

Unsymmetric bimetal(II) complexes: Synthesis, structures and catalytic behaviors toward ethylene

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Abstract

A series of unsymmetric bimetal(II) (Fe, Co and Ni) complexes ligated by 2-methyl-2,4-bis(6-iminopyridin-2-yl)-1*H*-1,5-benzodiazepines were synthesized and characterized by IR spectra and elemental analysis, while a representative nickel(II) complex (**5a**) was determined by single-crystal X-ray crystallography. These iron(II) complexes were found to exhibit good activities for ethylene oligomerization and polymerization in the presence of MMAO and afforded α -olefins in high selectivity, and the composition of oligomers followed the Schluz–Flory distribution. The nickel(II) complexes mainly dimerize ethylene with considerable activity. The influences of coordinative ligands and reaction parameters were fully investigated on the catalytic activity and properties of these complexes. © 2007 Elsevier B.V. All rights reserved.

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1. Introduction

α -Olefins are major industrial reactants and extensively used in the preparation of detergents, lubricants, plasticizers, oil field chemicals as well as monomers for copolymerization. The increasing demand of α -olefin industry has annually been growing around 5%. Therefore there is an increasing interest of developing new catalyst and process to produce α -olefins in both academic and industrial consideration. Recently, the investigation for ethylene polymerization and oligomerization with late transition metals has mushroomed over the past decade [1], which was initiated by the discovery of highly active catalysts of diimino Ni(II) and Pd(II) [2] as well as 2,6-bis(imino)pyridinyl Fe(II) and Co(II) precursors [3]. The products by the iron(II) and cobalt(II) catalysts varied from polyethylene to oligomers [4] through tuning the steric and electronic properties of the ligands, thereafter alternative catalysts'

models have been relied on designing new ligands [5] and recently effective ones such as 2-imino-1,10-phenanthrolines [6], 2-benzimidazolylpyridines [7] and 2-quinoxalinylnyl-6-iminopyridines [8] in our group. At the same time, the nickel complexes as homogeneous catalysts have also drawn many attentions toward ethylene activation with the complexes bearing bidentate [9] and tridentate ligands [6b,7a,10].

The use of compartmental ligands with multi-binding sites imposing close special confinement on two metal centers has drawn much attention [11]. Within the alkene polymerization/oligomerization, there are several examples of bimetallic compartmentalized LM₂ catalytic systems incorporating early transition metals [12], meanwhile there is a few of reports on the late transition metal [13] and heterobimetallic complexes [14]. Moreover, these ligands usually provided same coordination pockets for bimetallic catalytic systems. On the base of bis(imino)pyridyl metal (iron or cobalt) complexes [3] and the extensive works of monoiminopyridyl metal complexes [15], the bimetallic iron(II) and cobalt(II) complexes bearing 2-methyl-2,

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4-bis(6-iminopyridin-2-yl)-1*H*-1,5-benzodiazepines were recently synthesized and provided two different coordination environments for two active sites [16]. The iron and cobalt complexes showed good catalytic activity for ethylene oligomerization and polymerization with high α -olefin selectivity. Extensively more analogues of iron and cobalt complexes were prepared and investigated for the scope of ethylene reactivity with comparing the influences of the ligands' environments. Moreover, the bimetallic nickel(II) complexes were also prepared and could dimerize ethylene to butenes in the presence of diethylaluminum chloride (Et_2AlCl). Herein their results are going reported with discussions.

2. Results and discussion

2.1. Synthesis and characterization of the ligands and complexes

The ligands and their iron and cobalt complexes were efficiently synthesized according to our reported procedure [16]. The binickel complexes were easily formed in high yield by the reaction of nickel dichloride with the ligands (Scheme 1). All the organic compounds were characterized by IR spectra, ^1H NMR, ^{13}C NMR and elemental analysis while the complexes were characterized by elemental analysis and FT-IR spectra. In the IR spectra of bimetallic complexes, the $\text{C}=\text{N}$ stretching frequencies appeared in the range of $1614\text{--}1623\text{ cm}^{-1}$. The wave number shifted to lower and the peak intensity were greatly induced with comparing the corresponding ligands, indicating the coordination interaction between all the imino nitrogen atoms

and the metal cation. According to the elemental analysis data, nickel complexes were in accordant with the formula $\text{LNi}_2\text{Cl}_4 \cdot 2\text{H}_2\text{O}$. The unambiguous molecular structures of **1**, **4c** and **5a** were determined by X-ray diffraction analysis, and the molecular structure of **4c** was reported in our previous work [16].

2.2. Crystal structures

In the solid state of **1** (Fig. 1), two pyridine rings are linked by the seven-membered ring of the benzodiazepine. The $\text{N}(3)\text{--C}(10)$ bond length is $1.2772(2)\text{ \AA}$ with the typical character of $\text{C}=\text{N}$ double-bond. However, the $\text{N}(2)\text{--C}(8)$ ($1.4735(2)\text{ \AA}$) shows the character of $\text{C}\text{--}\text{N}$ single bond.

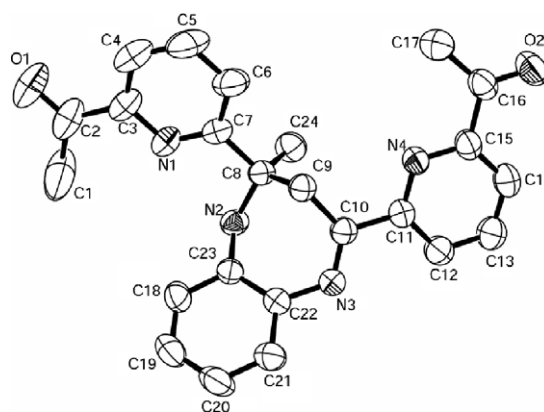
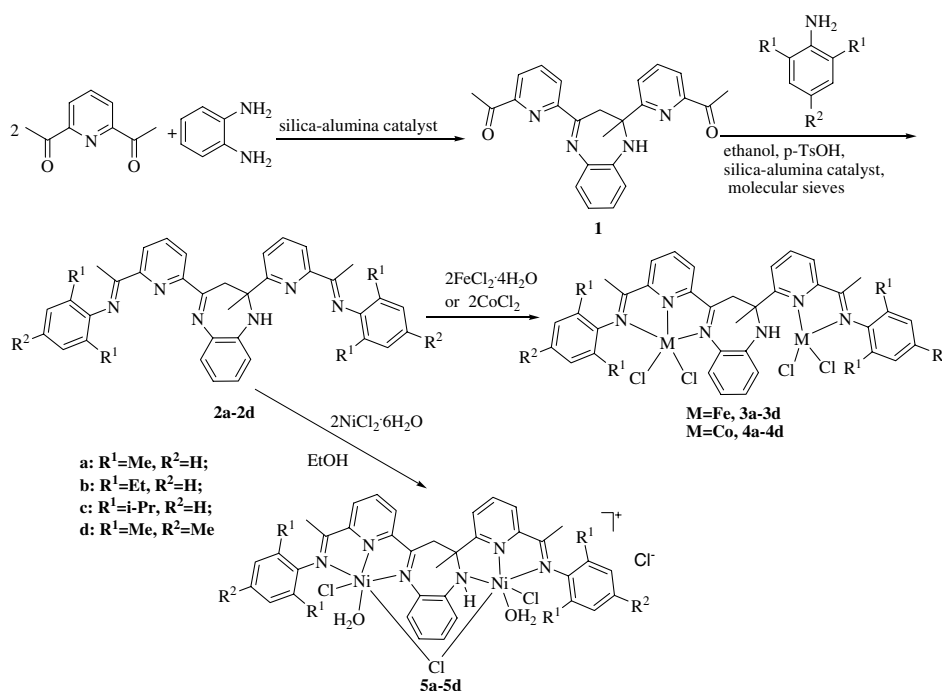


Fig. 1. Molecular structure of **1** with thermal ellipsoids at the 30% probability level. Hydrogen atoms have been omitted for clarity.



Scheme 1. Synthesis of ligands and bimetallic complexes.

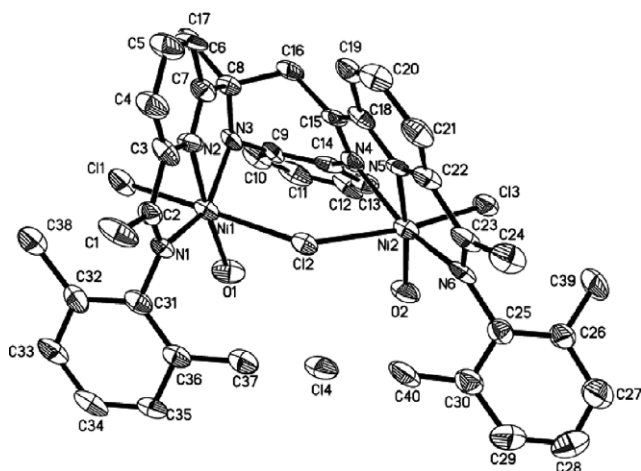


Fig. 2. Molecular structure of **5a** with thermal ellipsoids at the 30% probability. Hydrogen atoms and solvent have been omitted for clarity.

Single crystals of **5a**, grown by laying diethyl ether on a dichloromethane/methanol (v/v = 1:1) solution were used to determine its structure by single-crystal X-ray diffraction analysis (Fig. 2). Selected bond lengths and angles are reported in Table 1. The structure of **5a** consists of a binuclear asymmetric unit in which the ligand behaves as a bischelate and bridges two nickel(II) fragments. The geometry at each nickel center can be best described as distorted octahedral, in which each nickel atom is coordinated to three nitrogen atoms as one bridging chlorine atom connect the two metal centers. A chloride and an oxygen atom of water complete two independent six-coordinated geometries (Fig. 3). Some differences in the coordination sphere at each metal center are observed because of the unsymmetric ligand. The Ni1–N3 (benzodiazepine) bond length (2.126(1) Å) is longer about 0.09 Å than the Ni1–N2 (pyridine) bond length (2.034(1) Å) and about 0.14 Å than the Ni1–N1 (imino) bond length (1.990(1) Å), which can be due to the sp^3 N3. However, the difference is not as obvious as that in its cobalt analogues. The same trend as the cobalt complex **4c** for the M2–N bond lengths [16] is observed in **5a**. The Ni2–N5 (pyridine) bond (2.020(1) Å) is shorter by about 0.21 Å than the Ni2–N4 (benzodiazepine) bond (2.234(1) Å) and 0.24 Å than the Ni2–N6 (imino) bond (2.265(1) Å). The Ni1–Cl bond lengths (2.534(5) Å and 2.625(4) Å) are much longer than Ni2–Cl bond lengths (2.276(4) Å and 2.479(4) Å). As would be expected, the Ni–Cl (bridging) distance is longer than the Ni–Cl (terminal) distance for both Ni1 and Ni2. The imino N6–C23 bond length is 1.280(2) Å with the typical character of a C=N double bond. However, the N1–C2 (1.319(2) Å) and N4–C15 (1.347(2) Å) bond become longer compared with the free ligand. This could be explained as the distortion caused by the seven-membered ring and the bridging chloride. The phenyl rings link to the imino groups are oriented nearly perpendicular to the coordination plane with the dihedral angle of 76.5° (Ni1) and 79.9° (Ni2). A shorter intermetallic distance (4.717 Å) for Ni1⋯Ni2 is observed than the Co1⋯Co2

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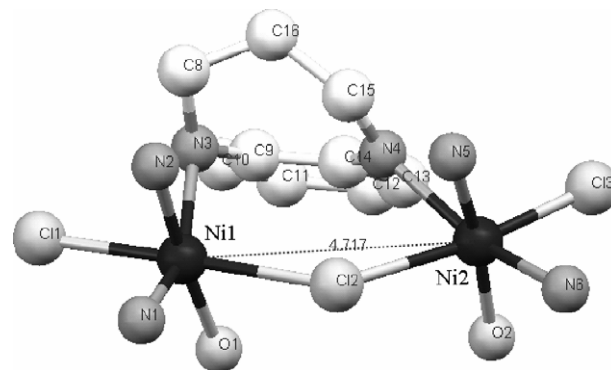


Fig. 3. Skeleton of complex **5a**. The Ni1⋯Ni2 distance is 4.717 Å.

Table 1
Selected bond lengths (Å) and angles (°) for complex **5a**

Bond lengths (Å)					
Ni1–N1	1.990(1)	Ni2–O2	2.026(1)	Ni2–Cl2	2.479(4)
Ni1–N2	2.034(1)	Ni2–N4	2.234(1)	N1–C2	1.319(2)
Ni1–N3	2.126(1)	Ni2–N5	2.020(1)	N3–C8	1.518(2)
Ni1–Cl1	2.534(5)	Ni2–N6	2.265(1)	N4–C15	1.347(2)
Ni1–Cl2	2.625(4)	Ni2–Cl3	2.276(4)	N6–C23	1.280(2)
Ni1–O1	2.074(1)				
Bond angles (°)					
N1–Ni1–N2	75.7(5)	N2–Ni1–O1	175.6(5)	N4–Ni2–Cl2	71.3(3)
N2–Ni1–N3	77.7(4)	N3–Ni1–O1	100.2(4)	N5–Ni2–Cl2	77.4(3)
N1–Ni1–N3	152.1(5)	O1–Ni1–Cl1	93.9(3)	N6–Ni2–Cl2	104.3(3)
N1–Ni1–Cl1	95.8(4)	O1–Ni1–Cl2	80.7(3)	Cl3–Ni2–Cl2	167.70(2)
N2–Ni1–Cl1	89.3(4)	N4–Ni2–N5	74.3(5)	N5–Ni2–O2	171.9(4)
N3–Ni1–Cl1	75.3(3)	N5–Ni2–N6	80.5(5)	O2–Ni2–N4	106.9(5)
N1–Ni1–Cl2	88.6(3)	N4–Ni2–N6	154.8(5)	O2–Ni2–N6	98.2(5)
N2–Ni1–Cl2	96.0(3)	N4–Ni2–Cl3	97.2(3)	O2–Ni2–Cl3	83.5(3)
N3–Ni1–Cl2	102.7(3)	N5–Ni2–Cl3	104.4(3)	O2–Ni2–Cl2	95.3(3)
Cl1–Ni1–Cl2	173.86(2)	N6–Ni2–Cl3	88.0(3)	Ni1–Cl2–Ni2	135.08(2)
N1–Ni1–O(1)	106.9(5)				

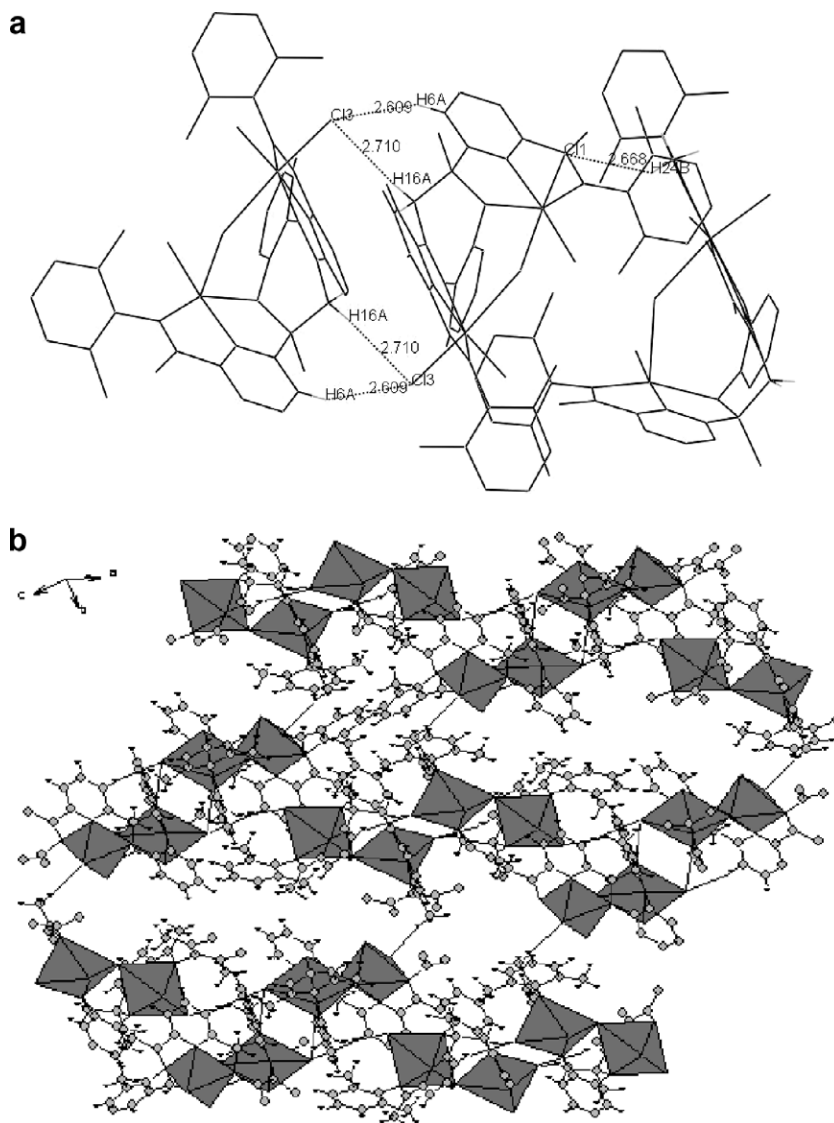


Fig. 4. (a) Hydrogen-bond interactions in complex **5a**. (b) Hydrogen-bond containing sheets in **5a**.

distance in **4c** [16], which could be attributed to the bridging chloride. However, it is longer than that in similar complexes [13m], which caused by the tension of the seven-membered ring.

In addition, extensive hydrogen bonds are formed between the chlorides and some hydrogen atoms of the ligand. As shown in Fig. 4a and Table 2, three kinds of hydrogen-bonding interaction exist in **5a**. The result is the creation of a polymeric hydrogen-bonded supermolecular sheet by self-assembly of the complex (Fig. 4b).

Table 2
Hydrogen-bond interactions in complex **5a**

D–H···A	D–H	H···A	D···A	∠DHA (°)
C6–H6A···Cl3	0.930	2.609	3.446	150.11
C16–H16A···Cl3	0.970	2.710	3.627	158.06
C24–H24B···Cl1	0.960	2.668	3.354	128.85

2.3. Catalytic behavior for ethylene

2.3.1. Ethylene oligomerization and polymerization of Fe(II) and Co(II) complexes

The iron complexes were studied for their catalytic activities with various alkylaluminums as co-catalysts. The catalytic system with modified methylaluminoxane (MMAO) showed best catalytic activity for ethylene oligomerization and polymerization with very high selectivity for α -olefin, and the detailed results of precursors **3a** and **3c** were reported [16]. Here, the effect of ligand environment on catalytic behavior was investigated in detail.

The variation of the R substituent on the imino-N of ligands resulted in great changes of the catalytic performance. In the presence of MMAO as cocatalyst, the biiron complexes **3a–d** showed high activities for ethylene reactivity (Table 3, entries 3–6). Based on these data, the oligomerization and the polymerization activities as well

Table 3
Results of ethylene oligomerization and polymerization by complexes **3a–d**, **4a–d**^a

Entry	Cat.	Cocat.	Al/Fe	<i>T</i> ^b (°C)	Oligomers			Polymer activity ^c	PE ^f (wt%)
					Activity ^c	<i>K</i>	% α -O ^d		
1	3a	MAO	1000	30	1.05	0.59	>99	2.62	71.4
2	3a	Et ₃ Al	1000	30	–	–	–	–	–
3	3a	MMAO	1000	30	6.17	0.71	>99	4.15	40.2
4	3b	MMAO	1000	30	1.36	0.61	>99	1.19	46.7
5	3c	MMAO	1000	30	0.46	0.59	>99	0.30	39.5
6	3d	MMAO	1000	30	2.98	0.62	>99	3.46	53.7
7	4a	MMAO	1000	30	1.83	0.64	>99	1.36	42.6
8	4b	MMAO	1000	30	0.81	0.57	>99	0.74	47.7
9	4c	MMAO	1000	30	0.73	0.53	>99	0.45	38.1
10	4d	MMAO	1000	30	2.02	0.57	>99	1.35	40.1
11	4a	MMAO	1500	60	7.38	0.80	>99	22.1	75.0
12	4a	MMAO	1500	80	1.58	0.74	>99	1.92	54.9
13	4b	MMAO	1500	60	1.06	0.68	>99	1.21	53.3
14	4c	MMAO	1500	60	2.13	0.40	>99	0.86	28.8
15	4d	MMAO	1500	50	1.81	0.56	>99	7.76	81.1
16	4d	MMAO	1500	60	1.16	0.60	>99	2.04	63.8

^a General conditions: cat: 2.5 μ mol; reaction time: 30 min; ethylene pressure: 30 atm; solvent: toluene (100 mL).

^b Reaction temperature.

^c Activity for oligomers: 10^6 g mol⁻¹(cat.) h⁻¹.

^d % α -olefin content determined by GC and GC-MS.

^e Activity for polyethylene wax: 10^6 g mol⁻¹(cat.) h⁻¹.

^f The percentage of polyethylene wax.

as the *K* value varied in the order of **3a** (with substituent of dimethyl) > **3b** (with diethyl) > **3c** (with diisopropyl). The introduction of the methyl group on *para*-position (**3d**) led to lower activity and higher percentage of polyethylene wax. The oligomer distribution was also influenced by the ligand environment which could be observed from Fig. 5. For the sterically bulkier catalyst **3c**, relatively smaller amount of longer-chain oligomers were produced with comparing its analogue **3a** and **3b**. In addition, the methyl substituted at the 4-position of the aryl ring also led to decreased productivity of longer-chain oligomers.

In similar manner, to compare the effect of the ligand environment on the catalytic activity, ethylene oligomeriza-

tion and polymerization with bimetallic cobalt analogues **4a–d**/MMAO system were investigated under the same conditions (Al/Co molar ratio of 1000 and 30 °C). Variation of the R¹ group at the *ortho*-positions of the imino-N aryl ring resulted in changes of the catalytic performance. It was observed that increase in steric hindrance of the R¹ group led to decreased activity and lower *K* value. Furthermore, the methyl group at 4-position of the aryl ring had slight influence on the catalytic activity with a decreased *K* value. The oligomer distribution obtained by **4a–d**/MMAO system was shown in Fig. 6. The catalytic performance of cobalt complex **4a** was greatly affected by the reaction temperature. Very high activity was

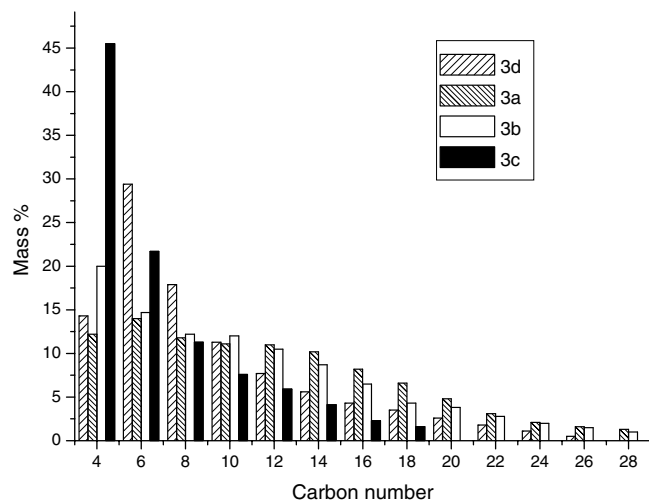


Fig. 5. Oligomers distribution obtained in entries 3–6 in Table 3.

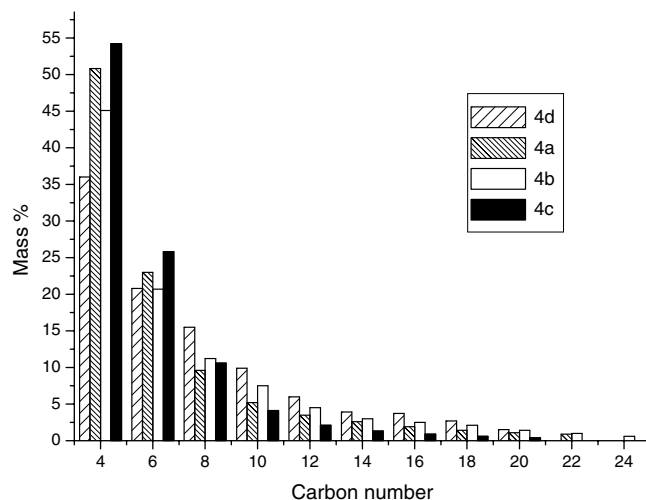


Fig. 6. Oligomers distribution obtained in entries 7–10 in Table 3.

Table 4
Ethylene oligomerization by **5a–d**^a

Entry	Complex	Cocat.	Al/Ni	T (°C)	Activity ^b	Oligomer distribution		
						C ₄ (%)	C ₆ (%)	α -C ₄ (%)
1	5a	Et ₃ Al	1000	25	1.86	95.5	4.5	93.2
2	5a	MAO	1000	25	0.25	64.9	35.1	99.2
3	5a	Et ₂ AlCl	100	25	0.69	100	0	95.3
4	5a	Et ₂ AlCl	200	25	3.56	95.2	4.8	97.1
5	5a	Et ₂ AlCl	300	25	7.55	95.9	4.1	97.5
6	5a	Et ₂ AlCl	400	25	6.65	97.0	3.0	97.2
7	5a	Et ₂ AlCl	500	25	5.73	96.5	3.5	95.2
8	5a	Et ₂ AlCl	300	40	6.91	96.7	3.3	97.7
9	5a	Et ₂ AlCl	300	60	3.77	96.4	3.6	96.5
10	5b	Et ₂ AlCl	300	25	9.12	96.8	3.2	94.1
11	5c	Et ₂ AlCl	300	25	3.37	94.7	5.3	92.7
12	5d	Et ₂ AlCl	300	25	5.62	95.8	4.2	92.5

^a General conditions: 5 μ mol cat.; 30 atm ethylene pressure; 100 mL toluene as solvent; 30 min; 25 °C.

^b Activity for oligomers: 10^5 g mol⁻¹(cat.) h⁻¹.

observed at 60 °C. However, further enhancement of reaction temperature to 80 °C resulted in sharply decrease of catalytic activity which can be attributed to the decomposition of the active species. The catalytic performance of complex **4b–d** was also investigated at 60 °C, and the catalytic activity was not greatly increased. It was noteworthy that complex **4d** showed higher polymerization activity and percentage of polyethylene wax at 50 °C.

2.3.2. Ethylene oligomerization of nickel(II) complexes

Various co-catalysts such as Et₂AlCl, Et₃Al and MAO were used to activate complex **5a** for ethylene reactivity at room temperature (Table 4). The nickel catalytic system containing Et₂AlCl showed the highest activity for ethylene oligomerization, and the butenes were observed as the major products. Therefore, further catalytic studies were performed using Et₂AlCl as cocatalyst, and the analyses of oligomers obtained were carried out by GC.

The effects of Al/Ni molar ratio on catalytic activities of ethylene oligomerization were investigated with complex **5a** in order to find the suitable molar ratio for better activity. When the Al/Ni ratio was enhanced from 100 to 500, the activity of **5a** was initially increased and then decreased with optimum catalytic activity with Al/Ni molar ratio of 300. In addition, the distribution of oligomers was not greatly affected by the Al/Ni molar ratio (Table 4, entries 3–7). The catalytic activity was also affected by the reaction temperature. Similar to the diiron complexes, the nickel complexes displayed lower activity at higher reaction temperature because of lower ethylene solubility and the possibility of less stability of nickel active species. Different substituents on the imino-N aryl ring could have some influences on their catalytic behavior. For the 2,6-dialkyl-substituted complexes **5a–c**, somewhat reduced catalytic activity and α -C₄ selectivity was observed for the sterically bulkier catalyst systems. This could be demonstrated by comparing the 2,6-diisopropyl-substituted **5c** with the 2,6-dimethyl-substituted **5a** or 2,6-diethyl-substituted **5b** (Table 4, entries 5, 10 and 11). The methyl group at 4-posi-

tion of the aryl ring led to lower catalytic activity and α -C₄ selectivity. However, ligand environments had no obvious influence on the distribution of oligomers.

3. Conclusion

A series of bimetallic iron(II), cobalt(II) and nickel(II) complexes had been synthesized and characterized. Upon treatment with MMAO, these iron(II) and cobalt(II) complexes showed high catalytic activity for ethylene oligomerization and polymerization with very high α -olefin selectivity. As an extensive work, the effect of ligand environment was investigated in detail, the increase in steric hindrance of the R¹ group led to decreased activity. The iron(II) complexes showed relative higher activity than their cobalt analogues. Furthermore, larger amount of longer-chain olefins were obtained with the iron complexes than those produced by cobalt analogues. In the presence of Et₂AlCl, the nickel(II) catalytic systems enable oligomerization of ethylene to dimerize mainly for butenes with high activity and α -C₄ selectivity. Complex **5b** with ethyl substituents in the *ortho*-positions of the aryl ring in the ligand backbone displayed the highest activity of 9.12×10^5 g mol⁻¹(cat.) h⁻¹.

4. Experimental

4.1. General considerations

All manipulations of air and/or moisture sensitive compounds were carried out under a nitrogen atmosphere using standard Schlenk techniques. NMR spectra were recorded on Bruker DMX-300 spectrometer, with TMS as the internal standard. IR spectra were recorded on a Perkin–Elmer FT-IR 2000 spectrometer using KBr disc in the range of 4000–400 cm⁻¹. Elemental analysis was performed on a Flash EA 1112 microanalyzer. GC analysis was performed with a VARIAN CP-3800 gas chromatograph equipped with a flame ionization detector and a

30 m (0.2 mm i.d., 0.25 μm film thickness) CP-Sil 5 CB column. The yields of oligomers were calculated by referencing with the mass of the solvent on the basis of the prerequisite that the mass of each fraction was approximately proportional to its integrated areas in the GC trace. GC–MS analysis was performed with HP 5890 SERIES II and HP 5971 SERIES mass detectors. ^1H NMR and ^{13}C NMR of the polymer samples were recorded on a Bruker DMS-300 instrument at 110 $^\circ\text{C}$ in 1,2-dichlorobenzene- d_4 using TMS as an internal standard. Solvents were dried by the appropriate drying reagents and distilled under nitrogen prior to use. Modified methylaluminumoxane (MMAO, 1.93 M in heptane, 3A) was purchased from Akzo Corp. Et_2AlCl (1.90 M) solution in hexane was purchased from Acros Chemicals. All other chemicals were obtained commercially and used without further purification unless otherwise stated.

4.2. Synthesis and characterization

4.2.1. Synthesis of ligands

4.2.1.1. 3,3-Dihydro-2-methyl-2,4-bis{[(2,6-diethylphenyl)imino]ethyl}pyridin-2-yl}-1H-1,5-benzodiazepine (**2b**)

In a manner similar to that described for **2a** [16], the ligand **2b** was synthesized as a yellow solid in 32% yield. Mp: 144–146 $^\circ\text{C}$. FT-IR (KBr disk, cm^{-1}): 3327 ($\nu_{\text{N-H}}$), 3060, 2965, 1646 ($\nu_{\text{C=N}}$), 1571, 1452, 1363, 1308, 1237, 1196, 1107, 818, 752. ^1H NMR (300 MHz, CDCl_3): δ 8.49 (d, $J = 7.7$ Hz, 1H, Py *Hm*); 8.42 (d, $J = 7.7$ Hz, 1H, Py *Hm*); 8.20 (d, $J = 7.7$ Hz, 1H, Py *Hm*); 7.89 (t, $J = 7.8$ Hz, 1H, Py *Hp*); 7.74 (t, $J = 7.7$ Hz, 1H, Py *Hp*); 7.60 (d, $J = 7.6$ Hz, 1H, Py *Hm*); 7.39 (d, $J = 7.7$ Hz, 1H, Ar *H*); 7.13–6.93 (m, 9H, Ar *H*); 5.27 (s, 1H); 4.11 (d, $J = 12.4$ Hz, 1H); 3.36 (d, $J = 12.7$ Hz, 1H); 2.57–2.29 (m, 8H, CH_2CH_3); 2.24 (s, 3H); 2.18 (s, 3H); 1.75 (s, 3H); 1.18–1.08 (m, 12H, CH_2CH_3). ^{13}C NMR (75 MHz, CDCl_3): δ 166.40, 166.22, 166.15, 164.06, 155.11, 154.48, 147.27, 138.63, 136.83, 136.48, 130.67, 129.00, 126.56, 125.49, 122.91, 121.87, 121.27, 120.93, 120.54, 120.16, 118.76, 72.67, 37.53, 31.16, 24.17, 16.45, 13.25. Anal. Calc. for $\text{C}_{44}\text{H}_{48}\text{N}_6$ (660.89): C, 79.96; H, 7.32; N, 12.72. Found: C, 79.83; H, 7.44; N, 12.33%.

4.2.1.2. 3,3-Dihydro-2-methyl-2,4-bis{[(2,4,6-trimethylphenyl)imino]ethyl}pyridin-2-yl}-1H-1,5-benzodiazepine (**2d**)

In a manner similar to that described for **2a** [16], the ligand **2d** was synthesized as a yellow solid in 26% yield. Mp: 161–162 $^\circ\text{C}$. FT-IR (KBr disk, cm^{-1}): 3327 ($\nu_{\text{N-H}}$), 3058, 2920, 1642 ($\nu_{\text{C=N}}$), 1572, 1475, 1452, 1362, 1311, 1216, 1129, 1036, 819, 752. ^1H NMR (300 MHz, CDCl_3): δ 8.51 (d, $J = 7.9$ Hz, 1H, Py *Hm*); 8.44 (d, $J = 6.9$ Hz, 1H, Py *Hm*); 8.24 (d, $J = 6.9$ Hz, 1H, Py *Hm*); 7.88 (t, $J = 7.7$ Hz, 1H, Py *Hp*); 7.73 (t, $J = 7.7$ Hz, 1H, Py *Hp*); 7.63 (d, $J = 7.6$ Hz, 1H, Py *Hm*); 7.41 (d, $J = 6.2$ Hz, 1H, Ar *H*); 7.07 (m, 2H, Ar *H*); 6.92 (m, 5H, Ar *H*); 5.20 (s, 1H); 4.09 (d, 1H, $J = 12.7$ Hz); 3.39 (d, 1H, $J = 12.0$ Hz); 2.33 (d, 6H, PhCH_3); 2.24 (s, 3H); 2.20

(s, 3H); 2.03 (m, 12H, PhCH_3); 1.97 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 167.33, 167.24, 164.67, 155.61, 155.18, 146.36, 139.43, 139.22, 137.34, 137.05, 132.37, 129.47, 128.74, 127.13, 125.42, 125.35, 122.47, 121.90, 121.62, 121.24, 120.75, 120.00, 119.37, 73.67, 38.08, 31.77, 20.92, 18.07, 16.67. Anal. Calc. for $\text{C}_{42}\text{H}_{44}\text{N}_6$ (632.84): C, 79.71; H, 7.01; N, 13.28. Found: C, 79.42; H, 7.02; N, 13.13%.

4.2.2. Synthesis of iron and cobalt complexes

All the iron and cobalt complexes were efficiently synthesized according to our reported procedure [16]. The data for **3b** are as follows. Yield: 96%. FT-IR (KBr disk, cm^{-1}): 3247 ($\nu_{\text{N-H}}$), 3067, 2967, 1622 ($\nu_{\text{C=N}}$), 1586, 1456, 1371, 1258, 1202, 814, 773. Anal. Calc. for $\text{C}_{44}\text{H}_{48}\text{Cl}_4\text{Fe}_2\text{N}_6$ (914.39): C, 57.79; H, 5.29; N, 9.19. Found: C, 57.93; H, 5.08; N, 8.85%.

Data for **3d** are as follows. Yield: 97%. FT-IR (KBr disk, cm^{-1}): 3184 ($\nu_{\text{N-H}}$), 3075, 2950, 1616 ($\nu_{\text{C=N}}$), 1590, 1470, 1371, 1258, 1216, 853, 814, 749. Anal. Calc. for $\text{C}_{42}\text{H}_{44}\text{Cl}_4\text{Fe}_2\text{N}_6$ (886.34): C, 56.91; H, 5.00; N, 9.48. Found: C, 56.95; H, 4.69; N, 9.28%.

Data for **4b** are as follows. Yield: 83%. FT-IR (KBr disk, cm^{-1}): 3237 ($\nu_{\text{N-H}}$), 3068, 2966, 1623 ($\nu_{\text{C=N}}$), 1586, 1466, 1372, 1259, 1203, 813, 772. Anal. Calc. for $\text{C}_{46}\text{H}_{54}\text{Cl}_4\text{Co}_2\text{N}_6\text{O}$ (966.64): C, 57.16; H, 5.63; N, 8.69. Found: C, 56.82; H, 5.81; N, 8.80%.

Data for **4d** are as follows. Yield: 85%. FT-IR (KBr disk, cm^{-1}): 3244 ($\nu_{\text{N-H}}$), 3071, 2915, 1619 ($\nu_{\text{C=N}}$), 1588, 1470, 1371, 1259, 1218, 1022, 855, 815, 749. Anal. Calc. for $\text{C}_{44}\text{H}_{50}\text{Cl}_4\text{Co}_2\text{N}_6\text{O}$ (938.59): C, 56.31; H, 5.37; N, 8.95. Found: C, 56.17; H, 5.22; N, 8.69%.

4.2.3. Synthesis of $L \cdot 2\text{NiCl}_2$ (**5a–d**)

Complexes **5a–d** were synthesized by the reaction of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ with the corresponding ligands in ethanol. A typical synthetic procedure for **5a** could be described as follows. The ligand **2a** (0.0901 g, 0.15 mmol) and 2.1 equiv. of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.0748 g, 0.31 mmol) were added together in a Schlenk tube which was purged three times with nitrogen and then charged with freshly distilled ethanol (3 mL). The reaction mixture was stirred at room temperature for 6 h and absolute diethyl ether was added to precipitate the complex. The resulted precipitate was filtered, washed with diethyl ether and dried in a vacuum to furnish the pure product as a yellow powder (0.1250 g, 0.14 mmol) in 93% yield. FT-IR (KBr disk, cm^{-1}): 3379, 3201 ($\nu_{\text{N-H}}$), 3071, 2916, 1614 ($\nu_{\text{C=N}}$), 1586, 1469, 1373, 1260, 1206, 815, 774. Anal. Calc. for $\text{C}_{40}\text{H}_{44}\text{Cl}_4\text{N}_6\text{Ni}_2\text{O}_2$ (900.02): C, 53.38; H, 4.93; N, 9.34. Found: C, 53.52; H, 4.78; N, 9.01%. Data for **5b** are as follows. Yield: 97%. FT-IR (KBr disk, cm^{-1}): 3380, 3188 ($\nu_{\text{N-H}}$), 3072, 2966, 1614 ($\nu_{\text{C=N}}$), 1585, 1469, 1373, 1261, 1204, 814, 773. Anal. Calc. for $\text{C}_{44}\text{H}_{52}\text{Cl}_4\text{N}_6\text{Ni}_2\text{O}_2$ (956.12): C, 55.27; H, 5.48; N, 8.79. Found: C, 55.62; H, 5.17; N, 8.56. Data for **5c** are as follows. Yield: 74%. FT-IR (KBr disk, cm^{-1}): 3368, 3190 ($\nu_{\text{N-H}}$), 3072, 2967, 1614 ($\nu_{\text{C=N}}$), 1585, 1468, 1370, 1263,

1203, 817, 771. Anal. Calc. for $C_{48}H_{60}Cl_4N_6Ni_2O_2$ (1012.23): C, 56.95; H, 5.97; N, 8.30. Found: C, 57.31; H, 5.66; N, 8.23%. Data for **5d** are as follows. Yield: 78%. FT-IR (KBr disk, cm^{-1}): 3379, 3188 (ν_{N-H}), 3063, 2957, 1614 ($\nu_{C=N}$), 1587, 1473, 1372, 1263, 1218, 856, 817, 750. Anal. Calc. for $C_{42}H_{48}Cl_4N_6Ni_2O_2$ (928.07): C, 54.35; H, 5.21; N, 9.06. Found: C, 54.16; H, 5.01; N, 8.77%.

4.3. General procedure for ethylene oligomerization and polymerization

Ethylene oligomerization and polymerization was carried out in a 500 mL autoclave stainless steel reactor equipped with a mechanical stirrer and a temperature controller. Briefly, toluene, the desired amount of cocatalyst and toluene solution of catalytic precursor (the total volume was 100 mL) was added to the reactor in this order under an ethylene atmosphere. Reaching the desired reaction temperature, ethylene with 30 atm pressure was introduced to start the reaction, and the ethylene pressure was kept by constant feeding of ethylene. After 30 min, the reaction was stopped. The catalytic reaction mixture was

quenched with 5% aqueous hydrogen chloride in ice-water base in accordance with the oligomers of C_4 and C_6 produced and then analyzed by gas chromatography (GC) for determining the distribution of oligomers obtained. The remaining solution was quenched with HCl-acidified ethanol (5%), and the precipitated polyethylene was filtrated, washed with ethanol, dried in a vacuum at 60 °C until constant weight.

4.4. Crystal structure determination

Crystals of **1** suitable for X-ray diffraction analysis were obtained by slow evaporation of their ethyl acetate solution. Crystals of **5a** suitable for X-ray diffraction analysis were obtained by laying diethyl ether on a dichloromethane/methanol ($v/v = 1:1$) solution at room temperature. Single-crystal X-ray diffraction study for **1** were carried out on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). Intensity data for a crystal of **5a** were collected on a Rigaku RAXIS Rapid IP diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on F^2 . All non-hydrogen atoms were refined anisotropically. Structure solution and refinement were performed by using the SHELXL-97 package [17]. Crystal data and processing parameters were summarized in Table 5.

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Appendix A. Supplementary material

CCDC 657365 and 657366 contain the supplementary crystallographic data for **1** and **5a**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/contents/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorgchem.2007.08.020](https://doi.org/10.1016/j.jorgchem.2007.08.020).

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Table 5
Crystal data and structure refinement for compound **1** and complex **5a**

Data	1	5a · 3H ₂ O
Formula	C ₂₄ H ₂₂ N ₄ O ₂	C ₄₀ H ₃₉ C ₁₄ N ₆ Ni ₂ O ₂ · 3H ₂ O
Formula weight	398.46	942.95
<i>T</i> (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 21/ <i>c</i>
<i>a</i> (Å)	8.42990(1)	14.397(3)
<i>b</i> (Å)	10.8619(2)	16.584(3)
<i>c</i> (Å)	12.2771(2)	22.753(7)
α (°)	104.3390(1)	90
β (°)	95.6480(1)	123.81(2)
γ (°)	92.5980(1)	90
Volume (Å ³)	1081.01(3)	4513.8(2)
<i>Z</i>	2	4
<i>D</i> _{calc.} (Mg m ⁻³)	1.224	1.388
μ (mm ⁻¹)	0.080	1.118
<i>F</i> (000)	420	1940
Crystal size (mm)	0.65 × 0.13 × 0.11	0.36 × 0.22 × 0.16
θ Range (°)	1.72–28.33	1.63–25.01
Limiting indices	–11 ≤ <i>h</i> ≤ 11, –14 ≤ <i>k</i> ≤ 14, –16 ≤ <i>l</i> ≤ 16	–16 ≤ <i>h</i> ≤ 17, –19 ≤ <i>k</i> ≤ 19, –27 ≤ <i>l</i> ≤ 27
No. of reflections collected	21309	11365
No. of unique reflections	5357	7239
<i>R</i> _{int}	0.0236	0.1046
Completeness to θ (%)	99.2	91.0
Absorption correction	Empirical	Empirical
Goodness-of-fit on F^2	1.102	1.213
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0552, <i>wR</i> ₂ = 0.1692	<i>R</i> ₁ = 0.1262, <i>wR</i> ₂ = 0.2981
<i>R</i> indices(all data)	<i>R</i> ₁ = 0.0757, <i>wR</i> ₂ = 0.1841	<i>R</i> ₁ = 0.2104, <i>wR</i> ₂ = 0.3491
Largest difference in peak and hole (e Å ⁻³)	0.489 and –0.442	0.969 and –0.709

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