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# Self-immobilizing binuclear neutral nickel catalyst for ethylene polymerization: Synthesis and catalytic studies

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ABSTRACT

A allyl-substituted salicylaldimine proligand (Scheme 1, Compound **5**) was prepared by a condensation reaction, which reacted with *trans*-[NiCl(Ph)($PPh_3$)$_2$] to give a binuclear neutral nickel (II) complex [((4-Allyl-2,6-i$Pr_2C_6H_2$) NCH)$C_6H_3$ONi($PPh_3$)Ph]$_2$ (Scheme 1, Complex **6**). The structure of the complex was characterized by $^1$H NMR, $^{13}$C NMR and elemental analysis. This novel complex bearing allyl groups can be used as a self-immobilizing catalyst for the polymerization of ethylene and does not need a cocatalyst for their catalytic performance. The self-immobilizing catalytic systems not only possess high activity (up to $5.23 \times 10^5$ g of PE/(mol of Ni h)) but also can produce high-molecular-weight polyethylenes ($Mw = (0.42–0.71) \times 10^6$) with relatively broad molecular weight distributions ($MWD = 2.83–3.11$). According to the $^{13}$C NMR analyses, the resultant polyethylenes contain a few branched chains mainly consisting of methyl branches.



## 1. Introduction

Recently, Grubbs and his co-workers have reported a new family of late-transition-metal catalysts based on neutral Ni(II) complexes containing substituted salicylaldiminato N, O ligands. These salicylaldimine-based neutral nickel (II) catalysts are capable of polymerizing ethylene to produce high-molecular-weight linear polyethylene even in aqueous emulsion. More important, such novel complexes not only have high activity for olefin polymerization but also can produce functionalized olefins due to their good tolerances to the polar functional groups during polymerization process [1–9]. However, the homogeneous catalysts can easily lead to a giant heat release effect and a serious reactor fouling in the slurry process of olefin polymerization. Thus the application of these catalysts in a continuous process is difficult. In general, the way to solve these problems is to immobilize the catalysts on suitable carriers. Up to now, three methods have been developed for the supporting of late transition metal catalysts [10–20]. The first method involves direct immobilization of the catalyst on the carrier surface, which usually significantly suppresses the catalytic activity, and changes the catalyst structure and the microstructure of the resultant polymer. The second method is the immobilization of the catalyst on the carrier pretreated with MAO or alkylaluminium compounds. It is expected that the carrier and MAO or alkylaluminium compounds are bound by loose ionic interactions. However, this fairly weak bond may lead to the easy departure of catalyst from carrier surface. The third method involves the covalent bonding between the ligand of catalyst and the carrier, which is commonly used in the ethylene polymerization.

As a new heterogenization strategy different from the three methods mentioned above, Alt [21] has developed the self-immobilizing metallocene catalysts, which can be used as a comonomer with an olefin or alkyne functional group in the polymerization. More recently, Herrmann [22], Alt [23] and Jin et al. [24] have reported the self-immobilizing Fe and single nuclear neutral Ni catalysts, respectively, for olefin polymerization. However, the self-immobilizing binuclear or multi neutral nickel catalysts were seldom studied. This prompted us to explore the self-immobilizing of binuclear or multi neutral nickel catalysts and study their catalytic behavior for ethylene polymerization so as to obtain polyethylene with high molecular weight.

According to Grubbs and his co-workers' work, the salicylaldimine-based neutral nickel(II) catalysts containing bulky substituents at the ortho position of a phenoxy group ($C_3$) not only shows high catalytic activities for ethylene polymerization to produce high-molecular-weight polyethylenes without using cocatalysts, but also can catalyze the copolymerization of ethylene and some functionalized olefins. If there is no bulky substituent at the *ortho* position of the phenoxy group, the catalysts exhibit no activity for ethylene polymerization. Even when $(COD)_2Ni$ or $B(C_6F_5)_3$ was used as a phosphine acceptor, only a low catalytic activity was obtained. This is due to the fact that the introduction of

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a bulky substituent at the *ortho* position of the phenoxy group ($C_3$) not only blocks the axial faces of the nickel center and retards the rate of chain termination but also enhances the catalytic activity by accelerating $PPh_3$ dissociation and decreases the rate of catalyst deactivation. Following this strategy, for the self-immobilized neutral catalysts, two important factors must be considered in the design of catalysts: one is introduction of bulky substituents *ortho* to the phenoxy group ($C_3$) in the salicylaldimine ligand, which favors obtaining high catalytic activity and polyethylene with high molecular weight, and the other is introduction of an active functional group such as allyl in the salicylaldimine ligand, which can simultaneously incorporate into the growing chain of polyethylene during polymerization.

Herein, we report the synthesis of a binuclear neutral nickel (II) complex with allyl groups (see Scheme 1) as a single-component self-immobilizing catalyst, which exhibit high activities for ethylene polymerization in the absence of cocatalyst and can produce high-molecular-weight branched polymers (see Scheme 2).

## 2. Experimental

### 2.1. General procedures and materials

All manipulations of air- and water-sensitive compounds were performed using standard Schlenk techniques. Solvents were dried by refluxing with appropriate drying agents (sodium/benzophenone for toluene, benzene, diethyl ether, THF, and *n*-pentane; $CaH_2$ for Methylene dichloride) and distilled under nitrogen prior to use. $(COD)_2Ni$ was purchased from Sigma–Aldrich and used as received. 4-Allyl-2, 6-diisoproylaniline was prepared according to a previously reported procedure [25]. All the other chemicals were purchased commercially, and used without further purification.

### 2.2. Synthesis of the proligands

#### 2.2.1. Synthesis of Compound **4**

In accordance with the reported method [24], Compound **4** was prepared from 2,2-biphenol. $^1$H NMR (500 MHz, $CDCl_3$, $\delta$ ppm): 7.11 (t, 2H, Ar—H), 7.61 (m, 4H, Ar—H), 9.88 (s, 2H, CHO), 11.21 (s, 2H, OH). IR (KBr) $\nu$, 1636 cm$^{-1}$ (CH=O), 3431 cm$^{-1}$ (OH). Elemental analysis: Calcd for $C_{14}H_{10}O_4$ (%): C, 69.42; H, 4.16. Found (%): C, 69.34; H, 4.12.

#### 2.2.2. Synthesis of Compound **5**

4-Allyl-2, 6-diisoproylaniline (5.43 g, 2.5 mmol) and formic acid (0.5 mL) as a catalyst were added to a solution of Compound **4** (2.42 g, 10 mmol) in dried methylene dichloride (60 mL) under stirring. The mixture was refluxed and stirred for 48 h. During the stirring period, a yellow solution was formed. The evaporation of solvent gave a yellow solid powder. The crude product was washed three with ethanol and dried in vacuum oven at 50 °C, affording a yellow solid powder (5.25 g, yield: 82.11%). $^1$H NMR (500 MHz, $CDCl_3$, $\delta$ ppm): 12.41 (s, 2H, —OH); 8.35 (s, 2H, —N=CH—Ar); 7.04, 7.16, 7.36,7.67 (m, 6H, —N=CH—Ar—H);6.82 (s,4H, CH=N—Ar—H); 1.21,1.19 (d, 24H, —CH($CH_3$)$_2$); 2.99 (d, 4H, —CH($CH_3$)$_2$); 3.29 (d,4H, —$CH_2$—CH=$CH_2$); 6.08 (m, 2H, —$CH_2$—CH=$CH_2$); 5.11, 5.09 (d, 4H, —$CH_2$—CH=$CH_2$). Elemental analysis: Calcd for $C_{44}H_{52}O_2N_2$ (%): C, 82.51; H, 8.13; N, 4.37. Found (%): C, 82.32; H, 8.18; N, 4.40.

### 2.3. Synthesis of the complex

#### 2.3.1. Synthesis of Complex **6**

A solution of Compound **5** (0.61 g, 0.95 mmol) in anhydrous THF (40 mL) was added to sodium hydride (0.058 g, 2.42 mmol). The resultant mixture was stirred at room temperature for 5 h and then filtered and evaporated. The solid residue was immediately used in the next step without further purification. The Na salt of Compound **5** obtained above and *trans*-[Ni($PPh_3$)$_2$PhCl] (1.48 g, 2.12 mmol) were dissolved in benzene (60 mL) in a Schlenk flask and stirred at room temperature for 24 h. The resultant mixture was filtered, and the filtrate was concentrated under vacuum to 10 mL. Pentane (50 mL) was added to the reaction mixture. A pale brown solid crystallized from solution, which was isolated by filtration to give Complex **6** (0.84 g, yield: 62%).

$^1$H NMR (500 MHz, $C_6D_6$, $\delta$ ppm): 5.92–7.79 (m, 52H, Ar—H); 7.60 (d, 2H, —N=CH—Ar); 1.29 (d, $J_{H,H}$, 6.6 Hz, 12H, —CH($CH_3$)$_2$); 1.38 (d, $J_{H,H}$, 6.3 Hz, 12H, —CH($CH_3$)$_2$); 4.32 (m, 4H, —CH($CH_3$)$_2$); 3.41 (d, 4H, —$CH_2$—CH=$CH_2$), 6.04 (m, 2H, —$CH_2$—CH=$CH_2$); 5.09 (d, 4H, —$CH_2$—CH=$CH_2$). $^{13}$C NMR (500 MHz, $C_6D_6$, $\delta$ ppm): 23.4, 28.2, 48.7, 117.1, 119.3, 122.6, 124.1, 124.9, 126.2, 128.3, 130.5, 132.4, 132.5, 134.8, 136.2, 137.8, 141.3, 149.4, 164.2, 165.6. Elemental analysis: Calcd for $C_{92}H_{90}N_2Ni_2O_2P_2$ (%): C, 77.03; H, 6.28; N, 1.95. Found (%): C, 77.12; H, 6.34; N, 1.89.

### 2.4. General procedure for ethylene polymerization

A 100-mL autoclave was heated under vacuum to 120 °C for 1 h and then was cooled to the desired reaction temperature in an oil bath with constant temperature. The autoclave was purged by ethylene three times and then was charged with 60 ml of toluene. A solution of the binuclear neutral nickel catalysts was added by a syringe. Next, the autoclave was sealed and pressurized to the desired level, and the polymerization was started by stirring. Finally, the polymerization was terminated by the addition of acidified ethanol. The solid polyethylene was filtered, washed with ethanol, and dried in vacuum oven at 60 °C.

### 2.5. Characterizations

The $^1$H NMR and $^{13}$C NMR spectra of the ligands and the complex were recorded on a Bruker-500 spectrometer. The $^{13}$C NMR spectroscopic data for polyethylene were obtained with a Varian INOVA-500 NMR spectrometer at 130 °C using *o*-dichlorobenzene as the solvent. Elemental analyses were performed on a Vario EL analyzer. The IR spectra were recorded on Bruker Equinox 55 spectrophotometer. Molecular weights ($M_n$ and $M_w$) and molecular weight distributions (*MWD*) of polyethylene were determined by high-temperature GPC using a Waters GPC-V200 RI detector. The measurements were recorded at 140 °C using 1,2,4-trichlorobenzene as a solvent. DSC measurements were performed with a Perkin-Elmer Pyris1 differential scanning calorimeter at a rate of 10 °C/min, and the melting temperatures were reported for the second heating cycle.

## 3. Results and discussion

### 3.1. Synthesis and characterization of proligands and complex

The general synthetic route for proligand Compound **4** and binuclear neutral nickel (II) Complex **6** containing ally group were shown in Scheme 1. In accordance with the reported method [26], Compound **4** was readily synthesized in good yield via a three-step reaction using 2,2-biphenol as a starting material. The ligand **5** was synthesized via the condensation reaction of Compound **4** and an excess of 4-allyl-2,6-diisoproylaniline in excellent yield. The deprotonation of ligand **5** was carried out with an excess of NaH in anhydrous THF and the sodium salt of the corresponding ligand was obtained in benzene. Without further purification, the sodium salt of ligand 5 was directly combined with *trans*-[NiCl(Ph)($PPh_3$)$_2$]