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# Trinuclear Fe(II)/Ni(II) complexes as catalysts for ethylene polymerizations

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# 1. Introduction

Multimetallic complexes are reasonable models, like enzymes, to achieve superior reactivity and selectivity, in part, by their efficacy in creating highly local reagent concentrations and conformationally advantageous active site–substrate proximities and interactions [1,2]. On the basis of these aspects, multinuclear metallocenes have been reported to provide novel and versatile polymerization catalysts by cooperative effects between multimetallic centers [2–4]. Within the context of the rapidly advancing and technologically significant field of homogeneous single-site olefin polymerization catalysis [5–7], the conjecture that cooperative effects involving two or more metal centers in close proximity might achieve more efficient chain propagation to yield novel polymer architectures.

Homogeneous catalyst systems based on late transition metal catalysts are currently regarded as being one of the interesting research fields in olefin polymerization catalysts due to their unique reactivity patterns and unusual catalytic properties [8–13]. Recently, a range of sterically encumbered multidentate binucleating ligands such as organo-bridged iminopyridines,  $\alpha$ -diimines, and iminophenolates have been found to be efficient systems achieving active dinickel, dipalladium and diiron catalysts for olefin polymerizations [11,14–18]. They are also expected to behave as promising catalysts in producing a wide range of olefinic com-

# ABSTRACT

A new trimetallic heterotrinuclear catalyst bearing two Fe and one Ni atoms of the general formula  $\{(2,6-C_{12}H_{17})N=C-(C_7H_9N)[FeCl_2]C-N=C-(C_{23}H_{34})-C\}_2=N-C-(C_{10}H_6)-C=N[NiBr_2]$  has been synthesized successfully. For comparison, monometallic Ni(II) and bimetallic Fe(II) complexes are also investigated. When activated with methylaluminoxane or common alkyl aluminums such as ethyl aluminum sesquichloride and triethylaluminum, all catalysts polymerize ethylene with activities exceeding  $10^5$  g-PE/mol-M h bar at 30 °C. The heteronuclear trimetallic complexes showed higher catalytic activity and longer life time, especially at high temperature, than monometallic Ni(II) and homonuclear bimetallic Fe analogues, due to the cooperative effect of the neighboring metals. The molecular weight, polydispersity and the degree of branching of polyethylene were drastically influenced by the type of the metal complex and experimental parameters.

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pounds including functionalized polyolefins. It is assumed that the active species of these homogeneous systems are a single metal center with a defined structure. However, the behavior of these complexes in polymerization was similar to mononuclear complexes and specific properties of late transition metal multinuclear complexes are yet unknown. The catalytic activities, sterioregularities, molecular weights and molecular weight distributions of the obtained polymer might be controlled by modifying the ligand structure of the monometallic complexes, and these might also be tuned by arranging multimetal centers at spatially confined positions. Although several syntheses of heterometalic complexes are known, only a few of them have been employed as polymerization catalysts [14,19–21].

Here we would like to report on the synthesis and characterization of a new class of multinuclear Ni(II)/Fe(II) complexes as catalysts for ethylene polymerizations. The Ni(II) and Fe(II) systems are so particular in that (1) the Ni(II)/Pd(II) diimine based catalysts are highly active and can convert ethylene directly to highly branched polyethylene without the addition of expensive  $\alpha$ -olefins, such as 1-hexene and 1-octene [11,22] and (2) the Fe(II)/Co(II) bis(imino)pyridine based catalysts are more active than its Ni(II) and Fe(II) monometallic counterparts. This new Fe(II)-Ni(II)-Fe(II) trinuclear trimetallic catalyst, when activated by various cocatalysts like methylaluminoxane (MAO) and common alkyl aluminums such as ethyl aluminum sesquichloride (EASC) and triethylaluminum (TEA), resulted in polyethylene (PE) with unique microstructure and broad molecular weight distribution, due to the formation of multiple active sites from each Fe(II) and Ni(II) metal centers.



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# 2. Experimental

# 2.1. Materials

All reactions were performed under a purified nitrogen atmosphere using standard glove box and Schlenk techniques. Polymerization grade of ethylene (SK Co., Korea) was purified by passing it through columns of Fisher RIDOX<sup>TM</sup> catalyst and molecular sieve 5 Å/13X. All organic solvents purchased from Aldrich Chemical Co. were purified by known procedures and stored over molecular sieves (4 Å). All reagents used in this study were purchased from Aldrich Chemical Co. and used without further purification. MAO (8.4 wt% total Al solution in toluene) was donated by LG Chemicals, Korea and was used without further purification.

#### 2.2. Characterization

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of ligands were recorded on a Varian Gemimi-2000 (300 MHz for <sup>1</sup>H NMR, 75 MHz for <sup>13</sup>C NMR) spectrometer. All chemical shifts were reported in parts per million (ppm) relative to residual CHCl<sub>3</sub> ( $\delta$  7.24) for <sup>1</sup>H and relative to  $CDCl_3$  ( $\delta$  77.00) for <sup>13</sup>C. <sup>1</sup>H and <sup>13</sup>C NMR spectra of PE were taken in C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> at 135 °C on an Inova-500 (500 MHz, 125 MHz) spectrometer. The elemental analysis of complexes was carried out using Vario EL analyzer. Metal concentrations (Fe and Ni) of the metal complexes were determined using inductively coupled plasma-atomic emission spectrometry (ICP-AES, Perkin-Elmer Optima 3300DV). Analytical thin layer chromatography (TLC) was conducted using Merck 0.25 mm silica gel 60F pre-coated aluminum plates with fluorescent indicator UV254. Ligands were purified by a Combi-Flash (Companion) auto-column machine. Elemental analysis was carried out using Vario EL analyzer and UV-vis spectra were recorded on a Shimadzu UV-1650PC UV-vis spectrophotometer at 30°C. FT-IR analyses were carried out in Shimadzu IR Prestige-21 spectrophotometer.

The molecular weight (MW) and polydispersity index (PDI) of PE were determined by GPC (PL-GPC220/FTIR) in 1,2,4-trichlorobenzene/THF using polystyrene columns as standard. Thermal analysis of PE was carried out by differential scanning calorimetry (Perkin-Elmer DSC, model: Pyris 1) at  $10^{\circ}$ C/min heating rate under nitrogen atmosphere. The results of the second scan were reported to eliminate any difference in sample history. The branching numbers for PE were determined by <sup>1</sup>H NMR spectroscopy using the ratio of the number of methyl groups to the overall number of carbons and were reported as branches per thousand carbons.

## 2.3. Synthesis of ligand precursors

The syntheses of trinuclear ligand (**C**) and metal monometallic Ni(II) complex **D**, bimetallic Fe(II) complex **E** and trimetallic Ni(II)/Fe(II) complex **F** are summarized in Scheme 1.

# 2.3.1. 1-(6-((E)-1-(2,6-diisopropylphenylimino)ethyl)pyridin-2yl)ethanone (**A**)

Compound **A** was synthesized by reacting 2,6-diacetylpyridine (1.630 g, 10.0 mmol) with 2,6-diisopropylaniline (1.70 mL, 9.0 mmol) in methanol (15 mL). A catalytic amount of formic acid was added. The yellow precipitate obtained was filtered and washed with cold methanol. The solid was suspended in refluxing ethanol and the resulting mixture was filtered in hot condition. The solvent was removed from the filtrate under reduced pressure to give pure compound **A** as pale yellow crystals in 67% yield (2.17 g, 6.73 mmol). m.p. 182–184 °C. IR:  $\nu_{(C=N)}$  1648 cm<sup>-1</sup>,  $\nu_{(C=0)}$  1698 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.16 [d, 6H, CH(CH<sub>3</sub>)(CH<sub>3</sub>)], 1.17 [d, 6H, CH(CH<sub>3</sub>)(CH<sub>3</sub>)], 2.28 [s, 3H,

C(NAr)CH<sub>3</sub>], 2.74 [sept, 2H, CH(CH<sub>3</sub>)(CH<sub>3</sub>)], 2.81 [s, 3H, C(O)CH<sub>3</sub>], 7.08–7.22 (m, 3H, CH Ar), 7.96 (t, 1H, CH Ar), 8.16 (d, 1H, CH Ar), 8.58 (d, 1H, CH Ar) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  17.7, 23.5, 23.9, 26.4, 29.0, 123.2, 123.7, 124.4, 125.2, 136.4, 138.4, 142.9, 153.1, 156.2, 167.8, 200.8 ppm. Calcd. for C<sub>21</sub>H<sub>26</sub>N<sub>2</sub>O (322.45): C 78.22, H 8.13, N 8.69, O 4.96; Found: C 78.39, H 8.17, N 8.84, O 4.6.

#### 2.3.2. 4-((4E)-4-(1-(6-((E)-1-(2,

6-diisopropylphenylimino)ethyl)pyridine-2-yl)ethyldene amino)-3,5-diisopropylbenzyl)-2,6-diisopropylbenzenamine (**B**)

Compound **B** (1.6 g, 5 mmol) and 4,4'-methylenebis(2,6diisopropylaniline) (5.5 g, 15 mmol) were dissolved in 15 mL of xylene and stirred at 100 °C until it become a clear solution. Acetic acid (100 µL) was added, and stirred for 5 days. The solution was dried under reduced pressure. The solid precipitate was washed with cold methanol several times and the product was purified via column chromatography [5% ethyl acetate (EA)/nhexane-alumina]. The solvent was evaporated to afford the product as a dark yellow powder in 60% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 1.27 [d, 6H, CH(CH<sub>3</sub>)(CH<sub>3</sub>)], 1.28 [d, 6H, CH(CH<sub>3</sub>)(CH<sub>3</sub>)], 2.30 [d, 6H, CH(CH<sub>3</sub>)(CH<sub>3</sub>)], 1.32 [d, 6H, CH(CH<sub>3</sub>)(CH<sub>3</sub>)], 1.38 [d, 6H, CH(CH<sub>3</sub>)(CH<sub>3</sub>)], 1.40 [d, 6H, CH(CH<sub>3</sub>)(CH<sub>3</sub>)], 2.2 [s, 6H, C(NAr)CH<sub>3</sub>], 2.68 [sept, 2H, CH(CH<sub>3</sub>)(CH<sub>3</sub>)], 2.72 [sept, 2H, CH(CH<sub>3</sub>)(CH<sub>3</sub>)], 2.86 [sept, 2H, CH(CH<sub>3</sub>)(CH<sub>3</sub>)], 3.56 (s, 2H, NH<sub>2</sub>), 3.88 (s, 2H, CH<sub>2</sub>), 6.82 (s, 2H, CHAr), 6.94 (s, 2H, CHAr), 7.09 (m, 3H, CHAr), 7.84 (t, 1H, CHAr), 8.42 (dd, 1H, CHAr) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 16.13, 21.51, 21.99, 22.20, 26.83, 26.95, 27.17, 27.28, 122.21, 122.58, 122.80, 130.32, 131.47, 134.54, 134.71, 135.29, 136.92, 143.20, 145.44, 154.02, 154.20, 165.88, 166.09. Anal. Calcd. for C<sub>46</sub>H<sub>62</sub>N<sub>4</sub> (671.01): C 82.34, H 9.31, N 8.35; Found: C 82.34, H 9.31, N 8.35.

## 2.4. Synthesis of trinuclear ligand C

Compound **B** (1.5 g, 2.2 mmol) and acenaphthenequinone (0.18 g, 1 mmol) were dissolved in 10 mL of xylene and stirred at 100 °C until it becomes a clear solution. Acetic acid (100 µL) was added, and sealed solution was stirred for 5 days. It was purified by auto-column using hexane and ethyl acetate as solvents. The product was then isolated and dried under vacuum to give 0.5 g (33%) trinuclear ligand as an orange powder. IR (KBr): v 1640 cm<sup>-1</sup> (C=N). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 0.873 [d, 12H, CH(CH<sub>3</sub>)(CH<sub>3</sub>)], 0.90 [d, 12H, CH(CH<sub>3</sub>)(CH<sub>3</sub>)], 1.09 [d, 12H, CH(CH<sub>3</sub>)(CH<sub>3</sub>)], 1.11 [d, 12H, CH(CH<sub>3</sub>)(CH<sub>3</sub>)], 1.14 [d, 12H, CH(CH<sub>3</sub>)(CH<sub>3</sub>)], 1.16 [d, 12H, CH(CH<sub>3</sub>)(CH<sub>3</sub>)], 2.21 [s, 6H, C(NAr)CH<sub>3</sub>], 2.25 [s, 6H, C(NAr)CH<sub>3</sub>], 2.71 [sept, 4H, CH(CH<sub>3</sub>)(CH<sub>3</sub>)], 2.73 [sept, 4H, CH(CH<sub>3</sub>)(CH<sub>3</sub>)], 2.96 [sept, 4H, CH(CH<sub>3</sub>)(CH<sub>3</sub>)], 4.07 (s, 2H, CH<sub>2</sub>), 6.73 (m, 4H, CHAr), 7.00 (m, 4H, CHAr), 7.08 (m, 6H, CHAr), 7.87 (m, 2H, CHAr), 8.44 (m, 4H, CHAr) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 16.16, 21.92, 22.10, 22.18, 22.31, 22.47, 27.24, 27.54, 40.42, 121.16, 121.96, 122.39, 123.49, 127.77, 128.58, 130.06, 134.19, 134.60, 134.74, 135.60, 135.82, 143.21, 144.35, 145.43, 154.03, 154.16, 160.06, 165.92, 166.19, 178.47. Anal. Calcd. for C104H126N8 (1487.01): C 83.94, H 8.53, N 7.53; Found: C 83.94, H 8.53, N 7.53.

# 2.5. Synthesis of complexes

#### 2.5.1. Monometallic Ni(II) complex D

Trinuclear ligand **C** (0.15 g, 0.1 mmol) and (DME)NiBr<sub>2</sub> (0.03 g, 0.1 mmol) (1:1) were stirred overnight in  $CH_2Cl_2$  (20 mL) at room temperature. The resulting mixture was filtered and the solvent was removed under reduced pressure. The complex precipitated in ether was filtered, washed and dried under vacuum at 60 °C. The brown powder was obtained in more than 90% yield. The NMR spectroscopic analysis was not informative due to the paramagnetic









Scheme 1. Synthesis of trinuclear ligand and mono-, bi- and tri-metallic complexes: (i) MeOH/formic acid; (ii) 4,4'-methylenebis(2,6-diisopropylaniline), xylene/acetic acid; (iii) acenaphthenequinone, xylene/acetic acid; (iv) (DME)NiBr<sub>2</sub>/CH<sub>2</sub>Cl<sub>2</sub>; (v) FeCl<sub>2</sub>/THF; (vi) (DME)NiBr<sub>2</sub>/CH<sub>2</sub>Cl<sub>2</sub>.

nature of the metal complexes. Anal. Calcd. for  $C_{104}H_{126}Br_2N_8Ni$ : C, 73.19; H, 7.44; N, 6.57; Ni, 3.44. Found: C, 73.81; H, 7.54; N, 6.45. Ni, 3.47 wt% (ICP-AES). IR (KBr):  $\nu$  1641, 1615 cm<sup>-1</sup> (C=N).

# 2.5.2. Bimetallic Fe(II) complex E

Trinuclear ligand **C** (0.3 g, 0.2 mmol) and ferrous chloride tetrahydrate (0.08 g, 0.4 mmol) were stirred overnight with THF (20 mL) at room temperature. The precipitated complex in ether was washed, filtered and dried under vacuum at 60 °C. The dark green powder was yielded above 90%. The NMR spectroscopic analysis was not informative due to the paramagnetic nature of the metal complexes. Anal. Calcd. for  $C_{104}H_{126}Cl_4Fe_2N_8$ : C, 71.72; H,

7.29; N, 6.43; Fe, 6.41. Found: C, 71.81; H, 7.45; N, 6.41. Fe, 6.52 wt% (ICP-AES). IR (KBr): ν 1641, 1617 cm<sup>-1</sup> (C=N).

#### 2.5.3. Trinuclear trimetallic 2Fe(II)/Ni(II) complex F

The complex **E** (0.2 g, 0.11 mmol) and (DME)NiBr<sub>2</sub> (0.04 g, 0.13 mmol) were added together in a Schlenk flask containing 20 mL of CH<sub>2</sub>Cl<sub>2</sub> at 30 °C and stirred for 24 h to ensure complete metallation. The complex precipitated in diethyether was filtered and washed with ether and dried in vacuum to get dark green powder (yield > 90%). The NMR spectroscopic analysis was not informative due to the paramagnetic nature of the metal complexes. Anal. Calcd. for C<sub>104</sub>H<sub>126</sub>Br<sub>2</sub>Cl<sub>4</sub>Fe<sub>2</sub>N<sub>8</sub>Ni: C, 63.72; H, 6.48;

N, 5.72; Fe, 5.70; Ni, 2.99. Found: C, 64.34; H, 6.45; N, 5.41. Ni, 2.86; Fe, 5.77 wt% (ICP-AES). IR (KBr): ν 1615 cm<sup>-1</sup> (C=N).

## 2.6. Polymerization procedure

Ethylene polymerizations were performed in a 250 mL roundbottom flask equipped with a magnetic stirrer and a thermometer. The catalyst was added to the flask and the reactor was charged with toluene (80 mL) by using syringe. The reactor was immersed in a constant temperature bath previously set to desired temperature. When the reactor temperature had been equilibrated to the bath temperature, ethylene was introduced into the reactor after removing nitrogen gas under vacuum. When no more absorption of ethylene into toluene was observed, the cocatalyst was injected into the reactor and then the polymerization was started. Polymerization rate was determined at every 0.01 s from the rate of consumption, measured by a hotwire flowmeter (model 5850 D from Brooks Instrument Div.) connected to a personal computer through an A/D converter. Polymerization was quenched by the addition of methanol containing HCl (5 vol.%) and then the unreacted monomer was vented. The polymer was washed with an excess amount of methanol and dried in vacuum at 50 °C. To make a worthy comparison of the effect of metal selection on catalytic activity and polymer structure and properties, all data were collected under similar conditions.

# 3. Results and discussion

## 3.1. Synthesis and characterization of the ligands and complexes

Trinuclear NNN-NN-NNN ligand was synthesized by a three step condensation reaction according to Scheme 1. Acenaphthenequinone and 2,6-diacetyl pyridine were utilized to provide bidentate and tridentate coordination vacancies, respectively. 4,4'-Methylenebis(2,6-diisopropylaniline) and 2,6-diisopropylaniline provide symmetrical environment for Ni center and unsymmetrical one for Fe centers. The methylene group in 4,4'-methylenebis(2,6diisopropylaniline) serves as a bridge between the tridentate and bidentate nuclei. Compound A (Scheme 1) was synthesized according to the reported procedure [23]. After column purification, compound A was treated with 4,4'-methylenebis(2,6diisopropylaniline) at 110°C using a little glacial acetic acid as promoter in a minimal solvent to give the expected unsymmetrical compound **B**. Trinuclear ligand **C** was prepared by the conventional Schiff-base condensation of 2.2 equiv. of compound **B** with acenaphthenequinone. Trinuclear ligand C was purified by column chromatography [2% ethyl acetate/n-hexane-alumina]. This trinuclear ligand was characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR and IR spectroscopies and elemental analysis.

Taking a glance at the structure of the trinuclear ligand C for the preparation of metal complexes with different metals, one of the most ambiguous problems related with the structure of the complexes can be realized. In fact late transition metal catalysts, such as bidentate  $(N_2) \alpha$ -diimine nickel and palladium catalyst developed by Brookhart [8] and tridentate (N<sub>3</sub>) pyridine diimine iron and cobalt catalysts by Brookhart and Gibson [24,25], have received a lot of attention because they can produce novel polyolefins with unique properties. When activated with MAO for the ethylene polymerizations,  $\alpha$ -diimine nickel and palladium catalyst yield highly branched polyethylene (PE) and pyridine diimine iron and cobalt complexes produce highly linear PE. However, tridentate pyridine diimine nickel complexes have been successfully prepared and utilized them for the vinyl polymerization of norbornene [26], and bidentate  $\alpha$ -diimine cobalt complexes have also been prepared for ethylene polymerization to give a moderate activity [27]. As a result the trinuclear ligand C bearing both  $N_2 \alpha$ -diimine and  $N_3$  pyridine diimine might give a mixture of complexes as illustrated in Fig. 1. Fortunately, as reported by Bianchini and coworkers [28] and Wang and coworkers [29], when the FeCl<sub>2</sub> was coordinated to a ligand **C**, the pyridine diimine was predominantly favored to be coordinated. In order to investigate the selectivity of the coordination of Fe and Ni, preliminary tests have been performed by using homonuclear N<sub>2</sub>  $\alpha$ -diimine [(0,0'-*i*Pr<sub>2</sub>Ar-DAB)(Ar-DAB = 1,4bis(aryl)-2,3-dimethyl-1,4-diaza-1,3-butadiene)] and N<sub>3</sub> pyridine diimine  $[(2-iPrC_6H_4N=C(Me))_2C_5H_3N]$  ligands. The reaction of 0.9 equiv. of FeCl<sub>2</sub> with the mixture of 1 equiv. of N<sub>2</sub>  $\alpha$ -diimine and 1 equiv. of N<sub>3</sub> pyridine diimine ligand in THF gave only N<sub>3</sub> pyridine diimine Co(II) complex. In a similar reaction by using 0.9 equiv. of (DME)NiBr<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub>, only N<sub>2</sub>  $\alpha$ -diimine Ni(II) complex was obtained as a pure product. These results indicate that in the presence of both pyridine diimine and  $\alpha$ -diimine ligands, iron has a high selectivity to the tridentate ligand and nickel to the bidentate ligand to give a desired product indicated in Fig. 1. Although these simple tests cannot be direct evidences for the formation of desired complex F (Scheme 1), other results such as element analysis, ICP-AES, IR spectroscopy, and ethylene polymerizations further support the selectivity of Ni to N<sub>2</sub> ligand and Fe to N<sub>3</sub> ligand at least in the preparation conditions employed in this study.

Thus, the complexes were synthesized by the addition of trinuclear ligand to appropriate metal salt [FeCl<sub>2</sub> or (DME)NiBr<sub>2</sub>] according to Scheme 1. Two equivalents of FeCl<sub>2</sub> were strictly used for the preferential coordination to tridentate ligand to form the complex E. To the homobimetallic Fe complex, one equivalent of (DME)NiBr<sub>2</sub> was added to obtain the final trinuclear complex F. It may be noted that both metallations were carried out separately. For comparison, mononuclear Ni(II) complex **D** was also prepared by treating the trinuclear ligand with one equivalent of (DME)NiBr<sub>2</sub>. Various efforts to achieve metal complexes that are suitable for crystallography were unsuccessful possibly due to the steric bulk of the complexes; however, the formation of the desired complexes was traced by element analysis and ICP-AES. In addition, the extremely low solubility of the metallic complexes with the NNN-NN-NNN ligands in either hydrocarbon or chlorinated solvents precluded their NMR characterization. Heating the solution to increase the solubility of the complexes resulted in forming some decomposed products that cannot be suitably assigned. The IR spectra of the metal complexes display medium absorption bands in the range  $\nu \sim 1615 \text{ cm}^{-1}$ , which is the absorption region for  $\nu$ (C=N). Bands assigned to the free ligand C=N stretching vibrations were observed in the range  $\nu \sim 1640 \,\mathrm{cm}^{-1}$ . In general, the bands in the complexes are shifted to lower wavenumbers which is a criterion of the coordination of the ligands to the Ni(II) and/or Fe(II) ion. The IR spectra of monometallic Ni(II) complex **D** and bimetallic Fe(II) complex **E** showed two  $\nu$ (C=N) bands. For example, compared with one single  $\nu$ (C=N) band at 1640 cm<sup>-1</sup> assigned to free imine group of ligand **C**, the medium absorption bands at  $1615 \text{ cm}^{-1}$  (for **D**) and  $1617 \text{ cm}^{-1}$  (for **E**) were assigned for the Ni(II) coordinated  $\alpha$ -diimine groups and the Fe(II) coordinated pyridine imine groups, respectively, and more intense ones at 1641 cm<sup>-1</sup> for the free pyridine imine and  $\alpha$ -diimine groups. This indicates that not all of the nitrogen atoms of the potentially NNN-NN-NNN ligand involved in the coordination to the nickel or iron center. The element analysis data and nickel and iron contents measured by ICP confirm that only one equivalent nickel or iron coordinates to each ligand to form complex **D** and **E**.

#### 3.2. UV-vis spectroscopic studies

The UV–vis spectroscopic investigation of modified  $\alpha$ -diimine Ni(II) catalyst/MAO systems has been recently reported [13,30]. This technique was found to be very effective for the observa-



Fig. 1. Possible coordinations of nickel and iron to the ligand comprised of bidentate (N<sub>2</sub>)  $\alpha$ -diimine and tridentate (N<sub>3</sub>) pyridine diimine and desired trinuclear Fe(II)/Ni(II) complex.

tion of the successive elementary steps leading to the formation of active species in metal (Fe or Ni) complex/MAO system [35]. Fig. 2 shows the UV-vis spectra of Ni(II), bimetallic Fe(II) and trimetallic Fe(II)/Ni(II) complexes activated by MAO at [A1]/[M] = 300 (M = Fe and/or Ni) at 30 °C. Since all the complexes show limited solubility in toluene, the UV investigation was carried out in CH<sub>2</sub>Cl<sub>2</sub> at nitrogen atmosphere. The addition of MAO to the CH<sub>2</sub>Cl<sub>2</sub> solution of the Ni(II) complex **D** results in the formation of three new absorption peaks (Fig. 2(a)). It was reported that the active species could exhibit absorptions at 523 and 565 nm, whereas the species corresponding to the band at 710 nm are likely inactive for polymerization [13]. The appearance of a UV absorption band centered at 624 nm for Fe(II) complex E corresponds to the active site formed by Fe(II) in the presence of MAO. Further the UV spectrum of the Fe-Ni trimetallic catalyst F shows both the absorption bands corresponding to active species of Ni and Fe, indicating the existence of Fe and Ni in the complex. It may be noted from Fig. 2(c) that the absorption peak for usual deactivation species of Ni complex around 700 nm is not appeared for complex F [13]. This is akin to the polymerization results (vide infra). The activity of the trimetallic catalyst is much higher than Ni and bimetallic Fe catalysts.

# 3.3. Polymerization of ethylene

Homogeneous catalysis is one of the most rapidly developing areas of synthetic organic chemistry. There are strong incentives



**Fig. 2.** UV-vis absorption spectra of reaction mixtures of precursors (a) Ni based catalyst (D), (b) Fe based bimetallic catalyst (E), and (c) Fe and Ni based trimetallic catalyst (F) with MAO ([AI]/[M] = 300; M = Fe and/or Ni) in  $CH_2CI_2$  at 30 °C.

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Selected resul	s of ethylene	polymerization <sup>a</sup>

Entry	Catalyst	Cocatalyst ([Al/M]) <sup>b</sup>	$T_{\rm p}~(^{\circ}{\rm C})$	Activity <sup>c</sup> $(10^{-4})$	Yield (g)	$M_n{}^{\rm d}(10^{-4})$	PDI <sup>d</sup>	$T_{\rm m}^{\rm e}(^{\circ}{\rm C})$	Branches/1000 C <sup>f</sup>
1	D	MAO(300)	30	1.2	0.6	36.3	3.5	n.d. <sup>g</sup>	103
2	D	EASC(300)	30	17.5	2.8	56.2	2.7	n.d.	92
3	E	MAO(300)	30	24.1	3.8	205.7	4.9	133.3	3
4	E	EASC(300)	30	0.4	0.2	249.2	5.7	134.2	3
5	F	MAO(300)	30	28.3	4.2	1.6	73.2	130.1	17
6	F	MAO(300)	10	14.6	2.7	5.3	46.4	133.5	10
7	F	MAO(300)	50	16.2	2.9	1.5	54.9	131.5	25
8	F	MAO(300)	70	11.5	1.8	1.1	19.6	128.9	59
9	F	EASC(300)	30	8.6	1.5	65.0	3.0	n.d	134
10	F	TEA(300)	30	9.9	1.3	0.7	144.0	130.8	33
11	F	MAO(50)	30	4.6	1.0	38.3	6.0	132.7	32
12	F	MAO(100)	30	13.9	2.1	45.5	6.3	134.3	30
13	F	MAO(500)	30	19.5	3.1	1.6	70.2	132.2	25

<sup>a</sup> Polymerization conditions: catalyst = 2 (mol, toluene = 80 mL, time = 30 min and  $P_{C_2H_4}$  = 1.3 bar.

<sup>b</sup> Al=EASC (ethylaluminum sesquichloride), MAO (methylaluminoxane) or TEA (triethylaluminum); M = Ni for complex **D**, Fe for **E** and (Fe + Ni) for **F**.

<sup>c</sup> Average rate of polymerization over the period of polymerization.

<sup>d</sup> Polydispersity index determined by gel permeation chromatography.

<sup>e</sup> Determined by differential scanning calorimetry (heating rate: 10 °C/min).

<sup>f</sup> Total degree of branching determined by <sup>1</sup>H NMR spectroscopy.

<sup>g</sup> Not detected.

to achieve environmentally friendly, high-economy processes and much research is performed to develop more selective catalysts. The most selective catalysts have been found in nature. The elucidation of the structure of the active sites of many enzymes and the nature of the key intermediates in enzyme catalyzed processes has both contributed to dramatic progress in recent years. It has been shown that a number of these active sites contain two metal ions, that operate cooperatively [31]. As a result, dinuclear complexes containing two metals in close proximity have become the subject of extensive investigations in order to design new trimetallic catalysts [32]. In order to investigate the scope of homo- and hetero-nuclear multimetallic enchainment cooperative effects in ethylene polymerization, the rate of polymerization of purified ethylene was followed using Fe(II) and Ni(II) complexes, in a dry toluene between 10 and 70 °C in combination with various cocatalvsts like MAO, EASC and TEA. A partial pressure of 1.3 bar was maintained by supply of ethylene, the consumption being measured every 0.1 s. In this way the characteristic rate curves can be followed consisting of rate growth and rate decay. Fig. 3 shows rate



**Fig. 3.** Rate of polymerization ( $R_p$ ) versus time plots of ethylene polymerizations catalyzed by (a) complex D, (b) complex E, and (c) complex F, in combination with MAO ([MAO]/[M] = 300; M = Fe and/or Ni). Polymerzation conditions: catalyst amount = 2  $\mu$ mol, toluene solvent = 80 mL,  $P_{C_2H_4} = 1.3$  bar and temperature = 30 °C.

curves obtained for Fe and Co catalyst systems using 0.6 mmol MAO, 2  $\mu$ mol catalyst. The results of polymerization are also summarized in Table 1.

There is a gradual increase in the rate of polymerization  $(R_p)$  in the build-up period where the  $R_p$  increases rapidly to a maximum until the almost stationary state is reached directly. Comparing the activity as the average rate of polymerization  $(R_{p,avg})$  over a polymerization period, homonuclear bimetallic Fe(II) catalyst E and heteronuclear trimetallic Fe(II)/Ni(II) catalyst F show significantly greater activities,  $R_{p,avg} = 24.1 \times 10^4 \text{ g-PE/mol-Fe}$  h bar (Entry 3 in Table 1) and  $28.3 \times 10^4$  g-PE/mol-(Fe + Ni) h bar (Entry 5), respectively, than monometallic Ni(II) catalyst **D**  $(1.2 \times 10^4 \text{ g-}$ PE/mol-Nihbar, Entry 1). These results show the cooperative nuclearity effect, probably minimizing monometallic "back coordination" of the last inserted monomer to the parent cationic metal centers [3]. Taking a careful look at the  $R_p$ 's obtained by using **D**-**F**, the activity of F is similar to the sum of the activity of D and E. The formation of active and inactive metal sites was traced by UV-vis spectral analysis (vide supra). Catalyst D and E yield high MW polymers, the number average molecular weight  $(M_n)$  of 36,300 and 205,700, respectively, with the polydispersity index (PDI) of 3.5 and 4.9, respectively. On the other hand trinuclear trimetallic Fe(II)/Ni(II) catalyst **F** yields low MW polymer ( $M_n$  = 1600) with a very broad polydispersity (PDI = 73.2). This is another evidence of the cooperative effect of the trimetallic complexes in an adverse direction. Even though it is too premature to conclude the effect on the MW, the sharply decreased MW value indicates that the cooperative effects provided by the two different metals crowded



**Fig. 4.** The complicated cooperations among three metals in a hetero-trimetallic catalyst, in which the three metals perform their own tasks influenced by the bulky ligands, incoming monomers and propagating polymer chains.

with bulky substituents on the aryl rings and by neighboring propagating chains (Fig. 4) play a significant role in controlling the rate of propagation and chain termination, thus influencing both activity and MW of the polymer. In addition each metal has its own characteristic active sites with different  $\beta$ -hydrogen transfer and chain transfer to Al, resulting in the formation of polymer with low MW and broad polydispersity. The low MW comes from accelerated chain terminations and the broad polydispersity from the fact that each metal has its own kinetics.

The cooperation of two metals in a heterotrimetallic system is an attractive approach because the each metal can perform different tasks. Recent advances in olefin polymerization catalysis using Fe are mainly based on developments around the bis(imino)pyridine systems [11]. This family of catalysts has attracted great interest, both in academia and in industry, since the Fe catalyst based on bis(imino)pyridine ligands with bulky aryl substituents is one of the most active examples. The catalysts show exceptionally high activities for ethylene polymerization, producing strictly linear, high MW polymer [11]. The similar behavior was observed for the bimetallic Fe catalyst (see Entry 3 in Table 1). The steric bulk provided by the substituents on the imino nitrogen donors plays a pivotal role in preventing the formation of bis-chelate complexes and controlling the rates of propagation and chain termination, thus influencing both activity and molecular weight of the polymer. The family of cationic α-diimine Ni(II) catalyst has also continued to attract much interest. The steric and electronic properties of the  $\alpha$ -diimine ligand can be readily adjusted by modifying the imino carbon and nitrogen substituents, and hence a large number of structural variations have been reported in the academic and patent literature [11]. The Ni(II)  $\alpha$ -diimine catalysts bearing isopropyl substituents on the aryl rings yield highly branched PE in the ethylene homopolymerizations. The similar behavior was observed for the monometallic Ni(II) catalyst (see Entry 1 in Table 1). The formation of highly branched polymer is the result of a series of B-hydrogen elimination/reinsertion reactions via the β-agostic cationic alkyl intermediate [8,11]. Considering these, it is worthy investigating the ethylene polymerization behavior of the complex **F** bearing Ni(II)  $\alpha$ -diimine complex as well as two Fe(II) bis(imino)pyridine complexes in some more detail.

Ethylene polymerizations were carried out with trinuclear complex **F** at temperatures between 10 and 70 °C in combination with various cocatalysts such as MAO, EASC and TEA. The results of polymerization are also summarized in Table 1. The polymerizations were carried out at very low catalyst concentrations; say 2 µmol of complex F, in 80 mL toluene to avoid the occurrence of mass transport limitations. The active catalysts are generated in situ in toluene by the addition of cocatalyst to the complex solution in the presence of ethylene. As the polymerization temperature increases, the degree of branching increases and the polymer MW and melting point decreases along with the decrease in activity as expected (Entries 5-8, Table 1), due to the deactivation of active species at high temperature [33]. The catalyst shows low activity at low temperature. At low temperature the catalytic structure might have blocked the bulky MAO accessing to the metal centers. As the temperature increases, the closed structures are slowly opened for the easy access of the cocatalyst. Even at high temperature, say 70 °C, the trimetallic catalyst showed considerable activity of  $(11.5 \times 10^{-4} \text{ g-PE/mol-(Fe + Ni)} \text{ h bar, Entry 8})$  and this may be due to the cooperative effect of adjacent metal centers present in the complex F. Note that its monometallic Fe and Ni(II) counterparts show only limited activity at this conditions [8,9,11,16].

The nature of alkylaluminum cocatalyst has an apparent effect on the catalytic activity and product distribution [34]. Chlorinated alkylaluminum as a coactivator has been reported to be more effective for homogeneous Ni(II)  $\alpha$ -diimine complexes than the most commonly used MAO (compare Entry

1 with 2 in Table 1) [13,15], while Fe(II) bis(imino)pyridine complex is more active with MAO than with EASC (compare Entry 3 with 4). The catalytic activity of **F**/EASC system shows much less activity  $(8.6 \times 10^4 \text{ g-PE/mol-(Fe+Ni)} \text{ h bar, Entry 9})$ than F/MAO (28.3 × 10<sup>4</sup> g-PE/mol-(Fe + Ni) h bar, Entry 5). Together with these results, considering the former system yields highly branched PE and the latter yields PE with moderate branches (17 branches/1000C), the EASC activates predominantly Ni centers and the MAO activates both Ni and Fe centers. In addition, the activity  $(9.9 \times 10^4 \text{ g-PE/mol-(Fe + Ni)})$  h bar, Entry 10) and the degree of branching (33 branches/1000 C) achieved by TEA demonstrate the TEA also activate both metal centers. Out of various concentrations of MAO used, the polymerization activity increases from  $4.6 \times 10^4$  g-PE/mol-(Fe + Ni) h bar (Entry 11) at 50 equiv. of MAO to  $28.3 \times 10^4$  g-PE/mol-(Fe + Ni) h bar (Entry 5) at 300 equiv. and then decreases along with higher amount of MAO (Entry 13). The amount of MAO to achieve the maximum activity is much lower than that needed in conventional metallocene catalyst systems [5-7,33], in which a gross excess (>10,000) of MAO is frequently needed.

Similar to the conventional metallocene and Ziegler-Natta catalysts [5–7], the MW was found to decrease as MAO concentration increases due to the chain transfer to MAO. It is interesting to note that at low MAO concentration, say up to [MAO]/[Fe+Ni] = 100, the polydispersity is found to be narrow (PDI = 6.0-6.3 (Entries 11 and 12)); however, at high MAO concentrations, the PDI values increase above 70. The polydispersity is found to be very high for the trimetallic Fe(II)/Ni(II) catalyst when compared to monometallic Ni(II) or homonuclear bimetallic Fe(II) analogues. For example, while Ni(II) and Fe(II) catalysts produce PE with PDI of 3.5 and 4.9, respectively (Entries 1 and 3), the trimetallic catalyst produces PE with very broad polydispersity system (PDI = 73.2 (Entry 5)) at the same conditions. The maximum PDI of 144 is recorded when TEA is used as a cocatalyst (Entry 10). These results demonstrate that the polydispersity is tunable by a suitable choice of heteronuclear multimetallic complexes together with the suitable selection of coactivators. The broad polydispersity of PE is favorable for the processibility, such as the high shear viscosity and low melt extensional viscosity of the product. The PE obtained by the trimetallic Fe(II)/Ni(II) catalyst is moderately branched, predominantly influenced by Ni(II) center, since the Fe(II) catalyst gives only highly linear PE. This observation was supported by DSC and NMR measurements. The  $T_{\rm m}$  values were not so affected by the Ni(II) catalyst, for example, T<sub>m</sub> value shifted from 133 to 130 for E and F respectively (Entries 3 and 5 in Table 1).

## 4. Conclusions

A new trinuclear ligand was synthesized successfully and utilized to coordinate late transition metals leading to a heterotrimetallic system. This Fe(II)/Ni(II) based trimetallic complexes were effective catalyst precursors for the polymerization of ethylene using various cocatalysts, with activities exceeding 10<sup>5</sup> g-PE/mol-metal h bar. Formation of active species resulting from the activation of Fe and Ni(II) complexes in the presence of MAO were studied by UV-vis spectroscopy. The trimetallic complexes showed high catalytic activity and a long life time, especially at high temperature, when compared to its bimetallic Fe(II) and monometallic Ni(II) analogues due to The cooperative effect of the heteronuclear Fe(II)/Ni(II) complex yielded PEs of moderate MW and of very broad polydispersity that were also influenced by the polymerization parameters such as the type and the amount of cocatalyst and temperature. The degree of branching was tunable from highly linear to highly branched by the type of catalyst, monometallic, homonuclear bimetallic and heteronuclear trimetallic, and polymerization parameters.

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