), 108.69 (benzenamine carbon connected with Br), 129.31 (benzenamine carbon connected with CH₃), 132.13 (benzenamine carbon), 139.48 (benzenamine carbon connected with NH_2).

2.4. Synthesis of 4-fluoro-2,6-diphenylbenzenamine 2a

(0.01 g. 0.04 mmol), 2,6-dibromo-4- $Pd(OAc)_{2}$ fluorobenzenamine (0.54 g, 2 mmol), K₂CO₃ (0.55 g, 4 mmol) and phenylboronic acid (0.54 g, 4.4 mmol) were placed in a 100 ml flask and allowed to stir at 25°C for 24h, in the presence of 10 ml PEG-400. The mixture was extracted three times with 10 ml diethyl ether. The combined organic phase was dried over MgSO₄, filtered, and the solvent was removed. The residue was purified by chromatography on silica gel with petroleum ether/ethyl ester (v/v=20:1) to give 4-fluoro-2,6-diphenylbenzenamine (0.35 g, 66% yield). ¹H NMR (400 MHz, CDCl₃): δ 3.66 (s, 2H, -NH₂), 6.85 (d, 2H, benzenamine), 7.34 (t, 2H, phenyl ring), 7.43-7.49 (m, 8H, phenyl ring). ¹³C NMR (400 MHz, CDCl₃): δ 115.81 (benzenamine carbon near F), 127.63 (benzenamine carbon connected with phenyl), 128.83 (phenyl carbon), 128.92 (phenyl carbon near benzenamine), 129.12 (phenyl carbon), 136.90 (phenyl carbon connected with benzenamine), 138.80 (benzenamine carbon connected with NH₂), 154.63 (benzenamine carbon connected with F).

2.5. Synthesis of 4-chloro-2,6-diphenylbenzenamine 2b

 $Pd(OAc)_2$ (0.01 g. 0.04 mmol), 2,6-dibromo-4chlorobenzenamine (0.57 g, 2 mmol), K₂CO₃ (0.55 g, 4 mmol) and phenylboronic acid (0.54 g, 4.4 mmol) were placed in a 100 ml flask and allowed to stir at 25°C for 24h, in the presence of 10 ml PEG-400. The mixture was extracted three times with 10 ml diethyl ether. The combined organic phase was dried over MgSO₄, filtered, and the solvent was removed. The residue was purified by chromatography on silica gel with petroleum ether/ethyl ester (v/v=20:1) to give 4-chloro-2,6-diphenylbenzenamine (0.34 g, 60% yield). ¹H NMR (400 MHz, CDCl₃): δ 3.71 (s, 2H, $-NH_2$), 7.00 (s, 2H, benzenamine), 7.28 (t, 2H, phenyl ring), 7.33-7.40 (m, 8H, phenyl ring). ¹³C NMR (400 MHz, CDCl₃): δ 124.82 (benzenamine carbon connected with Cl), 127.47 (benzenamine carbon connected with phenyl), 128.38 (benzenamine carbon near Cl), 128.98 (phenyl carbon), 129.58 (phenyl carbon near benzenamine), 130.46 (phenyl carbon), 138.46 (phenyl carbon connected with benzenamine), 139.74 (benzenamine carbon connected with NH_2).

2.6. Synthesis of 4-methyl-2,6-diphenylbenzenamine 2c

 $Pd(OAc)_2$ (0.01 g, 0.04 mmol), 2,6-dibromo-4methylbenzenamine $(0.53 g, 2 mmol), K_2CO_3 (0.55 g, 4 mmol)$ and phenylboronic acid (0.51 g, 4.2 mmol) were placed in a 100 ml flask and allowed to stir at 25°C for 24h, in the presence of 10 ml PEG-400. The mixture was extracted three times with 10 ml diethyl ether. The combined organic phase was dried over MgSO₄, filtered, and the solvent was removed. The residue was purified by chromatography on silica gel with petroleum ether/ethyl ester (v/v = 20:1) to give 4-methyl-2,6-diphenylbenzenamine (0.31 g, 58% yield). ¹H NMR (400 MHz, CDCl₃): δ 2.21 (s, 3H, CH₃ of benzenamine ring), 3.59 (s, 2H, -NH₂), 6.86 (s, 2H, benzenamine ring), 7.25 (t, 2H, phenyl ring), 7.34 (t, 4H, phenyl ring), 7.41 (d, 4H, phenyl ring near benzenamine). ¹³C NMR (400 MHz, CDCl₃): δ 20.41 (CH₃), 127.15 (benzenamine carbon connected with phenyl), 127.88 (phenyl carbon), 128.69 (phenyl carbon near benzenamine), 129.27 (phenyl carbon), 129.42 (benzenamine carbon connected with methyl), 130.23 (benzenamine carbon near methyl), 138.13 (phenyl carbon connected with benzenamine), 139.74 (benzenamine carbon connected with NH_2).

2.7. Synthesis of

bis[N,N'-(4-fluoro-2,6-diphenylphenyl)imino]acenaphthene 3a

4-Methylbenzenesulfonic acid (20 mg, 0.1 mmol) was added to a stirred solution of acenaphthenequinone (0.18 g, 1.00 mmol) and 4-fluoro-2,6-diphenylbenzenamine (0.58 g, 2.2 mmol) in benzene (20 ml). The mixture was refluxed for 24 h, and then the solvent was removed. The residue was purified by chromatography on silica gel with petroleum ether/ethyl ester (v/v = 20:1) to give ligand **3a** (0.45 g, 67% yield). ¹H NMR (400 MHz, CDCl₃): δ 6.76 (t, 2H, naphthyl ring), 6.93 (t, 4H, phenyl ring), 7.04 (d, 2H, naphthyl ring), 7.10 (t, 8H, phenyl ring), 7.27 (t, 8H, phenyl ring), 7.29 (d, 4H, benzenamine ring), 7.66 (d, 2H, naphthyl ring). ¹³C NMR (400 MHz, $CDCl_3$): δ 116.81 (naphthyl ring carbon), 122.53 (naphthyl ring carbon), 127.01 (benzenamine carbon near F), 127.11 (phenyl carbon), 128.10 (phenyl carbon near benzenamine), 129.01 (phenyl carbon), 129.69 (benzenamine carbon connected with phenyl), 130.37 (phenyl carbon connected with benzenamine), 133.27 (naphthyl ring carbon), 138.78 (naphthyl ring), 140.05 (naphthyl ring), 142.99 (naphthyl ring), 158.51 (benzenamine carbon connected with N), 161.13 (acenaphthoquinone ring carbon connected with N), 161.77 (benzenamine carbon connected with F). Anal. Calc. for C₄₈H₃₀F₂N₂: C, 85.69; H, 4.49; N, 4.16. Found: C, 85.66; H, 4.52; N, 4.18.

2.8. Synthesis of

bis[N,N'-(4-chloro-2,6-diphenylphenyl)imino]acenaphthene 3b

4-Methylbenzenesulfonic acid (20 mg, 0.1 mmol) was added to a stirred solution of acenaphthenequinone (0.18 g, 1.00 mmol) and 4-chloro-2,6-diphenylbenzenamine (0.62 g, 2.2 mmol) in benzene (20 ml). The mixture was refluxed for 24 h, and then the solvent was removed. The residue was purified by chromatography on silica gel with petroleum ether/ethyl ester (v/v = 20:1) to give ligand **3b** (0.46 g, 65% yield). ¹H NMR (400 MHz, CDCl₃): δ 6.83 (t, 2H, naphthyl ring), 6.92 (t, 8H, phenyl ring), 7.05 (t, 4H, phenyl ring), 7.26 (d, 8H, phenyl ring), 7.30 (d, 2H, naphthyl ring), 7.35 (s, 4H, benzenamine ring), 7.70 (d, 2H, naphthyl ring). ¹³C NMR (400 MHz, $CDCl_3$): δ 122.66 (naphthyl ring carbon), 127.10 (naphthyl ring carbon), 127.40 (phenyl carbon), 127.70 (benzenamine carbon near Cl), 128.00 (phenyl carbon near benzenamine), 129.06 (phenyl carbon), 129.66 (benzenamine carbon connected with phenyl), 130.18 (phenyl carbon connected with benzenamine), 130.64 (naphthyl ring), 131.76 (naphthyl ring), 132.82 (benzenamine carbon connected with Cl), 137.78 (naphthyl ring), 138.39 (naphthyl ring), 139.36 (benzenamine carbon connected with N), 160.36 (acenaphthoquinone ring carbon connected with N). Anal. Calcd. for C48H30Cl2N2: C, 81.70; H, 4.29; N, 3.97. Found: C, 81.73; H, 4.26; N, 3.95.

2.9. Synthesis of

bis[N,N'-(4-methyl-2,6-diphenylphenyl)imino]acenaphthene 3c

4-Methylbenzenesulfonic acid (20 mg, 0.1 mmol) was added to a stirred solution of acenaphthenequinone (0.18 g, 1.00 mmol) and 4-meyhyl-2,6-diphenylbenzenamine (0.57 g, 2.2 mmol) in benzene (20 ml). The mixture was refluxed for 24 h, and then the solvent was removed. The residue was purified by chromatography on silica gel with petroleum ether/ethyl ester (v/v = 20:1) to give ligand **3c** (0.41 g, 62% yield). ¹H NMR (400 MHz, CDCl₃): δ 2.37 (s, 6H, CH₃ of benzenamine ring), 6.84 (t, 8H, phenyl ring), 6.94 (t, 4H, phenyl ring), 7.07 (s, 4H, benzenamine ring), 7.21 (d, 8H, phenyl ring), 7.42 (t, 2H, naphthyl ring), 7.36 (d, 2H, naphthyl ring), 7.55 (d, 2H, naphthyl ring). ¹³C NMR (400 MHz, CDCl₃): δ 20.32 (–CH₃ of benzenamine ring), 122.65 (naphthyl ring carbon), 126.42 (naphthyl ring carbon), 126.72 (phenyl carbon), 127.25 (benzenamine carbon near CH₃), 127.85 (phenyl carbon near benzenamine), 128.68 (phenyl carbon), 129.68 (benzenamine carbon connected with phenyl), 130.41 (phenyl carbon connected with benzenamine), 130.71 (naphthyl ring), 131.69 (naphthyl ring), 134.85 (naphthyl ring), 137.93 (naphthyl ring), 139.21 (benzenamine carbon connected with CH₃), 139.74 (benzenamine carbon connected with N), 160.28 (acenaphthoquinone ring carbon connected with N). Anal. Calcd. for $C_{50}H_{36}N_2$: C, 90.33; H, 5.46; N, 4.21. Found: C, 90.31; H, 5.49; N, 4.23.

2.10. Synthesis of {bis[N,N'-(4-fluoro-2,6diphenylphenyl)imino]acenaphthene}dibromonicke **4a**

NiBr₂(DME) (0.16 g, 0.5 mmol), ligand **3a** (0.33 g, 0.5 mmol) and dichloromethane (40 ml) were mixed in a Schlenk flask and stirred at room temperature for 24 h. The resulting suspension was filtered. The solvent was removed under vacuum and the residue was washed with diethyl ether (3 × 15 ml), and then dried under vacuum at room temperature to give complex **4a** 0.37 g (82% yield). Anal. Calcd. for C₄₈H₃₀Br₂F₂N₂Ni: C, 64.68; H, 3.39; N, 3.14. Found: C, 64.64; H, 3.43; N, 3.17. FT-IR (KBr) 1,645 cm⁻¹ (C=N). Single crystals of complex **4a** suitable for X-ray analysis were obtained at $-30 \,^{\circ}$ C by dissolving the nickel complex in CH₂Cl₂, following by slow layering of the resulting solution with *n*-hexane.

2.11. Synthesis of {bis[N,N'-(4-chloro-2,6diphenylphenyl)imino]acenaphthene}dibromonicke **4b**

NiBr₂(DME) (0.16 g, 0.5 mmol), ligand **3b** (0.34 g, 0.5 mmol) and dichloromethane (40 ml) were mixed in a Schlenk flask and stirred at room temperature for 24 h. The resulting suspension was filtered. The solvent was removed under vacuum and the residue was washed with diethyl ether (3 × 16 ml), and then dried under vacuum at room temperature to give complex **4b** (0.39 g, 85% yield). Anal. Calcd. for C₄₈H₃₀N₂Cl₂NiBr₂: C, 62.38; H, 3.27; N, 3.03. Found: C, 62.35; H, 3.29; N, 3.06. FT-IR (KBr) 1647 cm⁻¹ (C=N).

2.12. Synthesis of {bis[N,N'-(4-methyl-2,6diphenylphenyl)imino]acenaphthene}dibromonicke **4c**

NiBr₂(DME) (0.16 g, 0.5 mmol), ligand **3c** (0.33 g, 0.5 mmol) and dichloromethane (40 ml) were mixed in a Schlenk flask and stirred at room temperature for 24 h. The resulting suspension was filtered. The solvent was removed under vacuum and the residue was washed with diethyl ether (3 × 15 ml), and then dried under vacuum at room temperature to give complex **4c** 0.41 g (93% yield). Anal. Calcd. for $C_{50}H_{36}Br_2N_2Ni$: C, 67.98; H, 4.11; N, 3.17. Found: C, 68.02; H, 4.09; N, 3.14. FT-IR (KBr) 1649 cm⁻¹ (C=N).

2.13. X-ray structure determinations

Single crystals of complex **4a** suitable for X-ray analysis were obtained at -30 °C by dissolving the nickel complex in CH₂Cl₂, following by slow layering of the resulting solution with *n*-hexane. Data collections were performed at 296(2)K on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite monochromated MoK α radiation ($\lambda = 0.71073$ Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. The structures were solved by using the SHELXTL program. Refinement was performed on *F*² anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure

 Table 1

 Summary of crystallographic data for complex 4a

Empirical formula $C_{48}H_{30}Br_2F_2N_2Ni$ Formula mass 891.27 Temperature (K) 296 K Wavelength (Å) 0.71073 Crystal size (mm ³) $0.29 \times 0.27 \times 0.26$ Crystal system Monoclinic Space group $C2/c$ a (Å) 16.390 (8) Å b (Å) 16.470 (8) Å c (Å) 18.445 (9) Å V (Å ³) 4530 (4) Å ³ Z 4 Density (calcd.) (mg/cm ³) 1.307 Absorption coefficient (mm ⁻¹) 2.23 $F(000)$ 1792 Theta range for data collection (°) 2.4-20.5 Limiting indices $-19 \le h \le 170 \le k \le 190 \le l \le 21$ Reflections collected 3919 Independent reflections 250 Rint 0.0000 Completeness to $\theta = 25.20^\circ$ 99.6% Final R indices ($1 > 2\sigma(I)$] $R_1 = 0.0396$, $wR_2 = 0.1104$ R indices (all data) $R_1 = 0.0396$, $wR_2 = 0.1285$ Refinement method Full-matrix least-squares on F^2 Gooo		
Formula mass 891.27 Temperature (K) 296 K Wavelength (Å) 0.71073 Crystal size (mm ³) $0.29 \times 0.27 \times 0.26$ Crystal size (mm ³) $0.29 \times 0.27 \times 0.26$ Crystal system Monoclinic Space group $C2/c$ a (Å) 16.390 (8) Å b (Å) 16.470 (8) Å c (Å) 18.445 (9) Å V (Å ³) 4530 (4) Å ³ Z 4 Density (calcd.) (mg/cm ³) 1.307 Absorption coefficient (mm ⁻¹) 2.23 $F(000)$ 1792 Theta range for data collection (°) $2.4-20.5$ Limiting indices $-19 \le h \le 170 \le k \le 190 \le l \le 21$ Reflections collected 3919 Independent reflections 250 Rint 0.0000 Completeness to $\theta = 25.20^\circ$ 99.6% Final R indices ($1 > 2\sigma(I)$] $R_1 = 0.0396$, $wR_2 = 0.1104$ R indices (all data) $R_1 = 0.0824$, $wR_2 = 0.1285$ Refinement method Full-matrix least-squares on F^2 Goodness-of-fit on F^2 1.015	Empirical formula	$C_{48}H_{30}Br_2F_2N_2Ni$
Temperature (K) 296 K Wavelength (Å) 0.71073 Crystal size (mm ³) 0.29 × 0.27 × 0.26 Crystal size (mm ³) 0.29 × 0.27 × 0.26 Crystal size (mm ³) 0.29 × 0.27 × 0.26 Crystal size (mm ³) 0.29 × 0.27 × 0.26 Crystal system Monoclinic Space group C2/c a (Å) 16.390 (8) Å b (Å) 16.470 (8) Å c (Å) 18.445 (9) Å V (Å ³) 4530 (4) Å ³ Z 4 Density (calcd.) (mg/cm ³) 1.307 Absorption coefficient (mm ⁻¹) 2.23 $F(000)$ 1792 Theta range for data collection (°) 2.4–20.5 Limiting indices $-19 \le h \le 170 \le k \le 190 \le l \le 21$ Reflections collected 3919 Independent reflections 250 Rint 0.0000 Completeness to $\theta = 25.20^\circ$ 99.6% Final R indices [$l > 2\sigma(l)$] $R_1 = 0.0396$, w $R_2 = 0.1104$ R indices (all data) $R_1 = 0.0396$, w $R_2 = 0.1285$ Refinement method Full-matrix least-squares on F^2	Formula mass	891.27
Wavelength (Å) 0.71073 Crystal size (mm ³) 0.29 × 0.27 × 0.26 Crystal system Monoclinic Space group $C2/c$ a (Å) 16.390 (8) Å b (Å) 16.470 (8) Å c (Å) 18.445 (9) Å V (Å ³) 4530 (4) Å ³ Z 4 Density (calcd.) (mg/cm ³) 1.307 Absorption coefficient (mm ⁻¹) 2.23 $F(000)$ 1792 Theta range for data collection (°) 2.4–20.5 Limiting indices $-19 \le h \le 170 \le k \le 190 \le l \le 21$ Reflections collected 3919 Independent reflections 250 Rint 0.0000 Completeness to $\theta = 25.20^\circ$ 99.6% Final R indices $[l > 2\sigma(l)]$ $R_1 = 0.0396$, $wR_2 = 0.1104$ R indices (all data) $R_1 = 0.0396$, $wR_2 = 0.1285$ Refinement method Full-matrix least-squares on F^2 Goodness-of-fit on F^2 1.015 Max. and min. transmission 0.5637 and 0.5945 Largest diff. peak and hole (e Å ⁻³) 0.37 and -0.32	Temperature (K)	296 K
Crystal size (mm ³) $0.29 \times 0.27 \times 0.26$ Crystal system Monoclinic Space group $C2/c$ a (Å) 16.390 (8) Å b (Å) 16.470 (8) Å c (Å) 18.445 (9) Å V (Å ³) 4530 (4) Å ³ Z 4 Density (calcd.) (mg/cm ³) 1.307 Absorption coefficient (mm ⁻¹) 2.23 $F(000)$ 1792 Theta range for data collection (°) $2.4-20.5$ Limiting indices $-19 \le h \le 170 \le k \le 190 \le l \le 21$ Reflections collected 3919 Independent reflections 250 Rint 0.0000 Completeness to $\theta = 25.20^\circ$ 99.6% Final R indices $[I > 2\sigma(I)]$ $R_1 = 0.0396$, $wR_2 = 0.1104$ R indices (all data) $R_1 = 0.0326$, $wR_2 = 0.1285$ Refinement method Full-matrix least-squares on F^2 Goodness-of-fit on F^2 1.015 Max. and min. transmission 0.5637 and 0.5945 Largest diff. peak and hole (e Å ⁻³) 0.37 and -0.32	Wavelength (Å)	0.71073
Crystal system Monoclinic Space group $C2/c$ a (Å) 16.390 (8) Å b (Å) 16.470 (8) Å c (Å) 18.445 (9) Å v (Å ³) 4530 (4) Å ³ Z 4 Density (calcd.) (mg/cm ³) 1.307 Absorption coefficient (mm ⁻¹) 2.23 $F(000)$ 1792 Theta range for data collection (°) 2.4-20.5 Limiting indices $-19 \le h \le 170 \le k \le 190 \le l \le 21$ Reflections collected 3919 Independent reflections 250 Rint 0.0000 Completeness to $\theta = 25.20^\circ$ 99.6% Final R indices ($l > 2\sigma(l)$] $R_1 = 0.0396$, $wR_2 = 0.1104$ R indices (all data) $R_1 = 0.0396$, $wR_2 = 0.1285$ Refinement method Full-matrix least-squares on F^2 Goodness-of-fit on F^2 1.015 Max. and min. transmission 0.5637 and 0.5945 Largest diff. peak and hole ($e Å^{-3}$) 0.37 and -0.32	Crystal size (mm ³)	$0.29 \times 0.27 \times 0.26$
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c (Å) 18.445 (9) Å V (Å ³) 4530 (4) Å ³ Z 4 Density (calcd.) (mg/cm ³) 1.307 Absorption coefficient (mm ⁻¹) 2.23 $F(000)$ 1792 Theta range for data collection (°) 2.4–20.5 Limiting indices $-19 \le h \le 170 \le k \le 190 \le l \le 21$ Reflections collected 3919 Independent reflections 250 Rint 0.0000 Completeness to $\theta = 25.20^{\circ}$ 99.6% Final R indices (all data) $R_1 = 0.03824, wR_2 = 0.1104$ R indices (all data) $R_1 = 0.0324, wR_2 = 0.1285$ Refinement method Full-matrix least-squares on F^2 Goodness-of-fit on F^2 1.015 Max. and min. transmission 0.5637 and 0.5945 Largest diff. peak and hole (e Å ⁻³) 0.37 and -0.32	b (Å)	16.470 (8)Å
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Z 4 Density (calcd.) (mg/cm ³) 1.307 Absorption coefficient (mm ⁻¹) 2.23 $F(000)$ 1792 Theta range for data collection (°) 2.4-20.5 Limiting indices -19 $\le h \le 170 \le k \le 190 \le l \le 21$ Reflections collected 3919 Independent reflections 250 Rint 0.0000 Completeness to $\theta = 25.20^\circ$ 99.6% Final R indices [I > $2\sigma(I)$] $R_1 = 0.0824$, $wR_2 = 0.1104$ R indices (all data) $R_1 = 0.0824$, $wR_2 = 0.1285$ Refinement method Full-matrix least-squares on F^2 Goodness-of-fit on F^2 1.015 Max. and min. transmission 0.5637 and 0.5945 Largest diff. peak and hole (e Å ⁻³) 0.37 and -0.32	V (Å ³)	4530 (4) Å ³
Density (calcd.) (mg/cm ³) 1.307 Absorption coefficient (mm ⁻¹) 2.23 $F(000)$ 1792 Theta range for data collection (°) 2.4–20.5 Limiting indices $-19 \le h \le 170 \le k \le 190 \le l \le 21$ Reflections collected 3919 Independent reflections 250 Rint 0.0000 Completeness to $\theta = 25.20^\circ$ 99.6% Final R indices [I > $2\sigma(I)$] $R_1 = 0.0396$, $wR_2 = 0.1104$ R indices (all data) $R_1 = 0.0324$, $wR_2 = 0.1285$ Refinement method Full-matrix least-squares on F^2 Goodness-of-fit on F^2 1.015 Max. and min. transmission 0.5637 and 0.5945 Largest diff. peak and hole (e Å ⁻³) 0.37 and -0.32	Ζ	4
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$F(000)$ 1792Theta range for data collection (°) $2.4-20.5$ Limiting indices $-19 \le h \le 170 \le k \le 190 \le l \le 21$ Reflections collected3919Independent reflections 250 Rint 0.0000 Completeness to $\theta = 25.20^{\circ}$ 99.6% Final R indices $[l > 2\sigma(l)]$ $R_1 = 0.0396$, $wR_2 = 0.1104$ R indices (all data) $R_1 = 0.0824$, $wR_2 = 0.1285$ Refinement methodFull-matrix least-squares on F^2 Goodness-of-fit on F^2 1.015 Max. and min. transmission 0.5637 and 0.5945 Largest diff. peak and hole (e Å-3) 0.37 and -0.32	Absorption coefficient (mm ⁻¹)	2.23
Theta range for data collection (°)2.4–20.5Limiting indices $-19 \le h \le 170 \le k \le 190 \le l \le 21$ Reflections collected3919Independent reflections250Rint0.0000Completeness to $\theta = 25.20^{\circ}$ 99.6%Final <i>R</i> indices $[l > 2\sigma(l)]$ $R_1 = 0.0396$, $wR_2 = 0.1104$ R indices (all data) $R_1 = 0.0324$, $wR_2 = 0.1285$ Refinement methodFull-matrix least-squares on F^2 Goodness-of-fit on F^2 1.015Max. and min. transmission0.5637 and 0.5945Largest diff. peak and hole (e Å ⁻³)0.37 and -0.32	F(000)	1792
Limiting indices $-19 \le h \le 170 \le k \le 190 \le l \le 21$ Reflections collected3919Independent reflections250Rint0.0000Completeness to $\theta = 25.20^{\circ}$ 99.6%Final R indices $[l > 2\sigma(l)]$ $R_1 = 0.0396, wR_2 = 0.1104$ R indices (all data) $R_1 = 0.0324, wR_2 = 0.1285$ Refinement methodFull-matrix least-squares on F^2 Goodness-of-fit on F^2 1.015Max. and min. transmission0.5637 and 0.5945Largest diff. peak and hole (e Å-3)0.37 and -0.32	Theta range for data collection (°)	2.4-20.5
Reflections collected3919Independent reflections250Rint0.0000Completeness to θ = 25.20°99.6%Final R indices $[I > 2\sigma(I)]$ $R_1 = 0.0396$, $wR_2 = 0.1104$ R indices (all data) $R_1 = 0.0324$, $wR_2 = 0.1285$ Refinement methodFull-matrix least-squares on F^2 Goodness-of-fit on F^2 1.015Max. and min. transmission0.5637 and 0.5945Largest diff. peak and hole (e Å-3)0.37 and -0.32	Limiting indices	$-19 \le h \le 170 \le k \le 190 \le l \le 21$
Independent reflections 250 Rint 0.0000 Completeness to θ = 25.20° 99.6% Final R indices [I > 2 σ (I)] R_1 = 0.0396, wR_2 = 0.1104 R indices (all data) R_1 = 0.0824, wR_2 = 0.1285 Refinement method Full-matrix least-squares on F^2 Goodness-of-fit on F^2 1.015 Max. and min. transmission 0.5637 and 0.5945 Largest diff. peak and hole (e Å-3) 0.37 and -0.32	Reflections collected	3919
Rint 0.0000 Completeness to $\theta = 25.20^{\circ}$ 99.6% Final R indices [I > $2\sigma(I)$] $R_1 = 0.0396$, $wR_2 = 0.1104$ R indices (all data) $R_1 = 0.0824$, $wR_2 = 0.1285$ Refinement method Full-matrix least-squares on F^2 Goodness-of-fit on F^2 1.015 Max. and min. transmission 0.5637 and 0.5945 Largest diff. peak and hole (e Å-3) 0.37 and -0.32	Independent reflections	250
Completeness to θ = 25.20° 99.6% Final R indices [I > 2 σ (I)] R_1 = 0.0396, wR ₂ = 0.1104 R indices (all data) R_1 = 0.0824, wR ₂ = 0.1285 Refinement method Full-matrix least-squares on F ² Goodness-of-fit on F ² 1.015 Max. and min. transmission 0.5637 and 0.5945 Largest diff. peak and hole (e Å ⁻³) 0.37 and -0.32	Rint	0.0000
Final R indices $[I > 2\sigma(I)]$ $R_1 = 0.0396, wR_2 = 0.1104$ R indices (all data) $R_1 = 0.0824, wR_2 = 0.1285$ Refinement method Full-matrix least-squares on F^2 Goodness-of-fit on F^2 1.015 Max. and min. transmission 0.5637 and 0.5945 Largest diff. peak and hole (e Å ⁻³) 0.37 and -0.32	Completeness to θ = 25.20°	99.6%
R indices (all data) $R_1 = 0.0824, wR_2 = 0.1285$ Refinement methodFull-matrix least-squares on F^2 Goodness-of-fit on F^2 1.015Max. and min. transmission0.5637 and 0.5945Largest diff. peak and hole (e Å-3)0.37 and -0.32	Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0396$, $wR_2 = 0.1104$
Refinement methodFull-matrix least-squares on F^2 Goodness-of-fit on F^2 1.015Max. and min. transmission0.5637 and 0.5945Largest diff. peak and hole (e Å-3)0.37 and -0.32	R indices (all data)	$R_1 = 0.0824$, $wR_2 = 0.1285$
Goodness-of-fit on F^2 1.015Max. and min. transmission0.5637 and 0.5945Largest diff. peak and hole (e Å-3)0.37 and -0.32	Refinement method	Full-matrix least-squares on F ²
Max. and min. transmission 0.5637 and 0.5945 Largest diff. peak and hole (e Å ⁻³) 0.37 and -0.32	Goodness-of-fit on F ²	1.015
Largest diff. peak and hole ($e Å^{-3}$)0.37 and -0.32	Max. and min. transmission	0.5637 and 0.5945
	Largest diff. peak and hole (e Å ⁻³)	0.37 and -0.32

calculation without further refinement of the parameters. Crystal data, data collection, and refinement parameters are listed in Table 1.

2.14. Procedure for the polymerization of ethylene

The polymerization of ethylene was carried out in a flame dried 250 ml crown capped pressure bottle sealed with neoprene septa. After drying the polymerization bottle under N₂ atmosphere, 50 ml of dry toluene was added to the polymerization bottle. The resulting solvent was then saturated with a prescribed ethylene pressure. The co-catalyst (DEAC) was then added in Al/Ni molar ratios in the range of 200–1000 to the polymerization bottle via a syringe. At this time, the solutions were thermostated to the desired temperature and allowed to equilibrate for 15 min. Subsequently, an *o*-dichlorobenzene solution of Ni catalyst was added to the polymerization reactor. The polymerization, conducted under a dynamic pressure of ethylene (0.2 bar), was terminated by quenching the reaction mixtures with 100 ml of a 2% HCl–MeOH solution. The precipitated polymer was filtered, washed with methanol and dried under vacuum at $60 \circ C$ to a constant weight.

3. Results and discussion

3.1. Synthesis and characterization of ligands **3a–c** and complexes **4a–c**

After protection of the amino group by acetic acid, 4-R-benzenamines were brominated to form 2,6-dibromo-4-Rbenzenamines **1a-c** (**1a**: R=F; **1b**: R=Cl; **1c**: R=CH₃) (Scheme 1). The Suzuki coupling reaction of 2,6-dibromo-4-R-benzenamines and phenylboronic acid catalyzed by Pd(OAc)₂, in PEG-400, led to the corresponding amine precursors 2,6-diphenyl-4-Rbenzenamines **2a–c** in 58–66% yield. The α -diimine ligands **3a–c** were finally obtained by acid catalyzed condensation of the 2,6diphenyl-4-R-benzenamines and acenaphthoquinone, and purified by chromatography on silica gel with petroleum ether/ethyl ester. The ligands (**3a–c**) were characterized by ¹H NMR. ¹³C NMR and elemental analysis. Compared with other α -diimine ligands, the synthesis of ligands (**3a-c**) was difficult due to two bulky orthophenyl groups of the anilines (2a-c). At the beginning, ligands (3a-c) were synthesized in methanol at 40-50 °C using formic acid as catalyst, but failed. Ligands (3a-c) were successfully synthesized at high temperature in benzene using 4-methylbenzenesulfonic acid as catalyst (yield, 62-67%).

The reaction of equimolar amounts of [NiBr₂(DME)] and the α -diimine ligands **3a–c** in CH₂Cl₂ led to the displacement of 1,2dimethoxyethane and afforded the catalyst precursors **4a–c** as moderately air-stable microcrystalline solids in high yields. The result of elemental analysis of complex **4a** is consistent with the theoretical value of the molecular structure obtained by X-ray crystallography (see below).

Suitable crystals of complex **4a** for X-ray diffraction were obtained at $-30 \,^{\circ}$ C by double layering a CH₂Cl₂ solution of the complex with n-hexane. The molecular structure complex **4a** was determined and the corresponding diagram is shown in Fig. 1, while selected bond distances and angles are summarized in Table 2. The structure of complex **4a** has pseudo-tetrahedral geometry about the nickel center, showing C_{2v} molecular symmetry. The two imino C=N bonds have typical double bond character with C=N bond lengths of 1.284 Å. Both aryl rings bonded to the iminic nitrogens of the α -diimine lie nearly perpendicular to the plane formed by the nickel and coordinated nitrogen atoms. The phenyl rings in the 2,6-position of the benzenamine fragments in **4a** point



Scheme 1. Syntheses of α -diimine ligands **3a–c** and their corresponding α -diimine nickel(II) dibromide complexes **4a–c**.



Fig. 1. ORTEP drawing of complex 4a with 30% probability displacement ellipsoid.

toward each other above and below the plane, thus shielding the apical positions of the Ni(II) center. Its structure is similar to those reported in the literature for other similar [NiBr₂(α -diimine)] compounds characterized by X-ray diffraction, {bis[*N*,*N'*-4-bromo-2,6-dimethylphenyl)imino]acenaphthene}dibromonickel [34] and {bis[*N*,*N'*-(2, 4, 6-trimethylphenyl)imino]acenaphthene}dibromonickel [35]. In fact, the Ni—N bond distances in complex **4a** (2.032 Å) are similar to those determined for these compounds (2.026 and 2.021 Å, respectively), as well as the Ni—Br bond distances (2.3336 Å for complex **4a** vs. 2.3229 and 2.323 Å, respectively). However, the N—Ni—Br angles (96.97° for complex **4a**) are very different to those determined for those compounds (113.32 and 114.4°, respectively) due to the great steric hindrance of the four *ortho* benzene rings of complex **4a** around Ni(II) center.

3.2. Polymerization of ethylene with nickel complexes 4a-c

The three α -diimine nickel (II) complexes **4a**, **4b**, and **4c**, activated by DEAC, were tested as catalyst precursors for the

 Table 2

 Selected bond lengths (Å) and angles (°) for complex 4a.

-		-	
Bond lengths	(Å)	Bond angles	(°)
Ni1—N1i	2.032 (3)	N1i—Ni1—N1	81.34(17)
Ni1-N1	2.032 (3)	N1i—Ni1—Br1	96.97 (9)
Ni1—Br1	2.3336 (9)	N1-Ni1-Br1	132.88 (9)
Ni1—Br1i	2.3337 (9)	N1i—Ni1—Br1i	132.88 (9)
C1-N1	1.435 (4)	N1—Ni1—Br1i	96.97 (9)
C4—F1	1.355 (5)	Br1—Ni1—Br1i	116.19(5)
C14-C15	1.377 (6)	C19-N1-Ni1	112.4(2)
C15-C16	1.360(8)	C1-N1-Ni1	122.2 (2)
C16-C17	1.385 (8)	C2-C1-N1	117.3 (3)
C17-C18	1.378(7)	C6-C1-N1	120.2 (3)
C19-N1	1.284(4)	C3-C4-F1	118.1 (4)
C19-C20	1.461 (5)	F1-C4-C5	119.0(4)
C19-C19i	1.485(7)	N1-C19-C20	135.4 (4)
C20-C25	1.376 (5)	N1-C19-C19i	116.9(2)
C20-C21	1.417 (5)	C19-N1-C1	124.5 (3)

polymerization of ethylene, under the same reaction conditions. The results of the polymerization experiments are shown in Table 3. Noteworthy is the fact that blank experiments carried out with DEAC alone, under similar conditions, showed its inability to polymerize ethylene on its own.

Three α -diimine Ni(II)/DEAC catalytic systems are highly active for ethylene polymerization due to the bulky *ortho*-phenyl substituents on the aryl rings of α -diimine Ni(II) complexes [the highest activities: **4a**: 4.95×10^6 g PE/(mol Ni h bar); **4b**: 2.89×10^6 g PE/(mol Ni h bar); **4c**: 4.00×10^6 g PE/(mol Ni h bar)] (Table 3).

The performances of the nickel precatalysts are also affected by 4-position substituents on the benzenamine rings of α -diimine Ni(II) complexes (Table 3). To our surprise, α -diimine nickel complex (4a) bearing strong electron-withdrawing 4-fluorine groups [the highest activity, 4.95×10^6 g PE/(mol Ni h bar) was obtained at 600 of Al/Ni ratio at 0°C, Run 3], activated by DEAC, shows higher activities for ethylene polymerization than those observed for 4b and 4c in same conditions (normally, a complex bearing 4-position electron-withdrawing substituents on the benzenamine rings shows lower activity than that of a complex bearing 4-position electron-donating substituents [8]). Complex 4b bearing electron-withdrawing 4-chlorine groups [the highest activity, 2.59×10^6 g PE/(mol Ni h bar) was obtained at 600 of Al/Ni ratio at 20°C, Run 11] exhibits an activity close to complex 4c bearing electron-donating 4-methyl groups [the highest activity, 4.00×10^6 g PE/(mol Ni h bar) was obtained at 600 of Al/Ni ratio at 20°C, Run 16]. This difference, observed between complex 4a and the others, may be partially due to the presence of the very strong electron-withdrawing F group in the 4-position of the 2,6-diphenylbenzenamine rings. In fact, the activity of these catalysts depends not only on the coordination step (π -complex formed between the metal atom of the catalyst and the double bond of the monomer), but also on the activation energy of the migratory insertion step. The barriers to migratory insertions as measured by low-temperature NMR spectroscopy in the nickel systems lie in the range of 13–14 kcal/mol with systems bearing

Table 3	
Polymerization of ethylene with complexes 4a-c/DEA	IC. ^a

Run	Complex	[Al]/[Ni]	$T(^{\circ}C)$	t(min)	Yield (g)	Activity ^b	TOF^{c} (h bar) ⁻¹	$M_{\rm n}~(\rm kg/mol)^{\rm d}$	$M_{\rm w}/M_{\rm n}{}^{\rm d}$	Branches ^e /1000 C	D ^f (nm)
1	4a	200	0	10	1.75	3.91	1.40	115.3	1.68	-	-
2	4a	400	0	10	1.78	3.97	1.42	109.8	1.68	-	-
3	4a	600	0	10	2.22	4.95	1.77	102.3	1.73	-	-
4	4a	800	0	10	1.98	4.42	1.58	16.2	1.78	-	-
5	4a	1000	0	10	1.77	3.94	1.41	16.0	1.82	-	-
6	4a	600	20	10	1.51	3.37	1.20	14.4	1.85	93.2	13.5 ± 5.1
7	4a	600	40	10	0.88	2.05	0.74	11.3	1.87	125.7	11.2 ± 4.9
8	4a	600	60	10	0.70	1.56	0.57	10.7	1.95	153.3	9.75 ± 1.2
9	4b	600	0	10	0.86	1.98	0.71	17.1	1.74	-	-
10	4b	600	10	10	1.01	2.43	0.87	19.1	1.79	-	-
11	4b	600	20	10	1.25	2.89	1.03	20.4	1.87	86.3	16.8 ± 3.2
12	4b	600	40	10	1.05	2.43	0.87	11.4	1.99	114.2	15.1 ± 3.5
13	4b	600	60	10	0.54	1.23	0.44	9.7	1.75	122.2	11.3 ± 2.4
14	4c	600	0	10	0.41	0.91	0.33	13.1	1.83	-	-
15	4c	600	10	10	1.72	2.84	1.01	14.6	1.88	-	-
16	4c	600	20	10	1.81	4.00	1.43	12.3	1.94	78.4	19.2 ± 4.1
17	4c	600	40	10	1.59	3.52	1.16	10.4	1.97	96.1	14.2 ± 3.2
18	4c	600	60	10	1.25	2.81	1.00	6.5	2.08	109.9	12.6 ± 2.1

^a Polymerization conditions: n(4a)=2.24 μmol, n(4b)=2.17 μmol, n(4c)=2.26 μmol; ethylene relative pressure=0.2 bar; ethylene absolute pressure=1.2 bar; *t* = polymerization time; solvent = toluene (50 ml); *T* = polymerization temperature.

Activity in 10⁶ g PE/(mol Ni h bar).

Turnover frequency in 10⁵ mol ethylene/(mol Ni h bar). d

Determined by GPC.

Estimated by ¹H NMR [39]. Branches/1000C = $(1/3)I_{CH_3}/(([I_{CH_2} - (1/3)I_{CH_3})]/2) + ((1/3)I_{CH_3})) \times 1000$

Estimated by particle size analyzer.

the bulkiest alkyl ligands (the most electron-donor character of the Ni atom) exhibiting the lowest insertion barriers (the highest insertion rate). Increased steric bulk of the diimine ligand aryl substituents (electron-donor character of the Ni atom) leads to an increase in the ground-state energy of the resting-state species relative to the migratory insertion transition state in nickel species (Scheme 2). Consequently, lower migratory insertion barriers (high insertion rate) were expected with bulkier diimine substituents (electron-donor character of the Ni atom) [20]. Thus, the increase of the electron-donor character of the metal atom is expected to increase the insertion rate while the increase of its electrophilicity is expected to increase the stability of resting state. Therefore, both factors must be balanced when predicting the effect of an electron donor or acceptor substituent on the catalyst activity. As a result, the following activity trend can be summarized for our substituted precatalysts under low ethylene pressure (0.2 bar), in the range 0–60 °C: **4a > 4b** ∼ **4c**.

At 0°C, the activity of complex **4a** increases slightly with the increase of [Al]/[Ni] ratio (Runs 1-3), the maximum around [Al]/[Ni] ratio 600 (Run 3), and then the activity decreases slightly with the increase of [Al]/[Ni] ratio (Runs 3-5). For a ratio [Al]/[Ni] 600, an increase in the polymerization temperature in the range 0-60 °C decreases slightly the activity of the precatalyst 4a (Runs 3, 6-8). However, precatalysts 4b and 4c show the highest activities around 20 °C (Runs 9–13 for complex 4b; Runs 14–18 for complex 4c).

3.3. Control of the polyethylene topology and size by α -diimine ligand structures and polymerization conditions

The type and amount of branches formed in the polymerization of ethylene promoted by typical α -diimine nickel precatalysts depend on reaction parameters such as the reaction temperature, ethylene pressure and ligand structure [20]. Generally, low ethylene pressure and high polymerization favor the Chain-Walking, and afford high branched polyethylenes [20]. However, the effect of ligand structure on polyethylene branching is much more complicated.

Previous studies by Guan and coworkers demonstrated that in ethylene polymerization the PE branching topology could be simply controlled by the pressure of ethylene, with linear PE being formed at high pressure and dendritic PE being obtained at very low pressure [36–38]. So, in this study, the low ethylene pressure (0.2 bar) was employed. Also, in order to keep the high productivity of polyethylene at low ethylene pressure, three new catalysts containing two bulky ortho-phenyl substituents on benzenamine rings were synthesized.

Our previous studies show that the more electron-rich catalyst affords a more linear polymer. Conversely, the more electrondeficient catalyst affords a more dendritic polymer [8]. So, complexes 4a and 4b containing electron-withdrawing para-F/Cl substituents on benzenamine rings were synthesized to prepared nanosized dendritic polyethylene.

As shown in Table 3 and Fig. 2, the catalyst systems 4a/DEAC, containing a strong electron-withdrawing F groups, generated polyethylene with high degrees of branching. The total branching degrees of the polymer samples prepared with 4a/DEAC (Runs 6-8, branching degree: 93.2, 125.7 and 153.3 branches/1000 C at 20, 40 and 60°C, respectively; diameter: 13.5, 11.2 and 9.75 nm at 20, 40 and 60 °C, respectively) are much higher than those observed for 4b/DEAC (Runs 11–13, branching degree: 86.3, 114.2 and 122.2 branches/1000 C at 20, 40 and 60 °C, respectively; diameter: 16.8, 15.1 and 11.3 nm at 20, 40 and 60 °C, respectively), and 4c/DEAC



Activation and Coordination **Resting State**

Scheme 2. Mechanism of ethylene insertion.



Fig. 2. ¹H NMR (CDCl₃/o-dichlorobenzene, v/v = 1:3) spectrum of the nanosized dendritic polyethylene catalyzed by 4a/DEAC at 60 °C (Table 3, Run 8).

systems (Runs 16-18, branching degree: 78.4, 96.1 and 109.9 branches/1000 C at 20, 40 and 60 °C, respectively; diameter: 19.2, 14.2 and 12.6 nm at 20, 40 and 60 °C, respectively). Also the total branching degrees of the polymer samples prepared with 4a/DEAC was higher than those observed for similar precatalyst/DEAC systems such as {bis[N,N'-(4-tert-butyl-diphenylsilyl-2,6-diisopropylphenyl)imino]acenaphthene}dibromonickel (45 branches/ 1000 C, at 20 °C) [20] or precatalyst/MAO systems such as {bis[N,N'-(2,6-diisopropylphenyl)imino]-1,2-dimethylethane} dibromonickel (30, 67, 80 and 90 branches/1000C, at 25, 50, 65 and 80°C, respectively) [20], and {bis[N,N'-(2,6diisopropylphenyl)imino]acenaphthene}dibromonickel (65)branches/1000 C, at $25 \circ C$) [20], although the reaction conditions are not exactly the same as in the present work. The total branching degree of the polymer sample obtained with 4c bearing electron-donating methyl groups is the lowest among our three complexes.

Our results (Table 3) indicate that the more electron deficient the catalyst, the more dendritic the polymer formed. A more electron-deficient ligand may better stabilize the transition state for monomer chain walking than for insertion, which should afford a more dendritic polymer. These results provide a strategy to control the branching topology by controlling the electronic effect of the catalysts and polymerization conditions.

The dendritic polyethylene particle size obtained by **4a**/DEAC can be controlled in the 1–20 nm under 0.2 bar ethylene pressure, and could be expected to become a nano-targeted drug carrier after modified with water-soluble oligo(ethylene glycol) (OEG).

4. Conclusions

Three new α -difficult ligands **3a–c**, and their Ni(II) complexes **4a–c** have been prepared and characterized. Ligands **3a–3c** were modified in an attempt to change steric effects and the electronic density of the metal center and eventually to improve the activity in the polymerization of ethylene and control the microstructure and size of the polyethylenes obtained. The results obtained show that complex 4a, activated by DEAC produces highly active catalyst system for the polymerization of ethylene. Complex 4a bearing strongly electron-withdrawing 4-fluorine groups produced nanosized dendritic polyethylene at 60°C. A more electron-deficient ligand may better stabilize the transition state for monomer chain walking than for insertion, which should afford a more dendritic polyethylene. The dendritic polyethylene particle size obtained by 4a/DEAC can be controlled in the 1–20 nm under 0.2 bar ethylene pressure, and could be expected to become a nano-targeted drug carrier after modified with water-soluble oligo(ethylene glycol) (OEG).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata. 2013.01.016.

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