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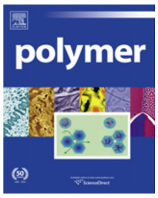

Selective activation of metallic center in heterobinuclear cobalt and nickel complex in ethylene polymerization

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ABSTRACT

Heterobinuclear cobalt and nickel complex $\{2\text{-}[2,6\text{-}R_2{-}C_6H_3N{=}C(CH_3){-}(CH_3)C{=}N{-}(3,5\text{-}R_2')C_6H_2{-}CH_2{-}(3',5'\text{-}R_2)C_6H_2N{=}C(CH_3)]\text{-}6\text{-}[2,6\text{-}R_2{-}C_6H_3N{=}C(CH_3)]$ pyridine$\}CoCl_2NiBr_2$ (R = isopropyl) (**N_5CoNi**) was prepared by reaction of pentadentate nitrogen ligand containing 2,6-bis(imino)-pyridine and α-diimine moieties with $CoCl_2$ and $NiBr_2$(DME) in turn. The complex was applied as catalyst for ethylene polymerization activated by $AlEt_3$, MMAO and $AlEt_3/[PhMe_2NH]$ $[B(C_6F_5)_4]$ respectively. The performance of the heterobinuclear complex in ethylene polymerization was compared with corresponding mononuclear complexes (α-diimine nickel bromide and 2,6-bis(imino)-pyridine cobalt chloride) and their equivalent mixture (binary complexes). When the complex **N_5CoNi** was activated by $AlEt_3$ or MMAO, its ethylene polymerization activity was lower than its control, the binary complexes. Both heterobinuclear complex and binary complex produced PE with bimodal molecular weight distribution. The amount of high-molecular-weight polyethylene produced by nickel center of **N_5CoNi** was less than the binary complexes, which reveals that productivity of nickel center of **N_5CoNi** is selectively suppressed. When the heterobinuclear complex **N_5CoNi** is activated by $AlEt_3/[PhMe_2NH]$ $[B(C_6F_5)_4]$, the relative productivity of nickel center increased, although the total activity of catalyst decreased compared with $AlEt_3$ as cocatalyst. With respect to $AlEt_3$, $[PhMe_2NH][B(C_6F_5)_4]$ can preferably activate nickel center of heterobinuclear complex. The results suggest that metal site in the heterobinuclear complex is selectively activated by cocatalyst.

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1. Introduction

Late transition metal catalysts, such as α-diimine nickel and palladium catalyst developed by Brookhart [1] and pyridine diimine iron and cobalt catalysts by Brookhart and Gibson [2,3], have received a lot of attention because they could produce novel polyolefin with unique properties. As shown in Scheme 1, **N_2Ni** is a typical α-diimine catalyst and **N_3Co** is a typical pyridine diimine catalyst for ethylene polymerization. When activated with methylaluminoxane (MAO), all of them show good activity towards olefin polymerization. α-Diimine nickel and palladium catalyst could convert ethylene into highly branched polyethylene (PE) and pyridine diimine iron and cobalt complexes catalyze ethylene polymerization to produce linear PE.

Polynuclear metal complexes as olefin polymerization catalyst present unique properties as compared with mononuclear one. Binuclear constrained-geometry catalyst(CGC), such as homobinuclear $CGCTi_2$ and $CGCZr_2$ and heterobinuclear CGCTiZr have been reported. Homobinuclear $CGCTi_2$ exhibits greatly enhanced polymerization activity, polyolefin molecular weight (MW), and comonomer incorporation efficiency compared with the zirconium analogues $CGCZr_2$ in the copolymerization of ethylene with 1-octene and isobutene [4]. They also exhibit higher styrene homopolymerization activity and can produce ethylene-styrene copolymers with broad range control of styrene enchainment than their mononuclear analogous [5]. Homobinuclear $CGCZr_2$ and bifunctional cocatalyst introduces more ethyl branches in ethylene homopolymerization compared to the mononuclear analogue [6]. The $CGCZr_2$ can also yield much higher MW in ethylene polymerization and higher hexene incorporation in the copolymerization of ethylene and hexane in comparison with its mononuclear analogous [7,8]. Heterobinuclear CGCTiZr produces long-chain branched PE in ethylene homopolymerization in sharp contrast to mononuclear zirconium and titanium catalyst mixtures [9]. The branch formation pathway is proposed to involve intramolecular cooperative effects. In ethylene homopolymerization and copolymerization of ethylene and olefin catalyzed by binuclear phenoxyiminato group 4 complex, substantial increments in catalytic activity and comonomer enchainment efficiency are observed for various

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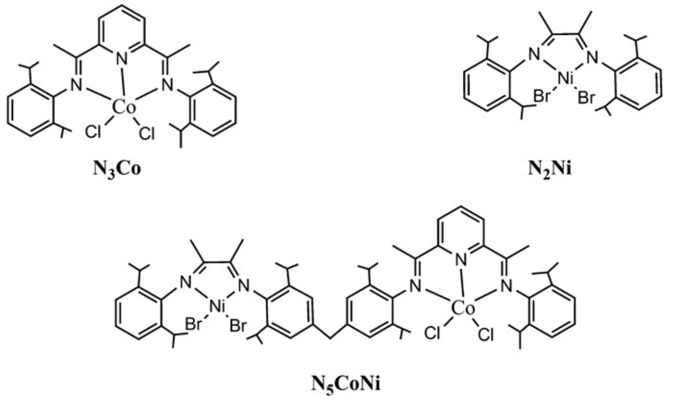


Scheme 1. Mononuclear and heterobinuclear cobalt and nickel complexes.

comonomers [10,11]. All results indicate that catalyst centers connected by electrostatical and covalently approaches in spatial proximity exhibit unique polymerization properties than single site.

Homopolynuclear late transition metal complex as olefin polymerization catalysts, such as bi- and polynuclear iron/cobalt complex [12–17] and bi- and polynuclear nickel/palladium complexes [18–23] have also been explored. Most of them show higher activity than their mononuclear complexes because the cooperative effect between closely adjacent metal centers modifies catalytic performance. The neutrally charged bimetallic phenoxyiminato Ni(II) complexes show twice of the ethylene homopolymerization activity, as well as an increased polar comonomer enchainment selectivity for functionalized norbornenes and for acrylates compared to their monometallic analogues, which is due to significant active center-active center cooperative effects [24]. There are few reports about synthesis and performance of the heterobinuclear or heteropolynuclear late transitional metal complexes. Bianchini reported that heterobinuclear cobalt and nickel complex based on tris-imino-bis-pyridine ligand, {6-[1-(2,6-Diisopropylphenylimino)ethyl]pyridin-2-yl}-{6-[1-(2,6-diisopropylphenylimino)ethyl]pyridin-3-yl}-methanone, showed lower activity than the typical mononuclear cobalt complex (**N$_3$Co**) for ethylene polymerization [25]. Trinuclear iron–nickel–iron complexes present better ethylene polymerization activity than mononuclear iron and nickel complexes with the same ligand at high temperature [26]. Some heterobinuclear complex of early/late transition metal complexes has also been reported for olefin polymerization [27–30].

To study the performance of heterobinuclear late transition metal complex as catalyst for ethylene polymerization, we synthesized the heterobinuclear cobalt and nickel complex **N$_5$CoNi** with ligand containing α-diimine and pyridine diimine moieties as shown in Scheme 1. The performance of the heterobinuclear complex in ethylene polymerization was compared with corresponding mononuclear complexes (**N$_2$Ni** and **N$_3$Co**) and their equivalent mixture (binary complexes, **N$_2$Ni** + **N$_3$Co**), in order to find the nature of two different active centers within one molecule, especially the interaction of two different metal centers with different cocatalysts.

2. Experimental section

All manipulations were carried out under nitrogen atmosphere using standard Schlenk techniques.

2.1. Materials

4,4′-methylene-bis(2,6-diisopropylaniline), 2,6-diisopropylaniline, 2,6-diacetyl-pyridine, [PhMe$_2$NH][B(C$_6$F$_5$)$_4$] were purchased from Acros and used as received. AlEt$_3$ was purchased from Albemarle, Modified methylaluminoxane (MMAO, obtained as a 2.59 M heptane solution from Albemarle) was dried under high vacuum for 48 h to remove excess volatile aluminum alkyls before use. CoCl$_2$ was purchased from Alfa Aesar. NiBr$_2$(DME) was purchased from Aldrich. All other chemicals were obtained commercially and used as received unless stated otherwise. Toluene, hexane, and diethyl ether were distilled from sodium benzophenone ketyl. CH$_2$Cl$_2$ and *n*-butanol were distilled under nitrogen from CaH$_2$ and Mg, respectively. Ethylene was purified with potassium sodium alloy. The mononuclear 2,6-bis-[1-(2,6-diisopropylphenylimino)ethyl]pyridine cobalt (II) chloride (**N$_3$Co**) [31] and 2,6-R$_2$–C$_6$H$_3$N=C(CH$_3$)–(CH$_3$)C=N(2,6-R$_2$C$_6$H$_3$)]NiBr$_2$ (R = isopropyl) (**N$_2$Ni**) [1] were synthesized as described.

2.2. Measurements

The ^{1}H NMR spectra were obtained on Bruker Advance DMX400 instrument with TMS as standard. Mass spectra were recorded using ESI-MS on Thermo Electron LCD Deca xp max. Elemental analyses were performed by Thermo Electron SPA EA1112. Metal content was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) over IRIS Interepid II XSP. The melting points of the polymer were measured with differential scanning calorimetry (DSC) on TA Q200 at a heating rate of 10 °C/min. Data reported were second heats. The MW of PE was measured by gel permeation chromatography (GPC) on PL-GPC220 at 150 °C with 1,2,4-C$_6$H$_3$Cl$_3$ as the eluant. Infrared spectra were recorded with a Thermo Nicolet 6700 FT-IR spectrophotometer. ^{13}C NMR spectra of the PE were measured on a Varian Mercury Plus 300 NMR spectrometer at 75 MHz *o*-Dichlorobenzene-d$_4$ was used as solvent, and the concentration of the polymer solution was 10 wt%. The spectra were recorded at 120 °C. Chromium triacetylacetone (6–9 mg) was added to each sample to shorten the relaxation time and ensure the quantitative results. Broadband decoupling with a pulse delay of 3 s was employed. Typically, 3500 scans were collected. The UV–visible absorption spectra of the catalytic system were recorded on a Varian Cary 100 Bio UV–visible spectrometer at room temperature under N$_2$ atmosphere, while keeping the concentration of all the catalyst as 0.33 M in 1.8 ml toluene and 0.6 ml CH$_2$Cl$_2$.

2.3. Preparation of N$_5$Co and N$_5$CoNi

2.3.1. 2-[2,6-R$_2$-4-(4-NH$_2$–3,5-R$_2$C$_6$H$_2$–CH$_2$)–C$_6$H$_2$N=CH$_3$]-6-[2,6-R$_2$–C$_6$H$_3$N=C(CH$_3$)] pyridine (R = i-Pr) (*2*)

Compound 2-[C(O)CH$_3$]-6-[2,6–R$_2$–C$_6$H$_3$N=C(CH$_3$)]pyridine(**1**) was synthesized by modified method reported in the reference [32]. Compound **1** (4.2 g, 13.0 mmol) and 4,4′-methylene-bis(2,6-biisopropylaniline) (16.9 g, 85% purity, 39.0 mmol) were dissolved in 50 ml 2-propanol in a round-bottom flask. Para-toluenesulfonic acid (50 mg, 0.3 mmol) was added, and the solution was refluxed for 48 h. After evaporation of solvent, the crude product was purified by column chromatography (silica, petroleum ether/ethyl acetate: 20/1). 3.8 g of compound **2** was obtained (yield 44%). ^{1}H NMR (400 MHz, CDCl$_3$, δ in ppm): 1.12–1.18(t, 24H, CH(CH_3)$_2$), 1.24–1.26(m, 12H, CH (CH_3)$_2$), 2.28(s, 6H, ArN=CCH_3), 2.76(m, 4H, CH(CH$_3$)$_2$), 2.94(m, 2H, CH(CH$_3$)$_2$), 3.64(s, 2H, NH_2), 3.96(s, 2H, Ar–CH_2–Ar), 6.90(s, 2H, Ar–H), 7.02(s, 2H, Ar–H), 7.10–7.19(m, 3H, Ar–H), 7.93(t, 1H, Py–H_p), 8.48(dd, 2H, Py–H_m). Anal. Calcd for C$_{46}$H$_{62}$N$_4$ (671.01): C, 82.34; H, 9.31; N, 8.35. Found: C, 82.10; H, 9.38; N, 8.36.

2.3.2. 2-[2,6-R$_2$–C$_6$H$_3$N=C(CH$_3$)–(CH$_3$)C=N-(3,5-iPr$_2$)C$_6$H$_2$–CH$_2$-(3′,5′-R$_2$)C$_6$H$_2$N=C(CH$_3$)]-6-[2,6-iPr$_2$–C$_6$H$_3$N=C(CH$_3$)] pyridine (R = i-Pr) (*N$_5$*)

2,6-R$_2$–C$_6$H$_3$N=C(CH$_3$)–C=O (**3**) was synthesized by modified method reported in the reference [33]. Compounds **2**(3.0 g, 4.5 mmol) and **3**(1.1 g, 4.3 mmol) were dissolved in 50 ml benzene. Para-toluenesulfonic acid (50 mg, 0.3 mmol) was added and the solution was refluxed for 48 h. After evaporation of solvent, the crude product was purified by column chromatography (silica, petroleum ether/ethyl acetate 40/1). 2.4 g of compound $\mathbf{N_5}$ was obtained (yield 60%). ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 1.12–1.20(m, 48H, $\mathrm{ArCH}(\mathit{CH}_3)_2$), 2.07 (d, 6H, $\mathrm{Ar{-}N{=}C}(\mathit{CH}_3){-}(\mathit{CH}_3)\mathrm{C{=}N{-}Ar}$), 2.27(s, 6H, $\mathrm{Py}{-}(\mathit{CH}_3)\mathrm{C{=}N}$), 2.75(m, 8H, $\mathrm{ArC}\mathit{H}(\mathrm{CH}_3)_2$), 4.03(s, 2H, $\mathrm{Ar}{-}\mathit{H}_2{-}\mathrm{Ar}$), 7.01(s, 4H, $\mathrm{Ar}{-}\mathit{H}$), 7.07–7.19(m, 6H, Ar–H), 7.93(t, 1H, $\mathrm{Py}{-}\mathit{H}_\mathrm{p}$), 8.47(dd, 2H, $\mathrm{Py}{-}\mathit{H}_\mathrm{m}$). Anal. Calcd for $C_{62}H_{83}N_5$ (898.36): C, 82.89; H, 9.31; N,7.80. Found: C, 82.49; H, 9.39; N, 7.84. ESI-MS: m/z 898.7$[M + H]^+$. m.p.: 255.3–257.8 °C. IR (KBr): ν 1641 cm^{-1} (C=N).

2.3.3. *{2-[2,6-$R_2{-}C_6H_3N{=}C(CH_3){-}(CH_3)C{=}N$-(3,5-$R_2$)$C_6H_2{-}CH_2$-(3′,5′-$R_2$)$C_6H_2N{=}C(CH_3)$]-6-[2,6-$R_2{-}C_6H_3N{=}C(CH_3)$]pyridine} $CoCl_2$ (R=i-Pr) (**$\mathbf{N_5Co}$**)*

A solution of $CoCl_2$ (0.137 g, 1.057 mmol) in 15 ml *n*-butanol was added dropwisely to a yellow solution of $\mathbf{N_5}$ (1.000 g, 1.113 mmol) in 20 ml *n*-butanol. After heated at 80 °C for 30 min, the mixture was cooled to room temperature. The reaction mixture was concentrated and 30 ml diethyl ether was added. The yellowish brown precipitate was isolated by decantation, washed with Et_2O (3 × 5 ml), and dried under vacuum to afford 1.025 g of complex $\mathbf{N_5Co}$ (yield 89%). ^{1}H NMR (400 MHz, CD_2Cl_2, δ in ppm): −82.73(d, 4H, $\mathrm{Py}{-}(\mathrm{CH}_3)\mathrm{C{=}N{-}ArC}\mathit{H}(\mathrm{CH}_3)_2$), −17.75(d, 12H, $\mathrm{Py}{-}(\mathrm{CH}_3)\mathrm{C{=}N{-}Ar}(\mathrm{CH}(\mathit{CH}_3)_2){-}\mathrm{CH}_2$), −16.93(d, 12H, $\mathrm{Py}{-}(\mathrm{CH}_3)\mathrm{C{=}N{-}ArCH}(\mathit{CH}_3)_2$), −8.36(s, 1H, $\mathrm{Py}{-}(\mathrm{CH}_3)\mathrm{C{=}N{-}Ar}{-}\mathit{H}_\mathrm{p}$), 0.94, 1.01(dd, 12H, $\mathrm{ArCH}(\mathit{CH}_3)_2\mathrm{N{=}C}(\mathrm{CH}_3){-}(\mathrm{CH}_3)\mathrm{C{=}N}$), 1.23, 1.48 (s, 12H, $\mathrm{Ar{-}N{=}C}(\mathrm{CH}_3){-}(\mathrm{CH}_3)\mathrm{C{=}N{-}Ar}(\mathrm{CH}(\mathit{CH}_3)_2){-}\mathrm{CH}_2$), 1.63, 1.79 (s, 6H, $\mathrm{N{=}C}(\mathit{CH}_3){-}(\mathit{CH}_3)\mathrm{C{=}N}$), 2.50, 2.63 (s, 4H, $\mathrm{ArC}\mathit{H}(\mathrm{CH}_3)_2{-}\mathrm{N{=}C}(\mathrm{CH}_3){-}(\mathrm{CH}_3)\mathrm{C{=}N}$), 4.78, 5.39 (s, 6H, $\mathrm{Py}{-}(\mathit{CH}_3)\mathrm{C{=}N}$), 7.02(m, 5H, $\mathit{H}{-}\mathrm{Ar{-}N{=}C}(\mathrm{CH}_3){-}(\mathrm{CH}_3)\mathrm{C{=}N}$), 10.32(d, 4H, $\mathrm{Py}{-}(\mathrm{CH}_3)\mathrm{C{=}N{-}Ar}{-}\mathit{H}_\mathrm{m}$), 19.89(s, 2H, $\mathrm{C}\mathit{H}_2$), δ = 49.94(s, 1H, H_p), 117.18(d, 2H, H_m). Anal. Calcd for $C_{62}H_{83}N_5Cl_2Co$ (1028.20): C, 72.42; H, 8.14; N, 6.81; Co, 5.73. Found: C, 72.02; H, 8.16; N, 6.59; Co, 5.69. ESI-MS: m/z 1027.4$[M + H]^+$, 991.7$[M{-}Cl]^+$, 898.7$[M{-}CoCl_2 + H]^+$. IR (KBr): ν 1618, 1637 cm^{-1} (C=N).

2.3.4. *{2-[2,6-$R_2{-}C_6H_3N{=}C(CH_3){-}(CH_3)C{=}N{-}$(3,5-$R_2$) $C_6H_2{-}CH_2{-}$(3′,5′-R_2)$C_6H_2N{=}C(CH_3)$]-6-[2,6-$R_2{-}C_6H_3N{=}C(CH_3)$] pyridine}$FeCl_2NiBr_2$ (R = i-Pr) (**$\mathbf{N_5CoNi}$**)*

A suspension of $NiBr_2$(DME) (0.180 g, 0.584 mmol) in CH_2Cl_2 (15 ml) was added to a solution of $\mathbf{N_5Co}$ (0.500 g, 0.486 mmol) in CH_2Cl_2 (20 ml) at room temperature. After 24 h, the mixture was filtered and the solvent was evaporated. The reddish-brown solid was washed with Et_2O (3 × 5 ml) and dried under vacuum to afford 0.496 g of product (yield 81%). Anal. Calcd for $C_{62}H_{83}N_5Br_2Cl_2CoNi$ (1246.70): C, 59.73; H, 6.71; N, 5.62; Co, 4.73 Ni, 4.71. Found: C, 59.79; H, 6.85; N, 5.50; Co, 5.05; Ni, 4.01. ESI MS: m/z 1239.8$[2M{-}Cl{+}Na]^{2+}$, 1210.8$[M{-}Cl]^+$, 1075.7 $[M{-}CoCl_2Br + K]^+$, 1034.5$[M{-}CoCl_2Br]^+$, 990.8$[M{-}NiBr_2Cl]^+$. IR (KBr): ν 1618, 1637 cm^{-1} (C=N).

2.4. *Ethylene polymerization*

The polymerization of ethylene was conducted in a 100-mL, three-necked flask. Toluene (50 mL) and required amount of cocatalyst were injected into the flask with vigorous stirring, and the system was saturated by ethylene. The polymerization was initiated by the addition of methylene dichloride solution of the catalyst. After 30 min, the polymerization was terminated by addition of the acidified ethanol. The resulting polymer was separated by filtration and dried in vacuum at 50 °C to constant weight.

3. Results and discussion

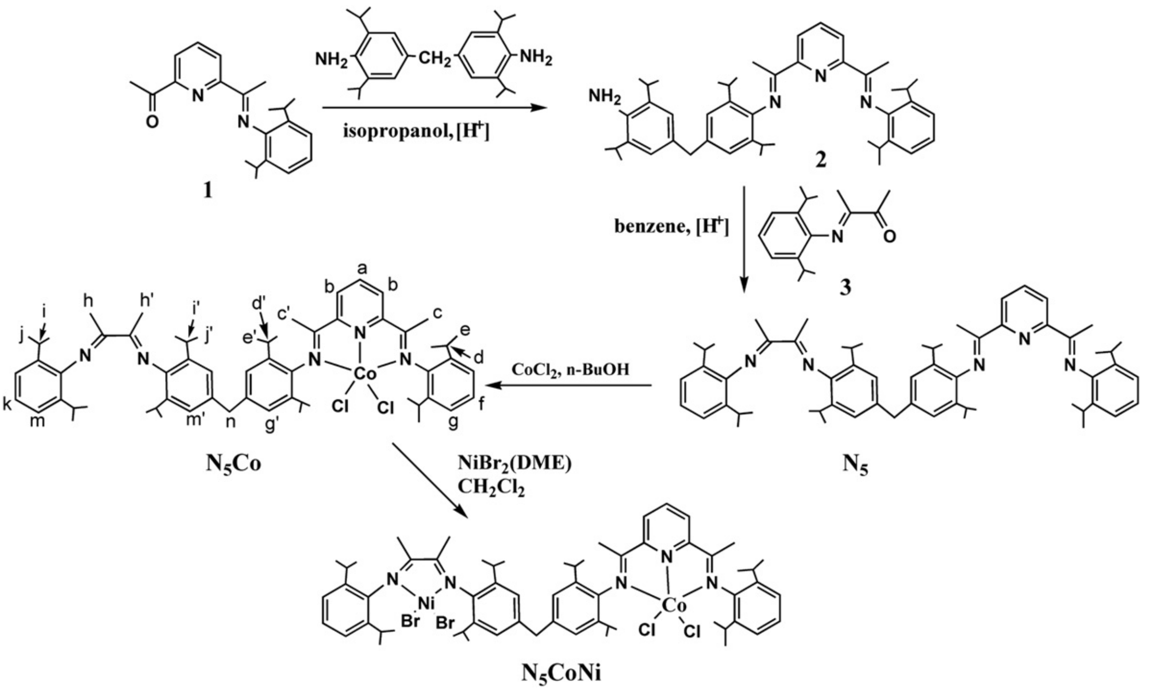
3.1. *Synthesis of heterobinuclear cobalt and nickel complex*

We designed the hybrid ligand containing α-diimine and pyridine diimine moieties according to common Brookhart [1] and Gibson [2,3] catalyst. The synthetic route of heterobinuclear cobalt and nickel complex $\mathbf{N_5CoNi}$ is described in Scheme 2. The 4,4′-methylene-bis(2,6-diisopropylaniline) was used as bridge to connect two monoketones. It was condensed with mono-(imino) pyridyl ketone catalyzed by para-toluenesulfonic acid, which produced compound **2**. Similar condensation reaction between compound **2** and ketimine **3** catalyzed by para-toluenesulfonic acid gave ligand $\mathbf{N_5}$. The ligand $\mathbf{N_5}$ was characterized by ^{1}H NMR spectrum (see Fig. S1), element analysis and mass spectrum. All results proved the successful synthesis of target ligand containing both pyridine imine and α-diimine moieties.

As reported by Bianchini and Kim [25,31], when the $CoCl_2$ or $FeCl_2$ was coordinated to a ligand which has both pyridine diimine and α-diimine moieties, the pyridine diimine was favored to be coordinated predominately. To confirm the selective coordination of $CoCl_2$ to pyridine diimine part of $\mathbf{N_5}$, the reaction of 0.95 equivalent $CoCl_2$ with the mixture of 1 equivalent ligand of $\mathbf{N_3Co}$ and 1 equivalent ligand of $\mathbf{N_2Ni}$ was conducted. Only cobalt complex $\mathbf{N_3Co}$ was obtained as product. The result indicates that in the presence of both pyridine diimine and α-diimine moieties, cobalt is predominantly coordinated to pyridine diimine.

The monometallic $\mathbf{N_5Co}$ was prepared by slowly addition of $CoCl_2$ in *n*-butanol to the 1.05 equivalent ligand $\mathbf{N_5}$ in *n*-butanol. The ^{1}H NMR spectrum of $\mathbf{N_5Co}$ is shown in Fig. 1, which is quite different from the spectrum of ligand $\mathbf{N_5}$ (see Fig. S1). The comparison of chemical shifts of all protons of ligand $\mathbf{N_5}$ with complex $\mathbf{N_5Co}$ is given in Table 1. It is evident that the chemical shifts of protons of pyridine diimine part of complex $\mathbf{N_5Co}$ are quite different from the ligand $\mathbf{N_5}$. On the other side, chemical shifts of protons of α-diimine part of $\mathbf{N_5Co}$ do not change so much compared with ligand $\mathbf{N_5}$. The peaks at 49.94 ppm (proton a in Scheme 2) and 117.18 ppm (proton b in Scheme 2) can be assigned to the signals of proton of pyridine ring, which is close to corresponding chemical shifts of mononuclear complex $\mathbf{N_3Co}$ [31]. The ^{1}H NMR result indicates that cobalt is selectively coordinated to the pyridine imine, and the $\mathbf{N_5Co}$ still keeps one free α-diimine moiety. In the ESI-MS of $\mathbf{N_5Co}$ (see Fig. S3), the peaks related to $[M + H]^+$, $[M{-}Cl]^+$ and $[M{-}CoCl_2{+}H]^+$ were found, no peak corresponding to $[M + CoCl_2]^+$ (1157.40) was found. This demonstrates no homobimetallic complexes $\mathbf{N_5Co_2}$ is formed during the reaction. Furthermore, The IR spectra of $\mathbf{N_5Co}$ (see Fig. S3) contained two ν(C=N) bands. Compared with one single ν(C=N) band at 1641 cm^{-1} assigned to free imine group of ligand $\mathbf{N_5}$ (see Fig. S3), the weak band at 1618 cm^{-1} was assigned for the coordinated pyridine imine groups, and more intense one at 1637 cm^{-1} for the free α-diimine group. This indicates that not all of the nitrogen atoms of the potentially pentadentate ligand involved in the coordination to the cobalt center. The element analysis data and cobalt content measured by ICP confirm that only one equivalent cobalt coordinates to each ligand $\mathbf{N_5}$. The polydispersity indexes of polymers prepared by $\mathbf{N_5Co}$ were around 2.0 (see Table 2), which also suggests only one kind of cobalt center exists in the structure of complex. Base on above characterizations, the $\mathbf{N_5Co}$ was successfully synthesized.

The heterobinuclear complex $\mathbf{N_5CoNi}$ was prepared by adding 1.20 equivalent of $NiBr_2$(DME) to the $\mathbf{N_5Co}$ in CH_2Cl_2. The ^{1}H NMR spectrum of final product is hardly to analyze due to the poor resolution of the spectra derived from the paramagnetic property of the complex. Attempt to obtain its crystal was failed. In the ESI-MS of $\mathbf{N_5CoNi}$ (see Fig. S4), the peaks related to $[M{-}Cl]^+$, $[M{-}CoCl_2Br + K]^+$,



Scheme 2. Preparation of heterobinuclear complexes N_5CoNi.

$[M{-}CoCl_2Br]^+$, $[M{-}NiBr_2Cl]^+$ were found, which demonstrates that both nickel and cobalt are coordinated to ligand $\mathbf{N_5}$. Its IR spectrum (see Fig. S3) showed the band at 1637 cm^{-1} became weak compared with that of $\mathbf{N_5Co}$, suggesting that nickel was coordinated to α-diimine group. The element analysis and cobalt and nickel content measured by ICP is consistent with the targeted formula as well.

3.2. *Ethylene polymerization*

Table 2 shows the results of ethylene polymerization catalyzed by various catalysts shown in Scheme 1 with $AlEt_3$ (TEA) and modified methylaluminoxane (MMAO) as cocatalyst. MMAO was dried under high vacuum for 48 h to remove excess volatile aluminum alkyls before use.

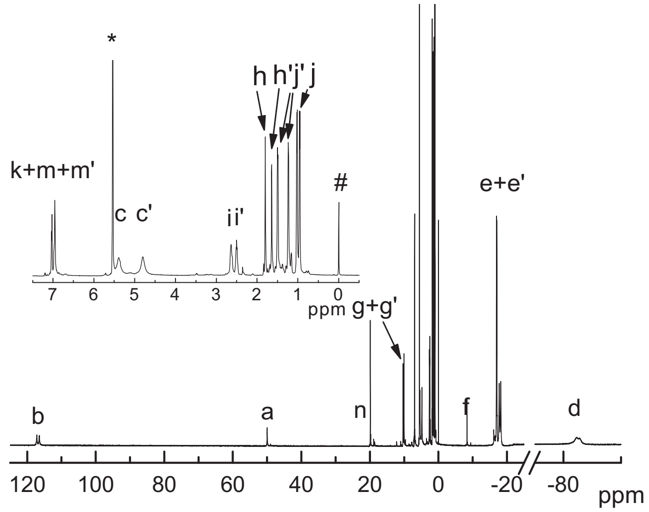


Fig. 1. ^1H NMR spectrum of complex N_5Co in CD_2Cl_2 (CD_2Cl_2 (*); TMS (#); protons marked same as in Scheme 2).

For both the monometallic $\mathbf{N_3Co}$ and $\mathbf{N_2Ni}$, the activity obtained with MMAO was higher than TEA. For $\mathbf{N_3Co}$, there was little influence of Al/Co ratio on the ethylene polymerization activity for two cocatalysts. When TEA used as cocatalyst For $\mathbf{N_2Ni}$, the activity decreased as the Al/Ni ratio increased. When using MMAO as cocatalyst, the activity of two mononuclear complexes slightly changed. The purpose of above study is to find the optimal polymerization condition for heterobinuclear complex. One molar binuclear complex has one molar nickel and one molar cobalt. If same amount of cocatalyst was used in both mononuclear and binuclear system, the ratio of Al/metal was different. The ratio of Al/metal in binuclear system is half as that in mononuclear system, although the ratio of Al/Co or Al/Ni in mononuclear is same as those in binuclear system. Because the ratio of Al/Co or Al/Ni don't affect the activity of the mononuclear complexes $\mathbf{N_3Co}$ and $\mathbf{N_2Ni}$ so much according to polymerization results, Al/Co (or Al/Ni) = 400 for mononuclear complex and Al/(Co + Ni) = 200 for binuclear complex are chosen for the following study.

Table 1
Comparison chemical shifts of protons of ligand N_5 and complex N_5Co.

Proton	**N_5**	**N_5Co**	Proton	**N_5**	**N_5Co**
pyridine imine part			*α-diimine part*		
a[a]	7.93[b]	49.94	h, h′	1.12–1.20	1.63, 1.79
b	8.47	117.18	i, i′	2.75	2.50, 2.63
c, c′	2.27	4.78,5.39	j, j′	1.12–1.20	0.94, 1.01,1.23,1.48
d, d′	2.75	−82.73	k, m, m′	7.07–7.19	7.02
e, e′	1.12–1.20	−16.93, −17.75			
f	7.01, 7.07–7.19	−8.37			
g, g′		10.32			
n	4.03	19.89			

[a] Proton marked same as in Scheme 2.
[b] δ in ppm.

Table 2
Results of ethylene polymerization catalyzed by mononuclear and binuclear complexes[a].

Entry	Catalyst	Cocatalyst	Al/(Co + Ni)	Activity[b]	M_w[c]	M_w/M_n[c]	T_m[d]
1	**N_3Co**	TEA	200	1.61	–[e]	–	132.7
2		TEA	400	1.58	2.18	2.68	132.9
3		TEA	800	1.54	–	–	132.4
4		MMAO	200	3.40	–	–	131.5
5		MMAO	400	3.80	1.98	2.69	132.2
6		MMAO	800	3.93	–	–	132.4
7	**N_2Ni**	TEA	200	0.83	–	–	no
8		TEA	400	0.44	10.15	2.82	no
9		TEA	800	0.37	–	–	no
10		MMAO	200	1.95	–	–	no
11		MMAO	400	2.06	27.17	1.95	no
12		MMAO	800	2.19	–	–	no
13	**N_5Co**	TEA	400	1.93	2.16	2.35	132.1
14		MMAO	400	4.22	1.91	2.25	131.5
15	**N_3Co + N_2Ni**	TEA	200	1.31	9.05	6.97	130.9
16		MMAO	200	2.21	9.38	8.65	131.6
17	**N_5CoNi**	TEA	200	0.82	2.88	3.60	131.7
18		MMAO	200	1.64	4.84	5.73	131.8

[a] Polymerization condition: 30 °C, 50 ml toluene, 1 atm ethylene pressure, 30 min, $[Co] = 1 \times 10^{-5}$ M, $[Ni] = 1 \times 10^{-5}$ M.
[b] 10^6 gPE/(mol(Co + Ni)·h bar).
[c] Measured by GPC, in 10^4 g/mol.
[d] Measured by DSC, in °C.
[e] Unmeasured.

We intentionally compare the following two catalytic systems: **N_5CoNi**, which is referred as binuclear system, and its control, mixed mononuclear complexes including equivalent molar **N_3Co** and **N_2Ni**, which is referred as binary system.

The activities of heterobinuclear complex were apparently lower than those of binary system and sum of the individual activity of **N_3Co** and **N_2Ni** for both TEA and MMAO. This result is different from performance of homobinuclear complex with respect to corresponding mononuclear complex. As reported by Sun [17], Li [12] and Schumann [20], binuclear and polynuclear nickel or iron complex normally showed higher activity than mononuclear one. On the other hand, the polymerization activities of binary system were higher than the sum of the individual activity of **N_3Co** and **N_2Ni** for both TEA and MMAO, which suggests that the cooperative effect between the two metal centers in the binary system exists. There are some reports on ethylene polymerization catalyzed by binary heteronuclear complexes. In ethylene polymerization catalyzed by combination of 2,6-bis[1-(2,6-dimethyphenylimino) pyridyl]-cobalt(II) dichloride and [1,4-bis(2,6-diisopropylphenyl)]acenaphthene diimine nickel(II) dibromide [34], the catalyst activity increased linearly with the fraction of nickel complex, suggesting that the interactions between catalysts were minimal, and the complexes performed independently from each other. For the binary system containing Ni(diimine)Cl_2 (diimine = 1,4-bis(2,6-diisopropylphenyl)-acenaphthenediimine) and {TpMs*}$TiCl_3$ (TpMs* = hydridobis(3-mesitylpyrazol-1-yl)(5-mesitylpyrazol-1-yl)) [35], the activity markedly depended upon the content of the late transition metal, suggesting a synergic effect between nickel and titanium complexes. Once mixture of 2,6-bis(imino)pyridyl iron dichloride complexes and 1,2-bis(imino)acenaphthyl nickel dibromide complexes used for ethylene polymerization [36], both the positive and negative deviation in activity have been observed, which depends on the component of iron and nickel. All the results indicate that the polymerization activity of the binary complexes with respect to mononuclear complex is determined by the combination of individual complexes, although the molar fraction of complex and the polymerization conditions, such as temperature and solvent, affect the activity as well.

In view of molecular structure, there are two main differences between binary and binuclear system. One is that binuclear complex has two metal sites in one molecular, while binary system is the mixture of mononuclear complex with different metal center. The other is that the ligand of binuclear complex contains both α-diimine and pyridine diimine units, which are chemically bonded. To check the influence of ligand on the performance of complex, mononuclear complex **N_5Co** was also used as catalyst for ethylene polymerization. The activity of **N_5Co** was higher than that of **N_3Co**, which indicates that bigger ligand results in higher activity. Since we could not prepare mononuclear nickel complex with nickel coordinated to the α-diimine of **N_5** and obtain its activity, we cannot know the influence of **N_5** on the nickel site. But from the performance of polynuclear nickel complex reported by Schumann [20], the large ligand normally increase the activity of the nickel centers. If the influence of ligand structure on the polymerization activity is excluded, there must be some other reasons leading to the low polymerization activity of heterobinuclear complex.

As expected, cobalt center produced linear PE with melting point around 132 °C, while nickel center generated branched PE without detectable melting point above room temperature, which is confirmed by DSC measurement.

MW and molecular weight distribution (MWD) are important parameters which could tell the different nature of metallic center. The GPC curves of PE prepared by various complexes are shown in Figs. 2 and 3. The GPC curves of PE produced by binuclear complex and binary catalyst show bimodal MWD, one major polymer population with low MW and one small population with high MW. All mononuclear complexes, **N_3Co**, **N_2Ni** and **N_5Co**, produced PE with unimodal MWD, and the cobalt and nickel complexes produced polymer with low and high MW respectively. It is noted that mononuclear cobalt complexes, **N_3Co** and **N_5Co**, produce PE with almost the same MW and MWD, which strongly demonstrates that cobalt selectively coordinates to the pyridyl imine moiety and no homobinuclear complex exists. Cocatalysts used in current study have little influence on the MW and MWD of polymer generated by **N_3Co**. The MW of polymer produced by **N_2Ni** increased in the order of MMAO > TEA.

According to the MWD of PE obtained by mononuclear cobalt and nickel complexes, it is confirmed that the high-MW fraction is produced by nickel center and the low-MW fraction produced by cobalt center. All cobalt centers produced polymer with similar MW. Nickel center in binary and binuclear system produced polymer with relatively higher MW than mononuclear one.

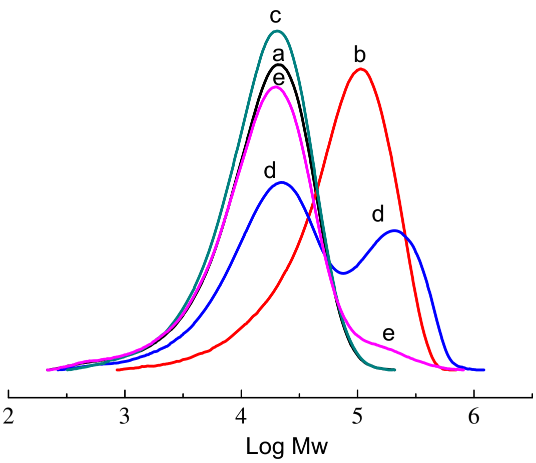


Fig. 2. The GPC curves of PE prepared by N_3Co (a), N_2Ni (b), N_5Co (c), N_3Co + N_2Ni (d) and N_5CoNi (e) activated by TEA.

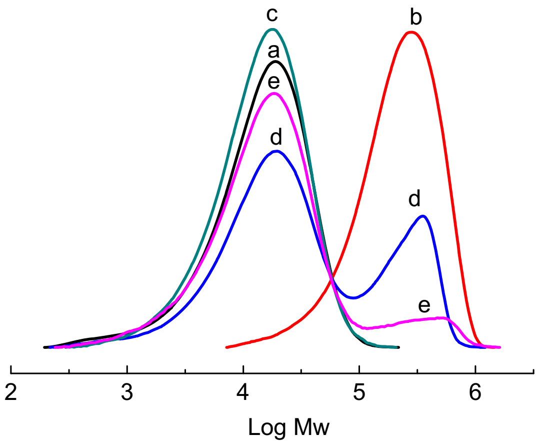


Fig. 3. The GPC curves of PE prepared by N_3Co (a), N_2Ni (b), N_5Co (c), $N_3Co + N_2Ni$ (d) and N_5CoNi (e) activated by MMAO.

Besides the polymerization activity, the prime difference between binuclear and binary system is the relative amount of two different PE populations. The relative amount of high-MW PE produced by binuclear system was far less than that by binary system, which suggests the productivity of nickel centers of binuclear complex is much lower than cobalt center. The productivity of each center in binuclear and binary complexes can be calculated from the their total activity and the weight fraction of each population, and the later can be obtained from the deconvolution of bimodal distribution. Table 3 gives the individual productivity of each metallic center in mononuclear, binuclear and binary complexes. When TEA was used as cocatalyst, the productivity of cobalt center in binuclear complex was almost the same as the mononuclear complex and binary system (Table 3 entry 5 vs 1 and 4). On the contrary, the productivity of nickel center in binuclear complex was much lower than mononuclear complex and binary system (Table 3 entry 5 vs 2 and 4). When MMAO was used as activator, the productivity of cobalt center in binuclear complex was almost the same as binary system, but lower than the mononuclear complex. (Table 3 entry 10 vs 6 and 9) The productivity of nickel center in binuclear complex was still much lower than binary system and mononuclear complex (Table 3 entry 10 vs 7 and 9). Therefore, the low polymerization activity of heterobinuclear complex is caused by the low productivity of nickel center.

Table 3
Individual productivity of metallic center in different complexes[a].

Entry	Catalyst	Cocatalyst	Activity[b]		
			Co	Ni	Co + Ni
1	**N_3Co**	TEA	1.58	–	–
2	**N_2Ni**		–	0.44	–
3	**N_5Co**		1.93	–	–
4	**$N_3Co + N_2Ni$**		1.55[c]	1.07[d]	1.31
5	**N_5CoNi**		1.51[c]	0.13[d]	0.82
6	**N_3Co**	MMAO	3.80	–	–
7	**N_2Ni**		–	2.06	–
8	**N_5Co**		4.22	–	–
9	**$N_3Co + N_2Ni$**		2.92[c]	1.50[d]	2.21
10	**N_5CoNi**		2.95[c]	0.33[d]	1.64

[a] Polymerization condition: 30 °C, 50 ml toluene, 1 atm ethylene pressure, 30 min, $[Co] = 1 \times 10^{-5}$ M, $[Ni] = 1 \times 10^{-5}$ M, Al/Co = 400, Al/Ni = 400.

[b] In 10^6 gPE/(mol(metal)·h atm).

[c] Calculated from percentage of low-MW × total activity.

[d] Calculated from percentage of high-MW × total activity.

To further investigate the influence of cocatalyst on the performance of binuclear complex, TEA/$[PhMe_2NH][B(C_6F_5)_4]$(B) was used as cocatalyst for various complexes and the results are listed in Table 4 and Fig. 4. When mononuclear complexes activated with TEA/B, the activity of **N_2Ni** significantly increased, while the activity of cobalt complexes **N_3Co** and **N_5Co** remarkably decreased. The same trend could also be found in the binary and binuclear catalysts, although the total polymerization activity decreased. For the binary catalysts, the amount of high-MW fraction produced by **N_2Ni** exceeded the amount of low-MW fraction generated by **N_3Co** (Fig. 4 curve d). The productivity of nickel center in binuclear complex also increased compared with the same complex activated with TEA (Table 4 entry 5 *vs* Table 2 entry 5). The above results indicate that TEA/B is better cocatalyst than TEA for nickel center. In order to improve polymerization activity, we further increased the Al/Metal ratio to 200 for binuclear complex (Table 4 entry 6). We obtained increased total activity together with the low productivity of nickel center, which is similar to the result obtained by TEA. This suggests that TEA is an more efficient cocatalyst than $[PhMe_2NH][B(C_6F_5)_4]$ for cobalt center of binuclear complex.

The branching degree of PE produced by various catalysts can be estimated from ^{13}C- NMR directly. (see Fig. S6) The branching degree of PE produced by nickel sites of binuclear and binary catalysts can be calculated according to its weight fraction, because cobalt site just produces linear PE. The branches per 1000 carbon atoms of PE produced by nickel sites of **N_2Ni**, **$N_3Co + N_2Ni$** and **N_5CoNi** were 84.5, 101.0 and 57.7 respectively. The results indicate that nickel site of binuclear complex produced less branches compared with mononuclear **N_2Ni**, which is probably due to the influence of cobalt site on its neighboring nickel site in binuclear complex. The binary catalyst produced PE with higher branching degree than mononuclear **N_2Ni**, the reason for this is not clear.

3.3. *UV–vis characterization of active center*

To understand the nature of active centers in binuclear complex during the polymerization, UV–vis spectroscopy was applied. Figs. 5 and 6 show the UV–vis absorption of all catalysts catalyzed by TEA and TEA/B respectively under N_2 atmosphere.

When activated by TEA, **N_3Co** presented a broad absorption band at 600 nm (Fig. 5a). It is suggested by previous work [37] that this absorption band can be assigned to its active center. Three absorption bands at 456 nm, 492 nm and 627 nm were found in the spectrum of **N_2Ni** (Fig. 5b). The bands at 456 nm and 492 nm correspond to active centers and band at 627 nm corresponds to inactive centers, which is consistent with previous work [38]. The UV–vis spectrum of the binary system showed four bands at 456 nm, 497 nm, 545 nm and 620 nm (Fig. 5d), which can be considered as the overlap of the individual spectra of the **N_3Co** and **N_2Ni**. **N_5Co** also has an absorption band in 590 nm (Fig. 5c). In the spectra of **N_5CoNi**, bands at 452 nm, 545 nm and 596 nm could be found (Fig. 5e). Compared with spectra of two mononuclear complexes, the two bands at 452 nm and 596 nm can be assigned to nickel center, and latter band corresponds to the band at 627 nm of **N_2Ni**. The left band at 545 is considered as the absorption of cobalt center, which shifts from 596 nm found in **N_3Co**. In the spectra of **N_5CoNi**, the band at around 497 nm (shown in the spectra of both **N_2Ni** and binary system) was not found, which indicates the poor activation of nickel center in heterobinuclear complex.

Table 4

Results of ethylene polymerization catalyzed by various complexes activated by TEA/[$PhMe_2NH$][$B(C_6F_5)_4$][a].

Entry	Catalyst	Activity[c]			M_w[e]	M_w/M_n[e]	T_m[f]	branches per 1000 °C
		Co	Ni	Co + Ni				
1	**N_3Co**	0.89	–	–	4.41	23.51	131.6	
2	**N_2Ni**	–	1.31	–	15.75	2.58	no	84.5[g,h]
3	**N_5Co**	1.48	–	–	2.17	2.62	131.9	
4	**N_3Co + N_2Ni**	0.49[d]	1.27[d]	0.88	15.61	8.18	130.1	59.8[g]/101.0[h]
5	**N_5CoNi**	0.63[d]	0.37[d]	0.50	12.12	11.08	132.1	20.1[g]/57.5[h]
6	**N_5CoNi**[b]	1.65[d]	0.05[d]	0.85	2.96	3.06	131.7	trace

[a] Polymerization condition: 30 °C, 50 ml toluene, 1 atm ethylene pressure, 30 min, [Co] = 1×10^{-5} M, [Ni] = 1×10^{-5} M, Al/Co = Al/Ni = 50, Al/(Co + Ni) = 25, B/(Co + Ni) = 1.2; [$PhMe_2NH$][$B(C_6F_5)_4$] was abbreviated as B.

[b] Same as condition (a) except Al/(Co + Ni) = 200.

[c] In 10^6 gPE/(mol(Co + Ni)·h bar).

[d] Calculated from weight percentage × activity.

[e] Measured by GPC, in 10^4 g/mol.

[f] Measured by DSC, in °C.

[g] Branches of whole polymer measured by ^{13}C NMR.

[h] Branches of polymer produced by nickel site measured by ^{13}C NMR.

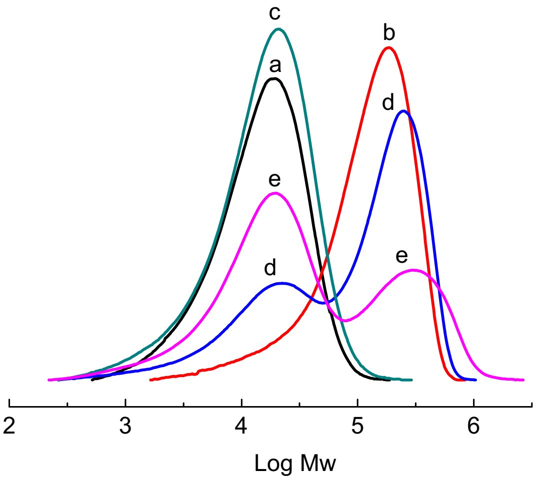


Fig. 4. The GPC curves of PE prepared by N_3Co(a), N_2Ni (b), N_5Co (c), N_3Co + N_2Ni (d) and N_5CoNi (e) activated by TEA/[$PhMe_2NH$][$B(C_6F_5)_4$].

When the cocatalyst was varied to TEA/B, the spectra of binary and binuclear complex displayed some changes. The band at around 545 nm disappeared (Fig. 6e, d), which was found in the spectra of binary system and binuclear complex activated by TEA (Fig. 5e, d). This band is probably the absorption band of cobalt center, which can explain the relative decrement of productivity of cobalt center in binuclear complex activated by TEA/B. The apparent discrepancy in the spectra of binary system and binuclear complex can account for the low productivity of nickel center in both systems.

According to the polymerization results and UV–vis spectra data, the key difference between heterobinuclear and binary system is that heterobinuclear complex **N_5CoNi** shows significant depression in the productivity of nickel center, while the cobalt center is only slightly influenced. The MW of PE produced by nickel center of heterobinuclear complex **N_5CoNi** is higher than its mononuclear and binary control. All these features combined suggests that metal site in the heterobinuclear complex is selectively activated by cocatalyst, which don't occur in its counterparts, such as binary system and homobinuclear complex. The possible reason of such depression and selective activation is that two different metallic sites exist in one molecule. Once one metal is activated by cocatalyst, the other one is less efficiently activated by

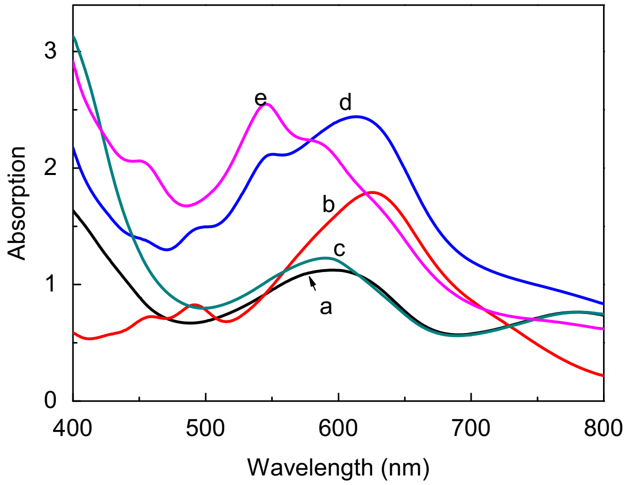


Fig. 5. UV–visible absorption spectrum of various catalysts/TEA under N_2 atmosphere. N_3Co (a), N_2Ni (b), N_5Co (c) N_3Co + N_2Ni (d), N_5CoNi (e). (Al/Co=Al/Ni = 400, [Cat] = 0.33 mM).

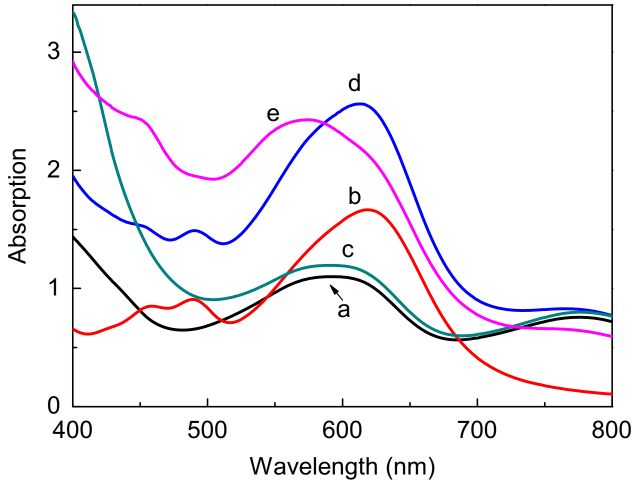


Fig. 6. UV–visible absorption spectrum of various catalysts/TEA/[$PhMe_2NH$] [$B(C_6F_5)_4$] under N_2 atmosphere. N_3Co (a), N_2Ni (b), N_3Co + N_2Ni (c), N_5Co (d), N_5CoNi (e). (Al/Co=Al/Ni = 50, [Cat] = 0.33 mM; B/(Co + Ni) = 1.2).

cocatalyst subsequently. Which one is efficiently activated by cocatalyst is determined by the type of cocatalyst used.

4. Conclusions

In this article, we prepared heterobinuclear cobalt and nickel complex **N_5CoNi**, which includes both pyridine diimine cobalt and α-diimine nickel units. Using TEA and MMAO as cocatalyst, the ethylene polymerization activity of **N_5CoNi** is less than that of mixed mononuclear complexes **N_3Co** and **N_2Ni**. The amount of high-MW PE produced by nickel center of binuclear complex is less than the binary system. When TEA/[$PhMe_2NH$][$B(C_6F_5)_4$] was applied as cocatalyst, the productivity of nickel site was improved, but it produced PE with less branching degree than mononuclear complex **N_2Ni**. In UV–vis spectra, the absorption band of active nickel center of **N_5CoNi** is weaker than in binary system. The results reveal that the productivity of nickel center of binuclear complex is predominantly suppressed due to selective activation of metallic center in heterobinuclear complex, which has not been reported previously.

Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2010.04.050.

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