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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_{2v} 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 [4.95×10^6 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).

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 water-soluble oligo(ethylene glycol) (OEG).

In this work, we report the synthesis and characterization of three new α-diimine Ni(II) complexes of the type [$NiBr_2$(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 4 Å molecular sieves and distilled from CaH_2 under dry nitrogen. Toluene, diethyl ether, and 1,2-dimethoxyethane (DME) were distilled from sodium/benzophenone under N_2 atmosphere. Anhydrous $NiBr_2$ (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**), 4-methylbenzenamine (98%), and 4-chlorobenzenamine (98%), were purchased from Alfa Aesar, and used without further purification. [$NiBr_2$(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 (2 ml) was added to a stirred solution of 4-chlorobenzenamine (0.64 g, 5 mmol) in CH_2Cl_2. The solution was stirred for 30 min. After the solution cooled to 5 °C with ice bath, Br_2 (2.00 g, 12.5 mmol) in 5 ml CH_2Cl_2 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 $MgSO_4$, 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). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.55 (s, 2H, —NH_2), 7.38 (s, 2H, $C_6H_2Br_2ClNH_2$). ^{13}C 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 (2 ml) was added to a stirred solution of 4-methylbenzenamine (0.54 g, 5 mmol) in CH_2Cl_2. The solution was stirred for 30 min. After the solution cooled to 5 °C with ice bath, Br_2 (2.00 g, 12.5 mmol) in 5 ml CH_2Cl_2 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 $MgSO_4$, 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). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.20 (s, 3H, —CH_3), 4.38 (s, 2H, —NH_2), 7.19 (s, 2H, $C_6H_2Br_2CH_3NH_2$). ^{13}C NMR (400 MHz, $CDCl_3$): δ 19.75 (—CH_3), 108.69 (benzenamine carbon connected with Br), 129.31 (benzenamine carbon connected with CH_3), 132.13 (benzenamine carbon), 139.48 (benzenamine carbon connected with NH_2).

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

$Pd(OAc)_2$ (0.01 g, 0.04 mmol), 2,6-dibromo-4-fluorobenzenamine (0.54 g, 2 mmol), K_2CO_3 (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 24 h, 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 $MgSO_4$, 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). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.66 (s, 2H, —NH_2), 6.85 (d, 2H, benzenamine), 7.34 (t, 2H, phenyl ring), 7.43–7.49 (m, 8H, phenyl ring). ^{13}C NMR (400 MHz, $CDCl_3$): 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 NH_2), 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-4-chlorobenzenamine (0.57 g, 2 mmol), K_2CO_3 (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 24 h, 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 $MgSO_4$, 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). ^{1}H NMR (400 MHz, $CDCl_3$): 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). ^{13}C NMR (400 MHz, $CDCl_3$): 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-4-methylbenzenamine (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 24 h, 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 $MgSO_4$, 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). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.21 (s, 3H, CH_3 of benzenamine ring), 3.59 (s, 2H, —NH_2), 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). ^{13}C NMR (400 MHz, $CDCl_3$): δ 20.41 (CH_3), 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).