

# Nickel(II) Complexes Containing RCOO-Substituent as Highly Active Single-Component Catalysts for Ethylene (Co) Polymerization

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**Abstract** Mononuclear nickel complexes  $[(2,6-R_2-C_6H_3)-N=C(H)-(3-Ph-5-PhCOO-2-O-C_6H_2)-\kappa^2-N,O]$  Ni(CH<sub>3</sub>)(pyridine)] (R = *i*Pr; 3,5-*t*Bu<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (**Ni**<sup>1</sup> ~ **Ni**<sup>2</sup>) and binuclear nickel complex (**Ni**<sup>3</sup>) were synthesized, characterized and applied in ethylene (co) polymerization. As single-component catalysts, all these complexes are capable of converting ethylene to branched polyethylenes (PE) with moderate relative molecular mass. The electron-donating group PhCOO— facilitates the initiation of catalyst **Ni**<sup>1</sup>, leading to better catalytic activity at low temperature compared to nickel methyl pyridine complex (**Ni**<sup>0</sup>). Introducing bulky 2,6-(3,5-(*t*-Bu)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N— moiety, the activities of **Ni**<sup>2</sup> up to 1.8 × 10<sup>6</sup> g of PE mol<sup>-1</sup> · Ni<sup>-1</sup> · h<sup>-1</sup> (at 5 × 10<sup>5</sup> Pa ethylene) were among the highest values using phenoxyiminato neutral nickel catalysts. Binuclear catalyst **Ni**<sup>3</sup> shows better tolerance toward PPh<sub>3</sub> donor additive than its mononuclear counterpart. In the presence of comonomers 1,5-hexadiene, 1,7-octadiene, 6-bromo-1-hexene, or methyl 10-undecenoate, these catalysts effectively enchain these comonomers into the polymer chain to give functionalized polyethylenes.

**Keywords** neutral nickel catalysts; electronic effects; olefin polymerization; functionalized polyolefin

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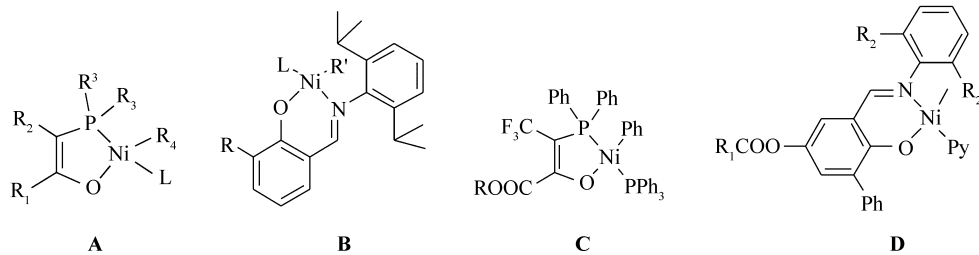
Shell higher olefin process (SHOP)-type catalysts<sup>[1]</sup> (Scheme 1, **A**) as the oldest neutral nickel catalysts have been successfully commercialized for the synthesis of linear  $\alpha$ -olefins. However, no noticeable improvement has been made in this field until Grubbs *et al.*<sup>[2-3]</sup> covered the phenoxyiminato neutral nickel catalysts (Scheme 1, **B**). These complexes, with bulky groups at the ortho position of the phenoxy moiety, generate high relative molecular mass polymers with excellent activities comparable to the classic metallocenes, and show substantial tolerance toward various polar additives. Since then, nickel catalysts<sup>[4-10]</sup> have attracted much attention, and the electronic and steric effects of the auxiliary ligands have been extensively studied. Neutral nickel (II) catalysts containing highly electron-withdrawing groups —CF<sub>3</sub> and —COOR<sup>[11]</sup> (Scheme 1, **C**) afford low relative molecular mass highly linear polyethylene (PE) with very high activity. Mecking group<sup>[12-13]</sup> reported the vital role of electron-donating groups in neutral nickel polymerization catalysts, which are responsible for the resultant hyperbranched ethylene oligomers. Generally speaking, electron-donating groups would enhance tolerance of the catalysts toward polar groups by increasing the electron density of nickel center, and facilitate polymerization initiation by promoting the dissociation of

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additional stabilizing ligand. As an electron-donating group, RCOO— has been rarely applied for nickel catalysts in olefin polymerization<sup>[14]</sup>. Thus, we designed a series of catalysts bearing RCOO— groups (Scheme 1, **D**) to study their properties in ethylene polymerization. Considering the vital role of effective blockage of the axial positions of nickel center, nickel complexes with 2,6-(3,5-*t*Bu<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NH<sub>2</sub> was also synthesized.



Scheme 1 Typical neutral nickel catalysts for olefin polymerization

Moreover, —OC(O)—R—COO— as excellent bridges for binuclear catalyst<sup>[15]</sup> have gained great success in various catalytic reactions<sup>[16-19]</sup>. We thus also designed and synthesized novel binuclear neutral nickel catalyst Ni<sup>3</sup> bearing OC(O)—R—COO— (R = *o*-C<sub>6</sub>H<sub>4</sub>) linkage to address their catalytic properties. Without any cocatalysts, all these complexes displayed very high activities up to  $1.8 \times 10^6$  g of PE mol<sup>-1</sup>·Ni<sup>-1</sup>·h<sup>-1</sup> even at low ethylene pressure ( $5 \times 10^5$  Pa), which are among the highest catalytic activities for phenoxyiminato neutral nickel catalysts in ethylene polymerization. These catalysts demonstrated good polar monomer tolerance, and were capable to catalyze the copolymerization of ethylene with 1,5-hexadiene, 1,7-octadiene, 6-bromo-1-hexene and methyl 10-undecenoate, yielding copolymers with moderate relative molecular mass at moderate activities.

## 1 Experimentals

### 1.1 Instruments and Reagents

All manipulations of air- and/or moisture-sensitive compounds were carried out using standard Schlenk techniques or in a Etelux lab2000 glovebox under a dry nitrogen atmosphere. Toluene, *n*-hexane, diethyl ether, dimethylformamide (DMF), and methylene dichloride were purified by an MBraun solvent purification system (SPS). Pyridine and *N,N,N*-triethylamine was distilled from sodium/benzophenone ketyl under nitrogen prior to use. BBr<sub>3</sub>, MeI, K<sub>2</sub>CO<sub>3</sub>, CH<sub>3</sub>COOH, CH<sub>3</sub>COONa, *p*-toluenesulfonate, 4-dimethylaminopyridine, benzoyl chloride and phthaloyl dichloride were purchased from Beijing Chemical Works and directly used without purification. 1,5-Hexadiene, 1,7-octadiene, and methyl 10-undecenoate were distilled after drying *via* calcium hydride for two days. These monomers were purchased from J&K Chemical. 2,5-Dimethoxy-3-phenylbenzaldehyde<sup>[20]</sup>, 2,6-(3,5-*t*Bu<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NH<sub>2</sub><sup>[13]</sup>, and (pyridine)<sub>2</sub>Ni(CH<sub>3</sub>)<sub>2</sub><sup>[21]</sup> were synthesized according to reported literature. Ethylene (99.999%) was purchased from Changchun Juyang Corporation and was used without further purification.

The nuclear magnetic resonance (NMR) spectra of polyethylene samples were all recorded on a Varian Unity 400 MHz spectrometer (Bruker Corporation) with *o*-dichlorobenzene-*d*<sub>4</sub> or 1,1,2,2-tetrachloroethane-*d*<sub>2</sub> as the solvent at 110 °C. All <sup>1</sup>H and <sup>13</sup>C NMR spectra of small organic and organometallic compounds were obtained on a Bruker 300 MHz spectrometer, a Varian Unity 400 MHz spectrometer or a Bruker 500 MHz spectrometer at ambient temperature with CDCl<sub>3</sub>, C<sub>6</sub>D<sub>6</sub> or dimethylsulfoxide-*d*<sub>6</sub> (DMSO-*d*<sub>6</sub>) as the solvent. The DSC measurements were performed on a Perkin-Elmer Pyris 1 differential scanning calorimeter at a heating rate of 20 °C/min. The mass-average relative molecular mass (*M*<sub>w</sub>) and the polydispersity index (PDI) of

polyethylene samples were determined *via* high-temperature gel permeation chromatography (GPC) in which 1, 2, 4-trichlorobenzene was used as mobile phase at a flow rate of 1.0 mL/min. The calibration was made by the polystyrene standard Easi-Cal PS-1 (PL Ltd., Agilen, Santa Clara, California, USA).

## 1.2 Synthesis of Compounds **b** ~ **d**

**3-phenyl-2,5-dihydroxy-benzaldehyde (b)**: In a flame dried two necked flask equipped with a pressure equalizing dropping funnel, 3-phenyl-2,5-dimethoxy-benzaldehyde (**a**) (2.2 g, 9.0 mol) was dissolved in dry dichloromethane (DCM, 20 mL). The resulting solution was cooled to  $-78\text{ }^{\circ}\text{C}$  and a solution of  $\text{BBr}_3$  in DCM (2 mol/L, 18 mL) was slowly added to the solution *via* the pressure equalizing dropping funnel in 20 min. The resulting solution was maintained at  $-78\text{ }^{\circ}\text{C}$  for 40 min, then was allowed to warm up to room temperature and left with stirring overnight under a nitrogen atmosphere. After 10 hours, the solution was quenched with ice to neutralise the excess  $\text{BBr}_3$ , and the DCM was removed under reduced pressure. The resulting mixture was extracted with ethyl acetate (EtOAc, 50 mL  $\times$  3) and the combined organic extracts were washed twice with brine (50 mL  $\times$  2), dried ( $\text{MgSO}_4$ ), and filtered. The solvent was removed in vacuo yielding 3-phenyl-2,5-dihydroxy-benzaldehyde (1.7 g, 89%) as yellow powder.  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-d}_6$ ),  $\delta$ : 10.65 (s, 1H), 10.02 (s, 1H), 9.51 (s, 1H), 7.54 (d,  $J = 7.0\text{ Hz}$ , 2H), 7.44 (t,  $J = 7.4\text{ Hz}$ , 2H), 7.36 (t,  $J = 7.3\text{ Hz}$ , 1H), 7.13 (d,  $J = 3.1\text{ Hz}$ , 1H), 7.09 (d,  $J = 3.1\text{ Hz}$ , 1H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{DMSO-d}_6$ ),  $\delta$ : 196.89, 150.64, 150.28, 136.46, 130.78, 129.08, 128.24, 127.44, 125.26, 121.85, 116.67.

$[(2,6\text{-}^i\text{Pr}_2\text{-C}_6\text{H}_3)\text{-N}=\text{C}(\text{H})\text{-}(3\text{-Ph-2,5-}(\text{OH})_2\text{-C}_6\text{H}_2)]$  (**c**): To an ethanol (5 mL) solution of compound **b** (0.63 g, 1.9 mmol) was added a catalytic amount of pyridinium *p*-toluenesulfonate (*p*-TSA) and 1.2 stoichiometric amount of 2,6-diisopropylaniline. The mixture was stirred for 12 hours at room temperature. The yellow solid that precipitated was filtered, washed with cold ethanol and dried to afford the Schiff base in 99% yield.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 13.25 (s, 1H, OH), 8.30 (s, 1H, ArH), 7.67 (d,  $J = 7.4\text{ Hz}$ , 2H, ArH), 7.47 (t,  $J = 7.6\text{ Hz}$ , 2H, ArH), 7.37 (t,  $J = 7.0\text{ Hz}$ , 1H, ArH), 7.20 (s, 3H, ArH), 7.08 (s, 1H, ArH), 5.46 (s, 1H, OH), 3.02 (hept,  $J = 6.8\text{ Hz}$ , 2H,  $\text{CH}(\text{CH}_3)_2$ ), 1.18 (d,  $J = 6.9\text{ Hz}$ , 12H,  $\text{CH}(\text{CH}_3)_2$ ).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 166.59, 152.73, 139.23, 137.01, 131.14, 129.44, 128.53, 127.76, 126.00, 123.49, 118.53, 116.88, 28.30, 23.73.

$[(2,6\text{-}(3,5\text{-}^t\text{Bu}_2\text{C}_6\text{H}_3)_2\text{C}_6\text{H}_3)\text{-N}=\text{C}(\text{H})\text{-}(3\text{-Ph-2,5-}(\text{OH})_2\text{-C}_6\text{H}_2)]$  (**d**): Using the same method for synthesizing compound **c**, reaction of compound **b** with 2,6-(3,5-*t*Bu<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NH<sub>2</sub> gave rise to compound **d** as yellow powder in 90% yield.  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO-d}_6$ ),  $\delta$ : 12.49 (s, 1H), 8.98 (s, 1H), 8.08 (s, 1H), 7.46 (d,  $J = 7.8\text{ Hz}$ , 2H), 7.42 ~ 7.33 (m, 5H), 7.29 (d,  $J = 7.1\text{ Hz}$ , 1H), 7.26 (t,  $J = 1.7\text{ Hz}$ , 2H), 7.19 (d,  $J = 1.7\text{ Hz}$ , 4H), 6.77 (d,  $J = 2.8\text{ Hz}$ , 1H), 6.37 (d,  $J = 3.0\text{ Hz}$ , 1H), 1.19 (s, 36H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO-d}_6$ ),  $\delta$ : 169.97, 150.51, 149.93, 148.87, 145.13, 138.02, 137.43, 134.81, 129.63, 129.09, 128.77, 127.92, 126.89, 125.73, 124.16, 121.24, 120.24, 118.86, 116.72, 34.43, 31.07.

## 1.3 Synthesis of ligands **L**<sup>0</sup> ~ **L**<sup>3</sup>

$[(2,6\text{-}^i\text{Pr}_2\text{-C}_6\text{H}_3)\text{-N}=\text{C}(\text{H})\text{-}(3\text{-Ph-2-}(\text{OH})\text{-C}_6\text{H}_3)]$  (**L**<sup>0</sup>): Ligand **L**<sup>0</sup> was synthesized according to the reported literature<sup>[31]</sup>.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 8.37 (s, 1H), 7.71 (d,  $J = 8.3\text{ Hz}$ , 2H), 7.53 (d,  $J = 7.6\text{ Hz}$ , 1H), 7.48 (t,  $J = 7.6\text{ Hz}$ , 2H), 7.37 (t,  $J = 7.1\text{ Hz}$ , 2H), 7.20 (s, 3H), 7.06 (t,  $J = 7.6\text{ Hz}$ , 1H), 3.02 (hept,  $J = 6.8\text{ Hz}$ , 2H), 1.18 (d,  $J = 6.9\text{ Hz}$ , 12H).

$[(2,6\text{-}^i\text{Pr}_2\text{-C}_6\text{H}_3)\text{-N}=\text{C}(\text{H})\text{-}(3\text{-Ph-5-PhCOO-2-}(\text{OH})\text{-C}_6\text{H}_2)]$  (**L**<sup>1</sup>) General procedure for the preparation of ligands **L**<sup>1</sup> ~ **L**<sup>3</sup>. The appropriate acid chloride (1.0 mmol) was added to a solution of compounds **c** or **d** (1.1 stoichiometric amount for **L**<sup>1</sup> and **L**<sup>2</sup>, 2.2 stoichiometric amount for **L**<sup>3</sup>), 4-dimethylaminopyridine (0.2 mmol), and triethylamine (3.0 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) at room temperature

under  $N_2$  atmosphere. After complete consumption of the acid chloride detected by TLC, the mixture was concentrated under reduced pressure and purified by silica gel chromatography. Ligand  $L^1$  was afforded as yellow powder in 84% yield.  $^1H$  NMR(500 MHz,  $CDCl_3$ ),  $\delta$ : 8.34(s, 1H), 8.22(dd,  $J = 8.3, 1.2$  Hz, 2H), 7.73(d,  $J = 7.1$  Hz, 2H), 7.65(t,  $J = 7.5$  Hz, 1H), 7.53(t,  $J = 7.8$  Hz, 2H), 7.47(t,  $J = 7.6$  Hz, 2H), 7.40~7.35(m, 2H), 7.25(s, 1H), 7.19(s, 3H), 3.01(hept,  $J = 6.8$  Hz, 2H), 1.18(d,  $J = 6.9$  Hz, 12H).  $^{13}C$  NMR(126 MHz,  $CDCl_3$ ),  $\delta$ : 166.34, 165.79, 156.65, 145.92, 142.84, 138.90, 136.76, 133.91, 131.41, 130.34, 129.55, 129.45, 128.79, 128.43, 127.83, 127.68, 125.84, 123.79, 123.45, 118.88, 28.27, 23.73.

[ (2,6-(3,5- $t$ -Bu $_2$ C $_6$ H $_3$ ) $_2$ C $_6$ H $_3$ —N=C(H)—(3-Ph-5-PhCOO-2-(OH)-C $_6$ H $_2$ ) ] ( $L^2$ ): Ligand  $L^2$  was afforded in 73% yield.  $^1H$  NMR(300 MHz,  $CDCl_3$ ),  $\delta$ : 8.14(d,  $J = 7.3$  Hz, 2H), 7.92(s, 1H), 7.62(t,  $J = 7.4$  Hz, 1H), 7.49(t,  $J = 7.4$  Hz, 6H), 7.35~7.39(m, 4H), 7.31(s, 2H), 7.23(d,  $J = 1.6$  Hz, 4H), 7.16(d,  $J = 2.8$  Hz, 1H), 6.60(d,  $J = 2.8$  Hz, 1H), 1.25(s, 36H).  $^{13}C$  NMR(126 MHz,  $CDCl_3$ ),  $\delta$ : 168.20, 165.30, 156.27, 150.76, 145.19, 142.35, 138.48, 137.02, 135.94, 133.70, 130.89, 130.22, 130.04, 129.64, 129.39, 128.70, 128.15, 127.49, 127.11, 125.98, 124.57, 123.07, 121.09, 119.08, 34.99, 31.51.

[ C $_6$ H $_4$ (COO) $_2$ - $\{$ (2,6- $i$ -Pr $_2$ -C $_6$ H $_3$ )—N=C(H)—(3-Ph-5-yl-2-(OH)-C $_6$ H $_2$ ) $\}_2$  ] ( $L^3$ ): Ligand  $L^3$  was afforded in 41% yield.  $^1H$  NMR(500 MHz,  $CDCl_3$ ),  $\delta$ : 8.27(s, 2H), 8.02(dd,  $J = 5.7, 3.3$  Hz, 2H), 7.73(dd,  $J = 5.7, 3.3$  Hz, 2H), 7.57(d,  $J = 7.0$  Hz, 2H), 7.38(dd,  $J = 8.9, 6.1$  Hz, 6H), 7.31(t,  $J = 7.4$  Hz, 2H), 7.28(d,  $J = 2.9$  Hz, 2H), 7.19(s, 6H), 2.96(hept,  $J = 6.8$  Hz, 4H), 1.14(d,  $J = 6.9$  Hz, 24H).  $^{13}C$  NMR(101 MHz, DMSO- $d_6$ ),  $\delta$ : 167.83, 165.93, 156.01, 145.22, 142.19, 138.10, 135.92, 132.63, 130.63, 129.99, 129.62, 128.95, 128.15, 127.56, 127.12, 125.71, 124.31, 123.20, 118.82, 27.75, 23.23.

#### 1.4 Synthesis of nickel complexes Ni $^0$ ~ Ni $^3$

[ [ (2,6- $i$ -Pr $_2$ -C $_6$ H $_3$ )—N=C(H)—(3-Ph-2-O-C $_6$ H $_3$ )- $\kappa^2$ -N, O ] Ni(CH $_3$ )(pyridine) ] ( $Ni^0$ ): According to the literature<sup>[22]</sup>, the nickel methyl pyridine complex  $Ni^0$  was prepared in excellent yield by adding dropwise the toluene solution of (pyridine) $_2$ NiMe $_2$  (0.295 g, 1.2 mmol) to toluene solution of ligand  $L^0$  (0.36 g, 1.0 mmol) with vigorous stirring at room temperature. The mixture was stirred at room temperature to give a dark red solution as the reaction proceeded. After 6 hours, the mixture was filtrated to remove nickel black, and the filtrate was directly taken to dryness, affording complex  $Ni^0$  in 95% yield as dark red solid.  $^1H$  NMR(500 MHz, C $_6$ D $_6$ ),  $\delta$ : 8.48(s, 2H), 7.61(s, 1H), 7.44(s, 3H), 7.08~7.16(m, 7H), 6.59(d,  $J = 40.9$  Hz, 2H), 6.18(s, 2H), 4.23(hept,  $J = 6.8$  Hz, 2H), 1.53(s, 6H), 1.11(s, 6H), -0.68(s, 3H, NiCH $_3$ ).  $^{13}C$  NMR(126 MHz, C $_6$ D $_6$ ),  $\delta$ : 166.59, 165.34, 151.97, 150.29, 141.21, 140.81, 135.51, 134.62, 133.91, 133.44, 129.97, 128.35, 127.51, 126.59, 123.65, 123.00, 120.73, 114.13, 28.60, 24.97, 23.23, -7.30(NiCH $_3$ ). Anal. Calcd for C $_{31}$ H $_{34}$ N $_2$ NiO: C 73.11, H 6.73, N 5.50. Found: C 73.09, H 6.76, N 5.48.

[ [ (2,6- $i$ -Pr $_2$ -C $_6$ H $_3$ )—N=C(H)—(3-Ph-5-PhCOO-2-O-C $_6$ H $_2$ )- $\kappa^2$ -N, O ] Ni(CH $_3$ )(pyridine) ] ( $Ni^1$ ): Using the same method for synthesizing  $Ni^0$ , complex  $Ni^1$  was obtained in 88% yield as yellow powder.  $^1H$  NMR(500 MHz, C $_6$ D $_6$ ),  $\delta$ : 8.50(dd,  $J = 6.4, 1.5$  Hz, 2H), 8.31~8.26(m, 1H), 7.53(s, 1H), 7.42(d,  $J = 3.0$  Hz, 1H), 7.37(dd,  $J = 8.2, 1.1$  Hz, 2H), 7.19~7.01(m, 6H), 6.93(t,  $J = 7.6$  Hz, 2H), 6.88(d,  $J = 3.0$  Hz, 1H), 6.64(tt,  $J = 7.6, 1.6$  Hz, 1H), 6.19(ddd,  $J = 7.5, 5.3, 1.3$  Hz, 2H), 4.21(hept,  $J = 6.8$  Hz, 2H), 1.56(d,  $J = 6.9$  Hz, 6H), 1.09(d,  $J = 6.8$  Hz, 6H), -0.65(s, 3H, NiCH $_3$ ).  $^{13}C$  NMR(101 MHz,  $CDCl_3$ ),  $\delta$ : 166.04, 165.50, 163.40, 151.91, 150.13, 141.10, 139.82, 139.34, 135.55, 134.06, 133.15, 130.88, 130.33, 129.94, 128.82, 128.66, 127.47, 126.62, 126.08, 124.21, 123.62, 123.02, 119.60, 28.59, 24.92, 23.22, -7.23(NiCH $_3$ ). Anal. Calcd for C $_{38}$ H $_{38}$ N $_2$ NiO $_3$ : C 72.51, H 6.09, N 4.45. Found: C 72.50, H 6.12, N 4.43.

[ [ (2,6-(3,5- $t$ -Bu $_2$ C $_6$ H $_3$ ) $_2$ C $_6$ H $_3$ —N=C(H)—(3-Ph-5-PhCOO-2-C $_6$ H $_2$ )- $\kappa^2$ -N, O ] Ni(CH $_3$ )(pyridine) ]

( $\text{Ni}^2$ ): Using the same method for synthesizing complexes  $\text{Ni}^0$ ,  $\text{Ni}^2$  was afforded in 91% yield as red powder.  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ),  $\delta$ : 8.21 ~ 8.16 (m, 4H), 7.87 (d,  $J = 1.8$  Hz, 4H), 7.65 (t,  $J = 1.7$  Hz, 2H), 7.55 (d,  $J = 7.6$  Hz, 2H), 7.34 (dd,  $J = 8.2, 1.2$  Hz, 2H), 7.29 ~ 7.25 (m, 2H), 7.22 (t,  $J = 7.6$  Hz, 1H), 7.11 (d,  $J = 7.4$  Hz, 1H), 7.05 (dd,  $J = 13.7, 6.6$  Hz, 3H), 6.95 (t,  $J = 7.5$  Hz, 2H), 6.65 (t,  $J = 7.6$  Hz, 1H), 6.54 (d,  $J = 3.1$  Hz, 1H), 6.29 ~ 6.25 (m, 2H), 1.45 (s, 36H), -0.54 (s, 3H,  $\text{NiCH}_3$ ).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 168.49, 165.23, 162.75, 151.52, 151.09, 150.89, 139.98, 139.91, 138.75, 137.45, 135.35, 133.27, 132.98, 130.98, 130.27, 129.87, 129.68, 128.58, 127.33, 126.36, 125.90, 124.12, 122.65, 121.04, 120.20, 35.28, 31.78, -7.96 ( $\text{NiCH}_3$ ). Anal. Calcd for  $\text{C}_{60}\text{H}_{66}\text{N}_2\text{NiO}_3$ : C 78.17, H 7.22, N 3.04. Found: C 78.18, H 7.20, N 3.05.

$[ \text{C}_6\text{H}_4(\text{COO})_2 ]_2 \cdot [ (2,6\text{-}^i\text{Pr}_2\text{-C}_6\text{H}_3\text{N}=\text{CH})-(3\text{-Ph-5-yl-2-O-C}_6\text{H}_2)\text{-}\kappa^2\text{-N,O}] \text{Ni}(\text{CH}_3)(\text{pyridine}) ]$

( $\text{Ni}^3$ ): The nickel methyl pyridine complex  $\text{Ni}^3$  was prepared by adding dropwise the toluene solution of (pyridine) $_2\text{NiMe}_2$  (0.15 g, 0.6 mmol) to toluene solution of ligand  $\text{L}^3$  (0.36 g, 0.25 mmol) with vigorous stirring at room temperature. The mixture was stirred at room temperature for 6 hours, then the mixture was filtrated to remove nickel black, and the filtrate was directly taken to dryness, affording complex  $\text{Ni}^3$  in 70% yield as yellow powder.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ),  $\delta$ : 8.52 (d,  $J = 5.4$  Hz, 4H), 7.81 ~ 7.75 (m, 2H), 7.53 (d,  $J = 2.9$  Hz, 2H), 7.41 (s, 2H), 7.25 (d,  $J = 7.6$  Hz, 4H), 7.14 ~ 6.93 (m, 16H), 6.65 (t,  $J = 7.2$  Hz, 2H), 6.27 ~ 6.16 (m, 4H), 4.15 (hept,  $J = 6.8$  Hz, 4H), 1.57 (d,  $J = 6.8$  Hz, 12H), 1.04 (d,  $J = 6.8$  Hz, 12H), -0.66 (s, 6H,  $\text{NiCH}_3$ ).  $^{13}\text{C}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ ),  $\delta$ : 165.67, 165.05, 162.50, 150.96, 149.08, 140.10, 138.68, 138.35, 134.58, 133.10, 131.88, 130.35, 128.90, 128.34, 127.57, 126.55, 125.01, 124.70, 123.25, 122.59, 122.07, 118.68, 27.60, 23.95, 22.33, -8.07 ( $\text{NiCH}_3$ ). Anal. Calcd for  $\text{C}_{70}\text{H}_{70}\text{N}_4\text{Ni}_2\text{O}_6$ : C 71.21, H 5.98, N 4.75. Found: C 71.18, H 5.61, N 4.73.

## 1.5 X-ray Structure Determination

Single crystals suitable for X-ray diffraction analysis were grown within one day after layering a solution of these complexes in toluene with *n*-hexane in a glove box. The intensity data were collected with the  $\omega$  scan mode (186 K) on a Bruker Smart APEX diffractometer with a CCD detector using  $\text{MoK}\alpha$  radiation ( $\lambda = 0.071073$  nm). Absorption corrections were performed using the SADABS program. The crystal structures were solved using the SHELXTL program and refined using full matrix least-squares techniques. The positions of hydrogen atoms were calculated theoretically and included in the final cycles of refinement in a riding model along with attached carbons. Crystal data collection and refinement details are given in Table S1 (see Supporting Information).

## 1.6 Procedure for Ethylene Polymerization

A 200 mL autoclave was heated under vacuum to 140 °C for 4 hours and was then cooled to the desired reaction temperature. The vessel was purged three times with ethylene and was charged with 30 mL toluene under ethylene pressure. A solution of nickel catalyst in 10 mL toluene was injected into the reactor. The reaction apparatus was then filled with ethylene and pressurized to the prescribed ethylene pressure immediately. The mixture was stirred for prescribed time for ethylene polymerization. After reaction, magnetic stirring was stopped, the reactor was vented, and the polymerization mixture was poured into 200 mL ethanol. The solid polymer was filtered, washed with ethanol several times, and dried to constant mass under vacuum.

## 1.7 Procedure for Ethylene Copolymerization

A 200 mL autoclave was heated under vacuum to 140 °C for 4 hours and was then cooled to the desired reaction temperature. The vessel was purged three times with ethylene and was charged with toluene under ethylene pressure. A solution of comonomer was injected into the reactor before a toluene solution of nickel catalyst was added by using a dry syringe. The total reaction volume was 40 mL. The reaction apparatus was then filled with ethylene and pressurized to the prescribed ethylene pressure immediately. The mixture was

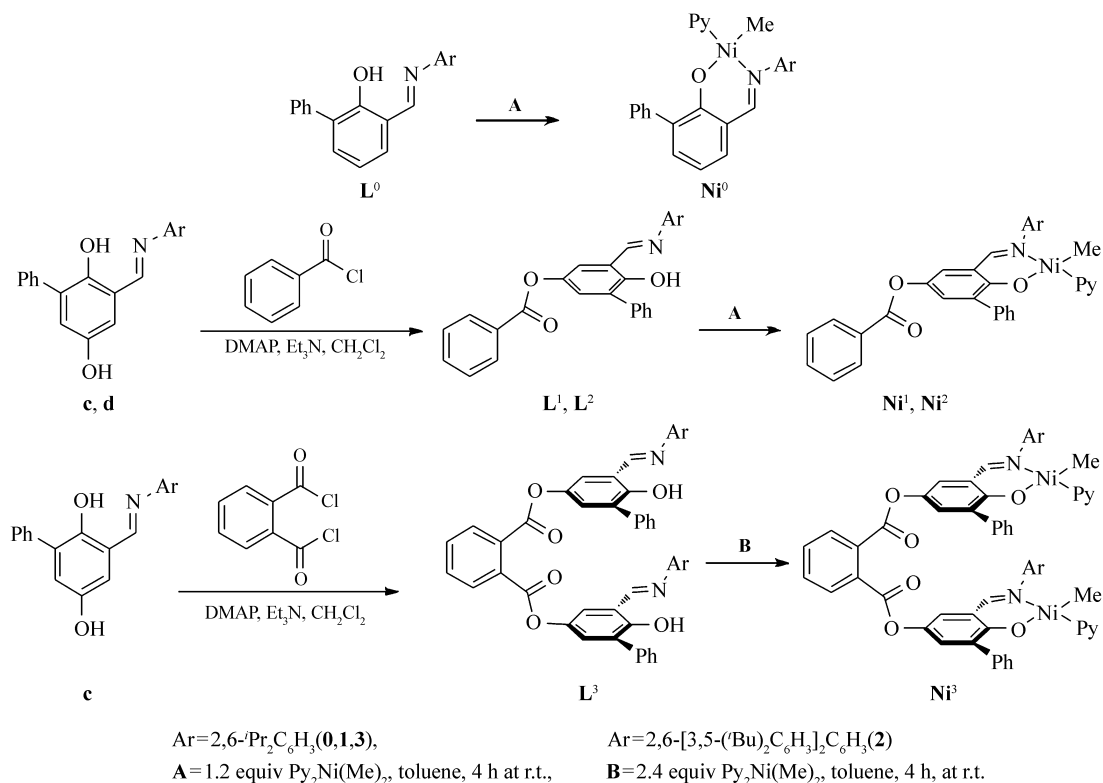
stirred for 90 min under prescribed temperature. After reaction, magnetic stirring was stopped, the reactor was vented, and the polymerization mixture was poured into ethanol. The solid polymer was filtered, washed with ethanol several times, and dried to constant mass under vacuum.

## 2 Results and Discussion

### 2.1 Synthesis of Ligands and Complexes

2,5-Dimethoxy-3-phenylbenzaldehyde (**a**) was synthesized at excellent yield from commercially available 2-hydroxy-5-methoxybenzaldehyde according to reported literature<sup>[20,23]</sup>. The key intermediate 3-phenyl-2,5-dihydroxy-benzaldehyde (**b**) was obtained after deprotection of compound **a** by  $\text{BBr}_3$  (Scheme S1, see Supporting Information). Condensation of compound **b** with 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NH<sub>2</sub> or 2,6-(3,5-*t*Bu<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NH<sub>2</sub> gave rise to compounds **c** and **d**, respectively (Scheme S1).

Ligands **L**<sup>1</sup> ~ **L**<sup>3</sup> were synthesized by the reaction of compounds **c** or **d** with corresponding acyl chlorides (Scheme 2). Using the procedure reported by Mecking *et al.*<sup>[22]</sup>, complexes **Ni**<sup>0</sup> ~ **Ni**<sup>3</sup> were prepared by reaction of corresponding ligands with (pyridine)<sub>2</sub>Ni(Me)<sub>2</sub> in 70% ~ 95% yields (see Scheme 2). All these

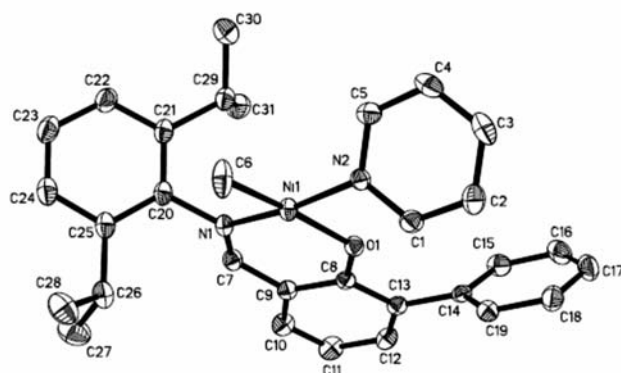


Scheme 2 Synthesis of ligands and complexes

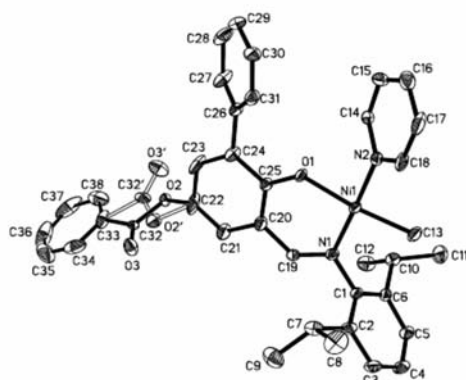
nickel complexes were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, and elemental analysis. Single crystals of **Ni**<sup>0</sup>, **Ni**<sup>1</sup> and **Ni**<sup>2</sup> were grown within one day after layering a solution of these complexes in toluene with *n*-hexane (1/3, volume ratio) and the structures of these complexes were determined by X-ray diffraction analysis (Fig. 1 ~ Fig. 3). The coordination geometry at the nickel center is slightly distorted square planar, and the methyl groups are located *trans* to the oxygen atoms. Obviously, the coordination environment of **Ni**<sup>2</sup> (see Fig. 3) was more congested than that of **Ni**<sup>1</sup> (Fig. 2). Due to the presence of bulkier substituted terphenyl imine moiety, the axial positions of the nickel center can be effectively shielded.

### 2.2 Ethylene polymerization

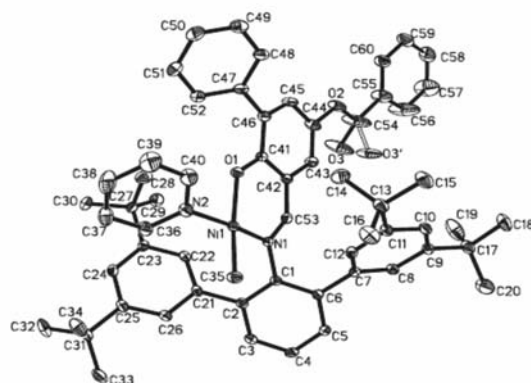
Ethylene polymerization trials were performed to determine the effects of polymerization temperature,

Fig. 1 Molecular structure of complex  $\text{Ni}^0$ 

Thermal ellipsoids are drawn at the 30% probability level, and H atoms are omitted for clarity. Selected bond distances (nm) and angles( $^\circ$ ): Ni1—N1 = 0.1888(2), Ni1—N2 = 0.1900(2), Ni1—O1 = 0.1922(2), Ni1—C6 = 0.1933(3), N1—Ni1—N2 = 171.08(9), N1—Ni1—O1 = 93.08(8), N1—Ni1—C6 = 93.42(11), N2—Ni1—O1 = 86.31(8), N2—Ni1—C6 = 88.42(11), O1—Ni1—C6 = 170.11(12)

Fig. 2 Molecular structure of complex  $\text{Ni}^1$ 

Thermal ellipsoids are drawn at the 30% probability level, and H atoms are omitted for clarity. Selected bond distances (nm) and angles( $^\circ$ ): Ni1—N1 = 0.1901(5), Ni1—N2 = 0.1915(5), Ni1—O1 = 0.1907(4), Ni1—C13 = 0.1921(6), N1—Ni1—N2 = 176.2(2), N1—Ni1—O1 = 92.82(18), N1—Ni1—C13 = 93.2(2), N2—Ni1—O1 = 85.82(19), N2—Ni1—C13 = 88.3(2), O1—Ni1—C13 = 173.2(2)

Fig. 3 Molecular structure of complex  $\text{Ni}^2$ 

Thermal ellipsoids are drawn at the 30% probability level, and H atoms are omitted for clarity. Selected bond distances (nm) and angles( $^\circ$ ): Ni1—N1 = 0.1886(2), Ni1—N2 = 0.1904(3), Ni1—O1 = 0.1907(2), Ni1—C35 = 0.1935(3), N1—Ni1—N2 = 168.47(11), N1—Ni1—O1 = 93.87(10), N1—Ni1—C35 = 95.02(13), N2—Ni1—O1 = 85.55(11), N2—Ni1—C35 = 88.21(13), O1—Ni1—C35 = 164.62(13)

reaction time, and additive triphenylphosphine (PPh<sub>3</sub>) (Table 1). All these nickel complexes (Ni<sup>0</sup> ~ Ni<sup>3</sup>) studied here can generate polyethylenes without cocatalysts such as expensive bis(1,5-cyclooctadiene) nickel(0) Ni(COD)<sub>2</sub> and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>. Relative molecular mass distributions of obtained polymers between 1.6 and 2.2 indicate that all these complexes were well-behaved single-site catalysts. Generally speaking, the relative molecular mass of polyethylenes produced by Ni<sup>0</sup> ~ Ni<sup>3</sup> decreased at elevated temperatures due to more extensive chain transfer reactions. Accordingly, the  $T_m$  values of polymers decreased at elevated temperatures as well.

Compared with Ni<sup>0</sup>, catalyst Ni<sup>1</sup> with PhCOO- remote from the nickel center exhibited higher activity at low reaction temperature (40 and 50 °C), implying an easier initiation process. This may result from the weaker coordination of pyridine ligand to the less oxophilic nickel center due to the presence of electron-donating group PhCOO—. Catalyst Ni<sup>1</sup> yields polyethylene with  $M_w = 1.9 \times 10^4$  and 61 branches with the activity of  $1.0 \times 10^6$  g of PE mol<sup>-1</sup>·Ni<sup>-1</sup>·h<sup>-1</sup> at 50 °C (entry 6, Table 1).

**Table 1** Ethylene polymerization using neutral nickel catalysts Ni<sup>0</sup> ~ Ni<sup>3a</sup>

Entry	Catalyst	Temperature/°C	Yield/g	Activity <sup>b</sup>	$M_w^c / (\text{kg} \cdot \text{mol}^{-1})$	$M_w/M_n^c$	$T_m^d / ^\circ\text{C}$
1	Ni <sup>0</sup>	40	0.19	1.5	45.4	2.2	114
2	Ni <sup>0</sup>	50	0.72	5.8	25.2	2.3	103
3	Ni <sup>0</sup>	60	1.23	9.8	15.1	2.2	96
4	Ni <sup>0</sup>	70	0.96	7.7	10.1	2.1	87
5	Ni <sup>1</sup>	40	0.22	1.8	51.7	2.2	115
6	Ni <sup>1</sup>	50	1.31	10.5	19.4	2.2	97
7	Ni <sup>1</sup>	60	0.82	6.6	11.6	2.2	89
8	Ni <sup>1</sup>	70	0.53	4.2	8.6	2.1	75
9 <sup>e</sup>	Ni <sup>1</sup>	50	2.24	6.0	17.0	2.2	92
10 <sup>f</sup>	Ni <sup>1</sup>	50	3.07	4.1	17.0	2.1	92
11 <sup>g</sup>	Ni <sup>1</sup>	50	0.016	0.13	4.9	1.8	—
12	Ni <sup>2</sup>	40	1.21	9.7	11.6	2.1	81
13	Ni <sup>2</sup>	50	1.91	15.3	6.9	2.0	68
14	Ni <sup>2</sup>	60	2.24	17.9	4.2	2.3	—
15	Ni <sup>2</sup>	70	1.75	14.0	3.5	1.1	—
16	Ni <sup>3</sup>	40	0.17	1.4	70.3	2.5	124
17	Ni <sup>3</sup>	50	1.11	8.9	27.3	2.4	99
18	Ni <sup>3</sup>	60	0.61	4.9	19.3	2.2	93
19	Ni <sup>3</sup>	70	trace	—	—	—	—
20 <sup>e</sup>	Ni <sup>3</sup>	50	2.52	3.4	16.6	2.1	91
21 <sup>f</sup>	Ni <sup>3</sup>	50	2.82	1.9	18.0	2.1	93
22 <sup>g</sup>	Ni <sup>3</sup>	50	0.021	0.17	5.4	1.9	—

a. Polymerizations conditions: toluene, 40 mL; nickel, 5 (mol); ethylene,  $5 \times 10^5$  Pa; 15 min; b. in the unit of  $10^5$  g PE mol<sup>-1</sup>·Ni<sup>-1</sup>·h<sup>-1</sup>; c. determined by GPC vs polystyrene standards; d. determined by DSC; e. reaction time: 45 min; f. reaction time: 90 min; g. 25 (mol PPh<sub>3</sub> as additives).

After introducing bulky terphenyl moiety, catalyst Ni<sup>2</sup> generated PE with  $M_w = 6900$  and 81 branches per 1000 carbon atoms (C<sup>-1</sup>) at  $1.5 \times 10^6$  g PE mol<sup>-1</sup>·Ni<sup>-1</sup>·h<sup>-1</sup> at 50 °C (entry 13, Table 1). With activities up to  $1.8 \times 10^6$  g of PE mol<sup>-1</sup>·Ni<sup>-1</sup>·h<sup>-1</sup> under  $5 \times 10^5$  Pa ethylene pressure at 60 °C (entry 14, Table 1), Ni<sup>2</sup> is among the most active phenoxyiminato nickel catalysts for ethylene homopolymerization<sup>[3,13,22,24-27]</sup>. The activity of Ni<sup>2</sup> has doubled relative to that of Ni<sup>1</sup>, which is ascribed to the bulky substituted *N*-terphenyl moiety playing a vital role in preventing the forming of bis-ligated complex<sup>[28]</sup>. However, the amorphous polymer  $M_w$  obtained by Ni<sup>2</sup> at 60 °C was much lower than that by Ni<sup>1</sup> under the same reaction conditions (4200 vs 11600, entry 14 vs 7, Table 1). Electron-donating tert-butyl groups are responsible for the lower  $M_w$  due to extensive chain transfer reaction, in good agreement with the findings by Mecking group<sup>[12]</sup>, that the electronic characteristics



of the remote substituents of terphenyl moieties govern the polymerization behavior.

Binuclear  $\text{Ni}^3$  shows similar optimal activity relative to mononuclear  $\text{Ni}^1$  (*ca.*  $1.0 \times 10^6$  g of PE  $\text{mol}^{-1} \cdot \text{Ni}^{-1} \cdot \text{h}^{-1}$ ) (entry 6 *vs* 17, Table 1). Compared with mononuclear  $\text{Ni}^1$ , binuclear catalyst  $\text{Ni}^3$  enhanced the  $M_w$  of polymer. This is consistent with the reported result of literatures<sup>[29-30]</sup> that binuclear catalysts enhanced polymer relative molecular mass. Catalyst  $\text{Ni}^3$  demonstrates slightly lower activity at low temperature than mononuclear  $\text{Ni}^1$ , and generates only trace amount of polymer at elevated temperature (70 °C, entry 19, Table 1), indicating an inferior thermal stability of binuclear catalyst  $\text{Ni}^3$  to mononuclear  $\text{Ni}^1$ . It was reported by Grubbs *et al.* that bis-ligated nickel species was isolated as the main deactivation product when ligand frameworks were not sufficiently bulky<sup>[31]</sup>. We thus proposed that inactive bis-ligated complex was more readily generated for binuclear complex  $\text{Ni}^3$  in which two nickel centers were close to each other, especially at elevated temperatures<sup>[32]</sup>. The drop of the catalytic activity with polymerization time may partly reflect the stability of catalysts, we thus conducted ethylene polymerization for different polymerization time using catalysts  $\text{Ni}^1$  and  $\text{Ni}^3$ . From 45 to 90 min, a 32% decrease in catalytic activity for  $\text{Ni}^1$  was observed and the value for binuclear  $\text{Ni}^3$  was 44%. This indicated a more serious catalyst deactivation with reaction time for binuclear  $\text{Ni}^3$ , which was similar to the effect of reaction temperature.

To further investigate the different performances of these catalysts, extra  $\text{PPh}_3$  was added to the catalytic systems during the ethylene polymerization. In the presence of 5 stoichiometric amount of  $\text{PPh}_3$ , the activity of mononuclear  $\text{Ni}^1$  was reduced to 1/80th of that without any additive due to the competitive coordination reaction of ethylene and  $\text{PPh}_3$ <sup>[33]</sup>. For binuclear  $\text{Ni}^3$ , the activity decreased sharply as well, but the activity in the presence of 5 stoichiometric amount of  $\text{PPh}_3$  was still 1/50th of the original value. The better tolerance toward  $\text{PPh}_3$  additives of the binuclear catalyst may be resulted from the close position of the nickel centers, which would prohibit simultaneous inhibition of the two metal centers by bulky  $\text{PPh}_3$  ligands<sup>[34-35]</sup>.

We also studied the microstructures of polyethylenes produced by these catalysts through  $^{13}\text{C}$  NMR. All these polymers obtained by  $\text{Ni}^0 \sim \text{Ni}^3$  at 50 °C possess similar branching pattern (Fig. 4). According to the  $^{13}\text{C}$  NMR, polymers generated by  $\text{Ni}^1$  contain main methyl branches and minor ethyl branches<sup>[36]</sup>.

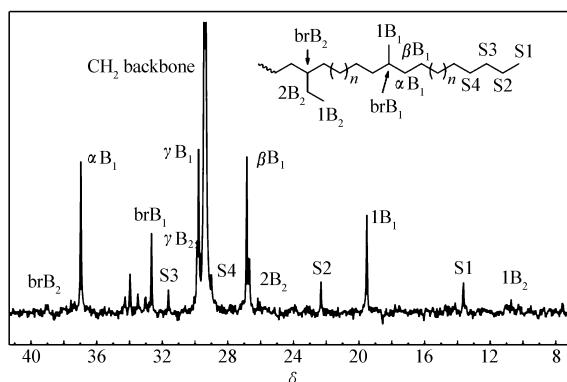


Fig. 4  $^{13}\text{C}$  NMR spectrum of PE obtained by  $\text{Ni}^1$  at 50 °C (entry 4, Table 1)

### 2.3 Ethylene Copolymerization

The typical results of ethylene copolymerization catalyzed by  $\text{Ni}^1 \sim \text{Ni}^3$  with 1,5-hexadiene, 1,7-octadiene, 6-bromo-1-hexene and methyl 10-undecenoate were summarized in Table 2. Both  $\text{Ni}^1$  and  $\text{Ni}^3$  could catalyze ethylene with 1,5-hexdiene at moderate activities ( $1.8 \sim 2.0 \times 10^4$  g of PE  $\text{mol}^{-1} \cdot \text{Ni}^{-1} \cdot \text{h}^{-1}$ ), but the incorporation of the comonomer was low. In stark contrast, 1,7-octadiene was efficiently incorporated into the polyethylenes by using  $\text{Ni}^1$  and  $\text{Ni}^3$ . The resulting copolymers with pendant double bonds were clearly evidenced by the significant increase of external double bonds versus polyethylenes by  $^1\text{H}$  NMR measurement (Fig. S1, *see Supporting Information*). Additionally, binuclear  $\text{Ni}^3$  demonstrated slightly higher activity and

polymer  $M_w$  than  $\text{Ni}^1$  (entry 9 *vs* 2, Table 2).

6-Bromo-1-hexene as a polar comonomer, could be efficiently incorporated into the copolymer backbone by  $\text{Ni}^1 \sim \text{Ni}^3$  (entry 3, 6, 10, Table 2) when copolymerizing with ethylene. According to the  $^1\text{H}$  NMR spectrum (Fig. 5) of copolymer obtained by  $\text{Ni}^1$  at 50 °C, the signal at  $\delta$  3.24 is clearly assigned to the  $-\text{CH}_2\text{Br}$  group<sup>[37]</sup>. The catalytic activity was much lower than that for ethylene homopolymerization, which is

**Table 2 Ethylene copolymerization using  $\text{Ni}^1$ - $\text{Ni}^3$  complexes<sup>a</sup>**

Entry	Catalyst	Comonomer	Yield/mg	Activity <sup>b</sup>	$M_w^c / (\text{kg} \cdot \text{mol}^{-1})$	$M_w/M_n^c$	$T_m^d / ^\circ\text{C}$	$X_c^e$
1	$\text{Ni}^1$		260	17.7	16.3	1.9	93	nd
2	$\text{Ni}^1$		230	15.3	16.6	2.0	94	nd
3	$\text{Ni}^1$		61	4.1	20.5	1.9	103	0.92
4	$\text{Ni}^1$		150	10.0	15.4	1.8	94	0.82
5 <sup>f</sup>	$\text{Ni}^1$		49	3.3	16.5	2.2	97	1.01
6	$\text{Ni}^2$		18	1.2	6.0	1.7	–	0.16
7	$\text{Ni}^2$		101	6.7	6.7	1.7	–	0.25
8	$\text{Ni}^3$		301	20.1	14.9	2.0	92	nd
9	$\text{Ni}^3$		252	16.8	17.6	1.7	94	nd
10	$\text{Ni}^3$		72	4.8	16.1	1.9	96	0.91
11	$\text{Ni}^3$		182	12.1	16.5	1.9	95	0.64
12 <sup>f</sup>	$\text{Ni}^3$		62	4.1	16.8	2.1	93	1.10

a. Polymerizations conditions: toluene, 40 mL; nickel, 10 (mol; ethylene,  $5 \times 10^5$  Pa; 90 min, 600 stoichiometric amount of comonomer; b. in the unit of  $10^3$  g PE  $\text{mol}^{-1} \cdot \text{Ni}^{-1} \cdot \text{h}^{-1}$ ; c. determined by GPC *vs.* polystyrene standards; d. determined by DSC; e. incorporation ratio was calculated according to  $^1\text{H}$  NMR spectra; f. 1000 stoichiometric amount of comonomer.

well consistent with that reported in literature<sup>[31]</sup>. The incorporation ratio by  $\text{Ni}^1$  is up to four times higher than that by  $\text{Ni}^2$  (entry 3 *vs* 6, Table 2). This may originate from the highly sterically hindered imine moiety of the nickel center in  $\text{Ni}^2$ .

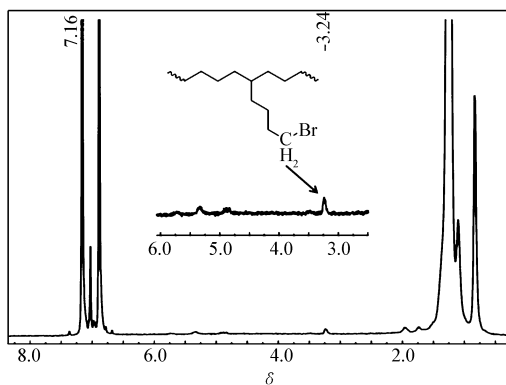


Fig. 5  $^1\text{H}$  NMR spectrum (400 MHz, *o*-dichlorobenzene- $d_4$ , 110 °C) of copolymer obtained by  $\text{Ni}^1$  at 50 °C (entry 3, Table 2)

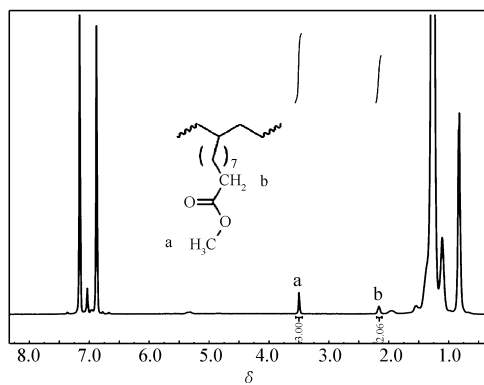


Fig. 6  $^1\text{H}$  NMR spectrum (400 MHz, *o*-dichlorobenzene- $d_4$ , 110 °C) of copolymer obtained by  $\text{Ni}^1$  at 50 °C (entry 4, Table 2)

Complexes  $\text{Ni}^1 \sim \text{Ni}^3$  also could efficiently initiate the copolymerization of ethylene with the methyl 10-undecenoate.  $^1\text{H}$  NMR signals (Fig. 6) at 3.49 and 2.16, assigned to  $-\text{COOCH}_3$  and  $-\text{CH}_2\text{COO}-$ ,

respectively, highlighted that methyl 10-undecenoate was effectively incorporated into the polymer backbone<sup>[38]</sup>. When the comonomer in the feed was increased from 600 to 1000 stoichiometric amount,  $\text{Ni}^1$  catalyzed the copolymerization with sharply decreased activity and higher comonomer incorporation (1.10% (molar fraction) *vs* 0.64% (molar fraction)) (entry 5 *vs* 4, Table 2). In this aspect, binuclear catalyst  $\text{Ni}^3$  displayed similar tendency (entry 13, 14, Table 2). When compared with  $\text{Ni}^2$  bearing bulky imine moieties, the mononuclear  $\text{Ni}^1$  yielded copolymer with higher relative molecular mass (15400 *vs* 6700) and comonomer incorporation (0.82% (molar fraction) *vs* 0.25% (molar fraction)). The bulky imine motif effectively shielded the axial positions of the nickel center, went against the coordination of comonomer with active center, and resulted in the sharply decreased incorporation ratio.

### 3 Conclusions

We have successfully synthesized and characterized a series of neutral nickel complexes containing benzyloxy groups. Without any cocatalyst, they can promote ethylene polymerization at very high activities generating polyethylenes with moderate relative molecular mass. For catalyst  $\text{Ni}^1$ , the electron-donating PhCOO— group promoted initiation of catalyst  $\text{Ni}^1$ , shows better activity at low temperature compared to catalyst  $\text{Ni}^0$ . Introducing bulky 2,6-(3,5-(*t*-Bu)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N- moiety, the activities of catalyst  $\text{Ni}^2$  up to  $1.8 \times 10^6$  g of PE mol<sup>-1</sup>·Ni<sup>-1</sup>·h<sup>-1</sup> (at  $5 \times 10^5$  Pa ethylene) are among the highest values using phenoxyimino to neutral nickel catalysts. However, lower relative molecular mass polymer was obtained due to the electron-donating 3,5-(*t*-Bu)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> groups. The microstructures of the polymers generated by these catalysts contain main methyl branches and minor ethyl branches. Compared with catalyst  $\text{Ni}^1$ , binuclear catalyst  $\text{Ni}^3$  produced polyethylene with higher  $M_w$  at similar activity and demonstrated better tolerance toward PPh<sub>3</sub>. These neutral nickel catalysts are also capable of copolymerizing ethylene with 1,7-octadiene and polar comonomers such as 6-bromo-1-hexene and methyl-10-undecenoate to give various functional polyolefins.

*Supporting Information [Synthesis of important intermediates; Crystal data and structure refinement for complexes  $\text{Ni}^0$ ,  $\text{Ni}^1$  and  $\text{Ni}^2$ ; <sup>1</sup>H NMR spectra of homo- and copolymers] is available free of charge at <http://yyhx.ciac.jl.cn>.*

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## RCOO-取代的镍(II)配合物单组分高效 催化乙烯均聚和共聚反应

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**摘要** 合成并表征了含 RCOO-基团的单核( $\text{Ni}^1 \sim \text{Ni}^2$ )及双核( $\text{Ni}^3$ )镍配合物  $[(2,6\text{-R}_2\text{-C}_6\text{H}_3)\text{-N}=\text{C}(\text{H})\text{-}(3\text{-Ph-5-PhCOO-2-O-C}_6\text{H}_2)\text{-}\kappa^2\text{-N,O}]\text{Ni}(\text{CH}_3)(\text{pyridine})$  ( $\text{R} = i\text{Pr}; 3,5\text{-tBu}_2\text{C}_6\text{H}_3$ ), 并用于催化乙烯均聚和共聚反应。作为单组分催化剂,这些配合物可以有效地催化乙烯聚合得到中等相对分子质量的支化聚乙烯(PE)。供电性的PhCOO-基团促进了催化剂 $\text{Ni}^1$ 的引发,从而在低温下比 $\text{Ni}^0$ 活性更高。引入大位阻的2,6-(3,5-二叔丁基苯基)苯胺基团,催化剂 $\text{Ni}^2$ 在 $5 \times 10^5$  Pa下的活性高达 $1.8 \times 10^6$  g PE  $\text{mol}^{-1} \cdot \text{Ni}^{-1} \cdot \text{h}^{-1}$ ,是活性最高的水杨醛亚胺中性镍催化剂之一。与相应的单核催化剂相比,双核催化剂 $\text{Ni}^3$ 对三苯基膦具有更好的耐受性。这些催化剂可催化乙烯与1,5-己二烯、1,7-辛二烯、6-溴-1-己烯或10-十一烯酸甲酯的共聚合,制备功能化聚乙烯。

**关键词** 中性镍催化剂;电子效应;烯烃聚合;功能化聚烯烃