Bimetallic (Iron or Cobalt) Complexes Bearing 2-Methyl-2,4-bis(6-iminopyridin-2-yl)-1*H*-1,5-benzodiazepines for Ethylene Reactivity

Shu Zhang, Igor Vystorop, Zhenghua Tang, and Wen-Hua Sun*

Key Laboratory of Engineering Plastics and Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

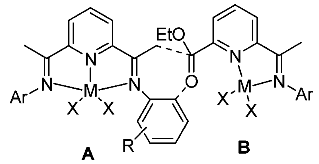
Received January 21, 2007

A series of bimetallic (ferrous and cobaltous) complexes ligated by 3,3-dihydro-2-methyl-2,4-bis(6-iminopyridin-2-yl)-1*H*-1,5-benzodiazepines were synthesized and evaluated as catalysts for ethylene oligomerization and polymerization with high activity and α-olefin selectivity in the presence of modified methylaluminoxane (MMAO).

Introduction

Combined catalytic systems have recently drawn more attention in general chemical processes, and extensive investigations have also covered their use in ethylene reactivity.[1] With polyolefin materials as the target, linear low-density polyethylene (LLDPE) was produced by two combined characteristic metallic complex systems which individually catalyzed ethylene oligomerization and polymerization. The technical combination of late-transition-metal complexes and metallocene with a cocatalyst of methylaluminoxane (MAO) indeed produced branched polyethylenes;[2] however, it was difficult to maintain the microstructural polyethylenes with the combined catalytic system when changing reaction parameters due to the different catalytic (dynamics and thermal stability) behaviors. It would be interesting to design bimetallic complexes in which two catalytic sites were held in close proximity to perform under the same conditions when reaction parameters are changed. A successful example of early−late heterobimetallic complexes for ethylene polymerization has been reported recently.[3] With the focus on iron and cobalt catalysts for use in ethylene reactivity, the most effective model was the N^N^N tridentate (bis(imino)pyridyl)metal (iron or cobalt) complexes (**A**)[4] as well as the recent (2-imino-1,10-phenanthrolinyl)iron and -cobalt complexes.[5] However, (mono(imino)pyridyl)metal complexes are promising, having moderate catalytic activity at this moment (**B**).[6] The fused framework of models **A** and **B** could be envisaged as a conceptual model of bimetallic complexes as catalysts for ethylene reactivity, as shown in Chart 1. To transform this model into reality, the two coordination pockets would be kept with some necessary adaptations through alternating atoms, forming a cyclic core between two active sites. Herein we report the synthesis of bimetallic complexes and their catalytic behavior for ethylene oligomerization and polymerization.

Chart 1. Concept of the Bimetallic Catalyst



Results and Discussion

1. Synthesis and Characterization of the Ligands and Complexes. The reaction of *o*-phenylenediamine with acetylarenes has been investigated, with a detailed consideration of the reaction mechanism.[7] In the first step, reaction of *o*-phenylenediamine with diacetylpyridine produced a novel compound, 3,3-dihydro-2-methyl-2,4-bis(6-acetylpyridin-2-yl)-1*H*-1,5-benzodiazepine, in considerable yield, which further reacted with aniline derivatives to form 3,3-dihydro-2-methyl-2,4-bis(6-iminopyridin-2-yl)-1*H*-1,5-benzodiazepines. The title bimetallic complexes were easily formed in high yield by the

---

* To whom correspondence should be addressed. E-mail: whsun@iccas.ac.cn. Tel: +86 10 62557955. Fax: +86 10 62618239.

[1] Wasilke, J.-C.; Obrey, S. J.; Baker, R. T.; Bazan, G. C. *Chem. Rev.* **2005**, *105*, 1001 and references therein.

[2] (a) Cui, Y.; Shao, C.; Sun, W.-H. *Central Eur. J. Chem.* **2003**, *1*, 325. (b) Li, Z.; Zhu, N.; Sun, W.-H.; Shao, C.; Ke, Y.; Hu Y.; He, J. *Polym. Int.* **2001**, *50*, 1275. (c) Mecking, S. *Macromol. Rapid Commun.* **1999**, *20*, 139. (d) Souza, R. F. D.; Casagrande, O. L. *Macromol. Rapid Commun.* **2001**, *22*, 1293. (e) Mota, F. F.; Mauler, R. S.; Souza, R. F. D.; Casagrande, O. L. *Macromol. Chem. Phys.* **2001**, *201*, 1016. (f) Kunrath, F. A.; Souza, R. F.; Casagrande, O. L. *Macromol. Rapid Commun.* **2000**, *21*, 277. (g) Wang, H.; Ma, Z.; Ke, Y.; Hu, Y. *Polym. Int.* **2003**, *52*, 1546. (h) Frediani, M.; Bianchini, C.; Kaminsky, W. *Kinet. Catal.* **2006**, *47*, 207.

[3] Kuwabara, J.; Takeuchi, D.; Osakada, K. *Chem. Commun.* **2006**, 3815.

[4] (a) Small, B. L.; Brookhart, M.; Bennett, A. M. A. *J. Am. Chem. Soc.* **1998**, *120*, 4049. (b) Britovsek, G. J. P.; Gibson, V. C.; McTavish, S. J.; Solan, G. A.; White, A. J. P.; Williams, D. J.; Kimberley, B. S.; Maddox, P. J. *Chem. Commun.* **1998**, 849.

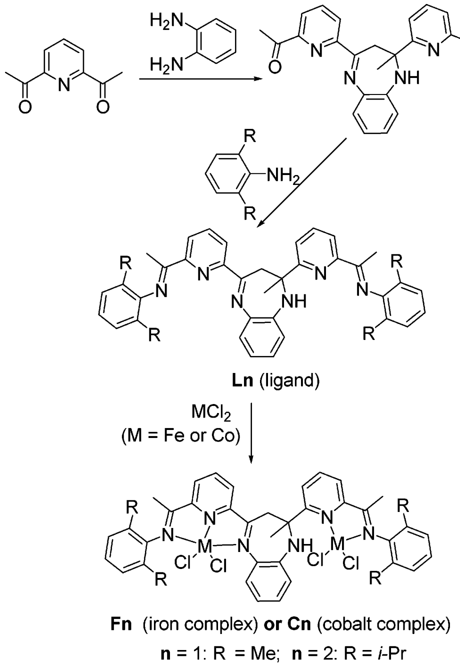
[5] (a) Sun, W.-H.; Jie, S.; Zhang, S.; Zhang, W.; Song, Y.; Ma, H.; Chen, J.; Wedeking, K.; Fröhlich, R. *Organometallics* **2006**, *25*, 666. (b) Jie, S.; Zhang, S.; Wedeking, K.; Zhang, W.; Ma, H.; Lu, X.; Deng, Y.; Sun, W.-H. *C. R. Chim.* **2006**, *9*, 1500. (c) Pelletier, J. D. A.; Champouret, Y. D. M.; Cadarso, J.; Clowes, L.; Gañete, M.; Singh, K.; Thanarajasingham, V.; Solan, G. A. *J. Organomet. Chem.* **2006**, *691*, 4114. (d) Sun, W.-H.; Zhang, S.; Jie, S.; Zhang, W.; Li, Y.; Ma, H.; Chen, J.; Wedeking, K.; Fröhlich, R. *J. Organomet. Chem.* **2006**, *691*, 4196. (e) Jie, S.; Zhang, S.; Sun, W.-H.; Kuang, X.; Liu, T.; Guo, J. *J. Mol. Catal. A: Chem.* **2007**, *269*, 85.

[6] (a) Sun, W.-H.; Tang, X.; Gao, T.; Wu, B.; Zhang, W.; Ma, H. *Organometallics* **2004**, *23*, 5037. (b) Bluhm, M. E.; Folli, C.; Döring, M. *J. Mol. Catal. A: Chem.* **2004**, *212*, 13. (c) Kaul, F. A. R.; Puchta, G. T.; Frey, G. D.; Herdtweck, D.; Herrmann, W. A. *Organometallics* **2007**, *26*, 988. (d) Tang, X.; Sun, W.-H.; Gao, T.; Hou, J.; Chen, J.; Chen, W. *J. Organomet. Chem.* **2005**, *690*, 1570. (e) Zhang, W.; Sun, W.-H.; Tang, X.; Gao, T.; Zhang, S.; Hao, P.; Chen, J. *J. Mol. Catal. A: Chem.* **2007**, *265*, 159.

[7] (a) Tang, X.; Cui, Y.; Sun, W.-H.; Miao, Z.; Yan, S. *Polym. Int.* **2004**, *53*, 2155. (b) Cui, Y.; Tang, X.; Shao, C.; Li, J.; Sun, W.-H. *Chin. J. Chem.* **2005**, *23*, 589.

10.1021/om070062z CCC: $37.00

Scheme 1. Synthetic Procedure



reaction of iron or cobalt chloride with the ligands (Scheme 1). All of the organic compounds were characterized by FT-IR, ^{1}H NMR, and ^{13}C NMR spectra and elemental analyses, while the complexes were characterized by elemental analyses and FT-IR spectra. The elemental analyses of the iron complexes were consistent with the composition $\mathbf{L}Fe_2Cl_4$. However, the cobalt complexes possess the molecular formula $\mathbf{L}Co_2Cl_4 \cdot EtOH$. The molecular structures of **L2 and C2** were determined by X-ray diffraction analysis.

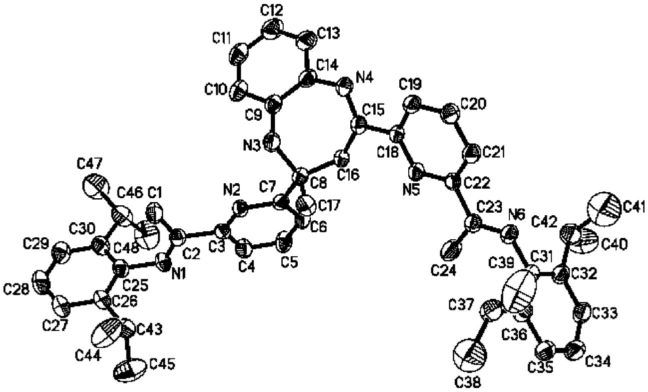


Figure 1. Molecular structure of **L2** with thermal ellipsoids at the 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): C2−N1 = 1.282(5), C8−N3 = 1.477(5), C15−N4 = 1.289(5), C23−N6 = 1.287(5); C2−N1−C25 = 120.5(4), C8−N3−C9 = 120.1(4), C14−N4−C15 = 118.2(4), C23−N6−C31 = 121.6(4).

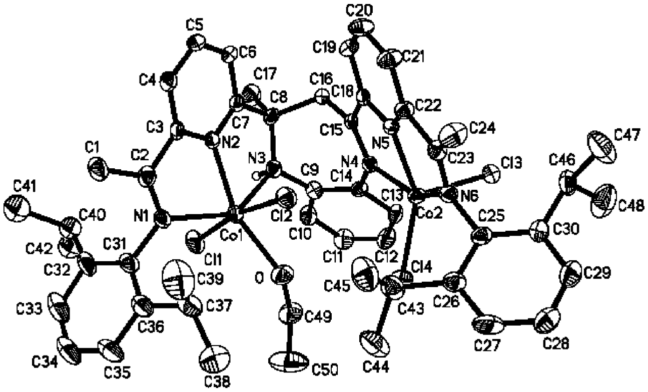


Figure 2. Molecular structure of **C2** with thermal ellipsoids at the 30% probability level. Hydrogen atoms and solvent have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Co1−N1 = 2.165(5), Co1−N2 = 2.092(5), Co1−N3 = 2.340(6), Co1−Cl1 = 2.421(2), Co1−Cl2 = 2.431(2), Co1−O = 2.082(5), Co2−N4 = 2.214(5), Co2−N5 = 2.051(5), Co2−N6 = 2.224(5), Co2−Cl3 = 2.325(2), Co2−Cl4 = 2.2541(2); N1−Co1−N2 = 75.5(2), N2−Co1−N3 = 71.9(2), N1−Co1−N3 = 140.3(2), N1−Co1−Cl1 = 87.29(2), N2−Co1−Cl1 = 104.53(2), N3−Co1−Cl1 = 79.62(2), N1−Co1−Cl2 = 95.88(2), N2−Co1−Cl2 = 85.11(2), N3−Co1−Cl2 = 103.25(2), Cl1−Co1−Cl2 = 170.34(7), N4−Co2−N5 = 75.14(2), N5−Co2−N6 = 75.15(2), N4−Co2−N6 = 149.96(2), N4−Co2−Cl3 = 94.06(1), N5−Co2−Cl3 = 102.98(1), N6−Co2−Cl3 = 96.80(1), N4−Co2−Cl4 = 99.02(1), N5−Co2−Cl4 = 148.33(2), N6−Co2−Cl4 = 103.88(1), Cl3−Co2−Cl4 = 108.51(7).

2. Crystal Structures. The molecular structures of **L2** and **C2** are shown in Figures 1 and 2, respectively, along with selected bond lengths and angles. Two imino groups of **L2** in the solid state are in the *E* conformation with the typical imino C═N double-bond lengths of 1.282(5) and 1.287(5) Å. The aryl rings on the imine are approximately perpendicular to the pyridine rings, and their dihedral angles are 98.8° (C3−C7, N2) and 87.5° (C18−C22, N4), respectively. The crystals of cobalt complex **C2,** with one incorporated ethanol molecule in the solid state, were obtained from the solvent mixture of dichloromethane and ethanol. The structure consists of one ligand molecule, two cobalt(II) cations, and four chlorides. One of the cobalt (Co1) atoms is six-coordinated with an additional ethanol molecule, while the second cobalt (Co2) atom is five-coordinated. The six-coordinated structure consists of a metal atom surrounded by three nitrogen atoms from the ligand, two chlorides, and one ethanol molecule linked by the oxygen atom, in a distorted-octahedral geometry. The Co1−N3 (2.340(6) Å) bond length is much longer than those of Co1−N1 (2.165(5) Å) and Co1−N2 (2.092(5) Å), which can be attributed to the sp^3 N3. The three nitrogen atoms and the oxygen atom occupied the equatorial plane, whereas the axial position is occupied by two chlorides. The geometry of the five-coordinated structure around Co2 can be described as a distorted trigonal bipyramid. The nitrogen (N5) of the pyridine and the two chlorides form an equatorial plane, while the axial plane consists of the other two nitrogen atoms (N4 and N6) and the cobalt core with a bond angle of 149.96(2)° for N4−Co2−N6. The cobalt atom deviates by 0.0491 Å from the equatorial plane. The Co2−N5(pyridine) bond (2.051(5) Å) is shorter by about 0.17 Å than the Co2−N4(benzodiazepine) bond (2.214(5) Å) and Co2−N6(imino) bond (2.224(5) Å), which is similar to the case for the (2,6-bis(imino)pyridyl)cobalt(II) complexes.[4] The two Co2−Cl bond lengths are slightly different: Co2−Cl3 = 2.325(2) Å and Co2−Cl4 = 2.2541(2) Å). The N4−C15 bond length in the benzodiazepine and the N6−C23 bond length are 1.283(7) and 1.278(8) Å, respectively, with the typical character for a C═N double bond. All the atoms of the pyridine ring (N5, C18, C19, C20, C21, C22) and N4, C15, N6, and C23 as well as the Co2 atom make an almost perfect plane, with the largest deviation from the plane being 0.1024 Å at Co2. The 2,6-diisopropylphenyl group C25−C26−C27−C28-C29−C30 is oriented to the basal coordination plane N4−C15−C18−N5−C22−C23-N6−Co2, with a dihedral angle of 79.9°. An inspection of the intermetallic distance (4.979 Å) reveals that there is no direct Co···Co interaction between the two metal centers.

Table 1. Ethylene Oligomerization and Polymerization Initiated by Bimetallic Complexes[a]

				oligomer				
entry	cat.	Al/M	T^b (°C)	activity[c]	K	α-O[d] (%)	polymer activity[e]	PE (wt %)[f]
1	**F1**	500	30	0.12	0.43	>99	trace	
2	**F1**	1000	30	2.06	0.71	>99	1.38	40.2
3	**F1**	1500	30	1.30	0.72	>99	3.00	69.8
4	**F1**	2000	30	1.33	0.66	>99	3.37	71.7
5	**F1**	2500	30	1.31	0.69	>99	3.40	72.2
6	**F1**	1500	40	0.38	0.66	>99	0.46	54.6
7	**F1**	1500	60	0.15	0.66	>99	trace	
8	**F2**	1000	30	0.15	0.59	>99	0.10	39.5
9	**C1**	500	30	0.03		>99	trace	
10	**C1**	1000	30	0.61	0.64	>99	0.45	42.6
11	**C1**	1500	30	0.91	0.64	>99	1.20	57.0
12	**C1**	2000	30	0.74	0.59	>99	1.49	66.7
13	**C1**	2500	30	0.29	0.57	>99	0.47	62.3
14	**C1**	1500	40	1.20	0.70	>99	2.50	67.6
15	**C1**	1500	60	2.46	0.80	>99	7.37	75.0
16	**C2**	1000	30	0.24	0.53	>99	0.15	38.1

[a] General conditions: cat., 2.5 μmol; cocat., MMAO; reaction time, 30 min; ethylene pressure, 30 atm; solvent, toluene (100 mL). [b] Reaction temperature. [c] Oligomerization activity: 10^5 g (mol of cat.)$^{-1}$ h^{-1} atm^{-1}. [d] Percent α-olefin content determined by GC and GC-MS. [e] Polymerization activity: 10^5 g (mol of cat.)$^{-1}$ h^{-1} atm^{-1}. [f] The percentage of polyethylene waxes.

3. Catalytic Behavior toward Ethylene Reactivity. The iron and cobalt complexes were studied for their catalytic activities with various alkylaluminums as cocatalysts. The catalytic system with modified methylaluminoxane (MMAO) showed high catalytic activities for ethylene oligomerization and polymerization with very high selectivity for α-olefin. The detailed results are summarized in Table 1. The distribution of oligomers obtained in all cases follows Schulz−Flory rules, which is characteristic of the constant *K*, where *K* represents the probability of chain propagation (K = (rate of propagation)/((rate of propagation) + (rate of chain transfer)) = (moles of C_{n+2})/(moles of C_n). The *K* values are determined by the molar ratio of C_{12} and C_{14} fractions.

The ligands greatly affected the catalytic behavior of their complexes. Under the same reaction conditions, noticeably reduced catalytic activities were observed for the sterically bulkier catalyst systems. This could be exemplified by comparing the 2,6-diisopropyl-substituted **F2** or **C2** with 2,6-dimethyl-substituted **F1** or **C1** (entries 2 vs 8 and 10 vs 16 in Table 1). The bulkiness at the ortho positions of the imino-N aryl ring may prevent the insertion of ethylene at the active center in the catalytic system, therefore resulting in decreased catalytic activity. When the Al/Fe molar ratio was increased from 500 to 1000, both oligomerization and polymerization activities of **F1** increased sharply (entries 1 and 2 in Table 1). A further increase of the Al/Fe molar ratio to 1500 resulted in decreased oligomerization activity and increased polymerization activity. Increasing the Al/Fe molar ratio from 1500 to 2500 led to almost constant production for both oligomers and polymers (entries 3−5 in Table 1). In addition, a higher Al/Fe molar ratio led to a higher proportion of polyethylene wax. With an Al/Fe molar ratio of 2500, the proportion of polyethylene wax peaked at 72.2%. Furthermore, the Al/Fe molar ratio had an obvious influence on oligomer distribution, as revealed by the different *K* values when the Al/Fe molar ratio was increased from 500 to 2500. The oligomer distributions obtained at different Al/Fe molar ratio with **F1** are shown in Figure 3. The *K* value peaked at 0.72 at an Al/Fe molar ratio of 1500. The effect of the Al/Co molar ratio on ethylene reactivity was also investigated using the cobalt complex **C1.** At an Al/Co molar ratio of 500, only very small amounts of oligomers and polymer were produced (entry 9 in Table 1). When the Al/Co molar ratio was further increased, the catalytic activity improved. At an Al/Co molar ratio of 1500, the catalytic system displayed the highest oligomerization activity of 0.91 × 10^5 g (mol of cat.)$^{-1}$ h^{-1} atm^{-1} (entry 11 in Table 1). However, the highest polymerization activity of 1.49 × 10^5 g (mol of cat.)$^{-1}$ h^{-1} atm^{-1} and the largest polymer percentage of 66.7% were obtained with an Al/Co molar ratio of 2000 (entry 12 in Table 1). In addition, the distribution of oligomers was also greatly influenced by the Al/Co molar ratio. The *K* value peaked at 0.64 with Al/Co molar ratios of 1000 and 1500. Elevating the reaction temperature of the **C1**/MMAO system from 30 to 60 °C resulted in a sharp increase in productivity and polymer percentage (entries 11, 14, and 15 in Table 1), suggesting that **C1** is thermally stable (under the experimental conditions) with a considerable lifetime. However, the activity of **F1** decreased sharply at higher reaction temperature, which could be attributed to the lower stability of iron active species.

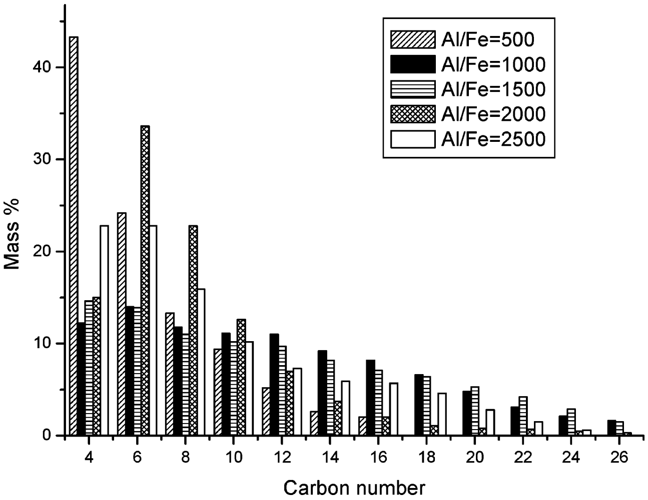


Figure 3. Oligomer distribution obtained in entries 1−5 in Table 1.

In most cases, some polyethylene waxes as higher oligomers were obtained, in addition to lower oligomers. The waxes were confirmed to be mainly linear α-olefins from the characteristic vibrations of C═C and various C−H bonds. ^{1}H and ^{13}C NMR spectra (Figure 4) of the waxes produced with complex **F1** were recorded in 1,2-dichlorobenzene-d_4 using TMS as an internal standard. The ^{13}C NMR spectra further demonstrated that linear α-olefins absolutely predominated in the waxes; also, the single peaks at δ 139 and 114 ppm showed the properties of a vinyl-unsaturated chain end. On the basis of ^{1}H NMR measurements, the average molecular weight indicated that the carbon number of the waxes obtained was about 60.

Conclusion

A series of new ligands with two different binding sites were synthesized and fully characterized. The reaction of these ligands with metal chlorides afforded bimetallic complexes. An X-ray crystallographic study revealed that one ligand coordinated with two metal cations with two different coordination geometries. Upon treatment with MMAO, the iron(II) complexes showed high catalytic activities of up to 3.40 × 10^5 g (mol of cat.)$^{-1}$ h^{-1} atm^{-1} for polymerization and 2.06 × 10^5 g (mol of cat.)$^{-1}$ h^{-1} atm^{-1} for oligomerization with high α-olefin selectivity. The cobalt complexes showed lower activity than their iron analogues under the same conditions. However, when the

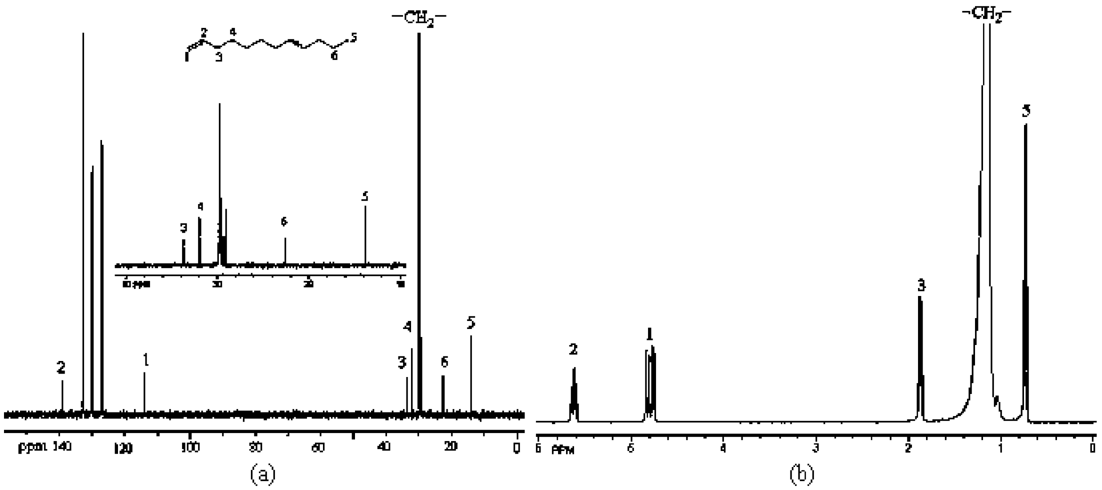


Figure 4. NMR spectra of the waxes obtained in entry 2 in Table 1: (a) ^{13}C NMR; (b) ^{1}H NMR.

reaction temperature increased to 60 °C, cobalt complexes displayed a higher polymerization activity of 7.37×10^5 g (mol of cat.)$^{-1}$ h^{-1} atm^{-1} and oligomerization activity of 2.46×10^5 g (mol of cat.)$^{-1}$ h^{-1} atm^{-1} with high α-olefin selectivity. The two metallic catalytic centers influenced each other during the ethylene oligomerization and polymerization. The investigation of their mononuclear analogues and cooperative effects of bimetallic complexes is in progress.

Experimental Section

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 a Bruker DMX-300 spectrometer, with TMS as the internal standard. IR spectra were recorded on a Perkin-Elmer FT-IR 2000 spectrometer using KBr disks in the range of 4000−400 cm^{-1}. Elemental analyses were performed on a Flash EA 1112 microanalyzer. GC analyses were 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 to the mass of the solvent, on the basis of the prerequisite that the mass of each fraction is 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. ^{1}H NMR and ^{13}C NMR spectra of the polymer samples were recorded on a Bruker DMS-300 instrument at 110 °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. Silica−alumina catalyst (support, grade 135) was purchased from Aldrich Chemicals. Modified methylaluminoxane (MMAO, 1.93 M in heptane, 3A) was purchased from Akzo Corp. All other chemicals were obtained commercially and used without further purification unless otherwise stated.

2. Synthesis and Characterization. 3,3-Dihydro-2-methyl-2,4-bis(6-iminopyridin-2-yl)-1*H*-1,5-benzodiazepines. A mixture of 2,6-diacetylpyridine (4.750 g, 29.1 mmol) and silicon−aluminum catalyst (2 g) was heated to 80 °C under a nitrogen atmosphere. Benzene-1,2-diamine (1.794 g, 16.6 mmol) was then added to the melting 2,6-diacetylpyridine. After 2 min, the mixture was cooled and eluted on an alumina column. The second part to elute was collected and concentrated to give a yellow solid in 41% yield. Mp: 126−128 °C. FT-IR (KBr disk, cm^{-1}): 3304 (ν_{N-H}), 3004, 2972, 1696 ($\nu_{C=O}$), 1621, 1581, 1475, 1360, 1254, 771. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.54 (d, J = 7.8 Hz, 1H, Py H_m); 8.04 (d, J = 7.4 Hz, 1H, Py H_m); 7.87 (t, J = 7.8 Hz, 1H, Py H_p); 7.84 (t, J = 7.8 Hz, 1H, Py H_p); 7.73 (d, 2H, Py H_m); 7.35 (d, J = 7.1 Hz, 1H, Ar H); 7.10 (t, J = 7.3 Hz, 1H, Ar H); 7.04 (t, J = 7.5 Hz, 1H, Ar H); 6.92 (t, J = 7.5 Hz, 1H, Ar H); 4.93 (s, 1H); 3.87 (d, 1H, J = 12.7 Hz); 3.47 (d, 1H, J = 12.7 Hz); 2.72 (s, 3H); 2.71 (s, 3H); 1.71 (s, 3H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 199.3, 199.2, 165.7, 164.7, 155.3, 151.9, 151.8, 138.6, 138.3, 137.2, 136.9, 129.0, 126.9, 124.2, 122.8, 121.7, 121.0, 119.3, 73.1, 37.5, 30.8, 25.2. Anal. Calcd for $C_{24}H_{22}N_4O_2$ (398.46): C, 72.34; H, 5.57; N, 14.06. Found: C, 72.03; H, 5.66; N, 13.81.

3,3-Dihydro-2-methyl-2,4-bis((((2,6-dimethylphenyl)imino)ethyl)pyridin-2-yl)-1*H*-1,5-benzodiazepine (L1). A solution of 3,3-dihydro-2-methyl-2,4-bis(6-acetylpyridin-2-yl)-1*H*-1,5-benzodiazepine (1.20 g, 3.01 mmol), 2,6-dimethylaniline (1.06 g, 8.73 mmol), and a catalytic amount of *p*-toluenesulfonic acid and silica−alumina catalyst in ethanol (25 mL) were refluxed for 24 h, and 4 Å molecular sieves (2 g) were added to remove water. After filtration and solvent evaporation, the crude product was purified by column chromatography on alumina with petroleum ether/ethyl acetate (20/1) as eluent. The second part to elute was collected and concentrated to give a yellow solid. The third and the fourth parts to elute were collected, and the reaction was repeated with the first part to elute. This process was carried out four times to obtain the products (**L1**) in 27% yield (0.50 g). Mp: 103−105 °C. FT-IR (KBr disk, cm^{-1}): 3342 (ν_{N-H}), 3016, 2920, 1645 ($\nu_{C=N}$), 1572, 1469, 1362, 1308, 1243, 1206, 821, 759. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.47 (d, J = 7.7 Hz, 1H, Py H_m); 8.41 (d, J = 7.7 Hz, 1H, Py H_m); 8.20 (d, J = 7.8 Hz, 1H, Py H_m); 7.90 (t, J = 7.6 Hz, 1H, Py H_p); 7.74 (t, J = 7.6 Hz, 1H, Py H_p); 7.60 (d, J = 7.7 Hz, 1H, Py H_m); 7.37 (d, J = 7.5 Hz, 1H, Ar H); 7.07−6.88 (m, 9H, Ar H); 5.17 (s, 1H); 4.05 (d, J = 12.3 Hz, 1H); 3.35 (d, J = 12.6 Hz, 1H); 2.19 (s, 3H); 2.16 (s, 3H); 2.07−2.02 (m, 12H, PhCH_3); 1.74 (s, 3H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 166.6, 166.5, 164.1, 155.1, 154.4, 148.2, 138.8, 138.6, 136.8, 136.5, 128.9, 127.5, 126.6, 124.9, 122.6, 122.0, 121.3, 121.0, 120.7, 120.3, 118.8, 73.1, 37.5, 31.0, 17.5, 16.1. Anal. Calcd for $C_{40}H_{40}N_6$ (604.79): C, 79.44; H, 6.67; N, 13.90. Found: C, 79.69; H, 6.72; N, 13.62.

3,3-Dihydro-2-methyl-2,4-bis((((2,6-diisopropylphenyl)imino)ethyl)pyridin-2-yl)-1*H*-1,5-benzodiazepine (L2). In a manner similar to that described for **L1**, **L2** was also prepared in 39% yield. Mp: 202−204 °C. FT-IR (KBr disk, cm^{-1}): 3307 (ν_{N-H}), 3056, 2961, 1645 ($\nu_{C=N}$), 1570, 1455, 1363, 1312, 1235, 1122, 1109, 815, 771. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.49 (d, J = 7.8 Hz, 1H, Py H_m); 8.41 (d, J = 7.6 Hz, 1H, Py H_m); 8.19 (d, J = 7.6 Hz, 1H, Py H_m); 7.86 (t, J = 7.8 Hz, 1H, Py H_p); 7.71 (t, J = 7.8 Hz, 1H, Py H_p); 7.58 (d, J = 7.6 Hz, 1H, Py H_m); 7.38 (d, J = 6.6 Hz, 1H, Ar H); 7.04 (m, 9H, Ar H); 5.28 (s, 1H); 4.08 (d, 1H, J = 12.7 Hz); 3.40 (d, 1H, J = 12.6 Hz); 2.68 (m, 4H, $CH(CH_3)_2$); 2.25 (s, 3H);

2.17 (s, 3H); 1.74 (s, 3H); 1.14 (m, 24H, CH(CH_3)$_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.29, 166.17, 164.06, 155.15, 154.54, 145.98, 138.68, 138.56, 136.88, 136.49, 135.26, 129.10, 126.59, 123.17, 122.56, 121.88, 121.33, 120.92, 120.52, 120.11, 118.83, 72.43, 37.55, 31.28, 27.85, 22.73, 22.47. Anal. Calcd for $C_{48}H_{56}N_6$ (717.00): C, 80.41; H, 7.87; N, 11.72. Found: C, 80.27; H, 7.86; N, 11.39.

F1. Ligand **L1** (0.1210 g, 0.20 mmol) and 2.1 equiv of $FeCl_2 \cdot 4H_2O$ (0.084 g, 0.42 mmol) were added together in a Schlenk which was purged three times with nitrogen and then charged with freshly distilled ethanol. The reaction mixture was stirred at room temperature for 6 h, and absolute diethyl ether was added to precipitate the complex. The resulting precipitate was filtered, washed with diethyl ether, and dried under vacuum to furnish the product **F1** (0.163 g, 0.19 mmol) as a green powder in 95% yield. FT-IR (KBr disk, cm^{-1}): 3246 (ν_{N-H}), 3071, 2971, 1620 ($\nu_{C=N}$), 1590, 1469, 1371, 1258, 1208, 814, 776. Anal. Calcd for $C_{40}H_{40}Cl_4Fe_2N_6$ (858.29): C, 55.98; H, 4.70; N, 9.79. Found: C, 55.79; H, 4.56; N, 9.58. Complexes **F2**, **C1**, and **C2** were also prepared by this manner.

F2. Yield: 97%. FT-IR (KBr disk, cm^{-1}): 3258 (ν_{N-H}), 3063, 2964, 1616 ($\nu_{C=N}$), 1588, 1467, 1370, 1257, 1200, 815, 770. Anal. Calcd for $C_{48}H_{56}Cl_4Fe_2N_6$ (970.50): C, 59.40; H, 5.82; N, 8.66. Found: C, 59.45; H, 5.70; N, 8.50.

C1. Yield: 96%. FT-IR (KBr disk, cm^{-1}): 3246 (ν_{N-H}), 3071, 2916, 1621 ($\nu_{C=N}$), 1589, 1470, 1371, 1259, 1218, 816, 750. Anal. Calcd for $C_{40}H_{40}Cl_4Co_2N_6 \cdot C_2H_5OH$ (910.53): C, 55.40; H, 5.09; N, 9.23. Found: C, 55.12; H, 4.88; N, 9.20.

C2. Yield: 83%. FT-IR (KBr disk, cm^{-1}): 3217 (ν_{N-H}), 3069, 2965, 1620 ($\nu_{C=N}$), 1587, 1467, 1369, 1258, 1202, 817, 770. Anal. Calcd for $C_{48}H_{56}Cl_4Co_2N_6 \cdot C_2H_5OH$ (1022.75): C, 58.72; H, 6.11; N, 8.22. Found: C, 58.64; H, 5.79; N, 8.21.

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 a toluene solution of the catalytic precursor (the total volume was 100 mL) were added to the reactor in this order under an ethylene atmosphere. When the desired reaction temperature was reached, ethylene at 30 atm pressure was introduced to start the reaction, and the ethylene pressure was maintained by constant feeding of ethylene. After 30 min, the reaction was stopped. A small amount of the reaction solution was collected, the reaction was terminated by the addition of 5% aqueous hydrogen chloride, and then this mixture was analyzed by gas chromatography (GC) to determine the distribution of oligomers obtained. The remaining solution was quenched with HCl-acidified ethanol (5%), and the precipitated polyethylene was filtered, washed with ethanol, and dried under vacuum at 60 °C to constant weight.

4. Crystal Structure Determination. Single crystals of **L2** suitable for X-ray diffraction analysis were obtained by slow evaporation of its ethyl acetate solution. Crystals of **C2** suitable for single-crystal X-ray diffraction analysis were obtained by layering diethyl ether on a dichloromethane/ethanol (1/1 v/v) solution at room temperature. Single-crystal X-ray diffraction studies for **L2** were carried out on a Bruker P4 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Intensity data for a crystal of **C2** were collected on a Rigaku RAXIS Rapid IP diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 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.[8] Crystal data and processing parameters are summarized in Table 2.

Table 2. Crystal Data and Structure Refinement Details for L2 and C2

	L2	**C2**$\cdot EtOH \cdot 2CH_2Cl_2$
formula	$C_{48}H_{56}N_6$	$C_{50}H_{61}Cl_4Co_2N_6O \cdot 2CH_2Cl_2$
formula wt	716.99	1191.56
T (K)	293(2)	293(2)
wavelength (Å)	0.710 73	0.710 73
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	11.5337(5)	11.198(2)
b (Å)	12.2438(6)	16.308(3)
c (Å)	15.7362(7)	16.371(3)
α (deg)	98.347(3)	103.77(3)
β (deg)	90.241(3)	91.89(3)
γ (deg)	104.096(2)	96.22(3)
V (Å^3)	2130.65(2)	2881.2(1)
Z	2	2
D_{calcd} (Mg m^{-3})	1.118	1.373
μ (mm^{-1})	0.066	0.988
F(000)	772	1234
cryst size (mm)	0.19 × 0.17 × 0.11	0.22 × 0.15 × 0.10
θ range (deg)	1.31−25.01	1.28−25.01
limiting indices	$-13 \le h \le 13$, $-14 \le k \le 14$, $-18 \le l \le 18$	$0 \le h \le 13$, $-19 \le k \le 19$, $-19 \le l \le 19$
no. of rflns collected	37 180	9464
no. of unique rflns	7504	5716
R_{int}	0.0914	0.0610
completeness to θ (%)	99.8	93.0
abs cor	empirical	empirical
goodness of fit on F^2	0.971	1.010
final R indices ($I > 2\sigma(I)$)	R1 = 0.0825, wR2 = 0.2360	R1 = 0.0726, wR2 = 0.1891
R indices (all data)	R1 = 0.1849, wR2 = 0.2872	R1 = 0.1286, wR2 = 0.2216
largest diff peak, hole (e Å^{-3})	0.637, −0.322	0.967, −1.010

Acknowledgment. This work was supported by NSFC Grant No. 20674089 and MOST Grant No. 2006AA03Z553. We thank Mr. Sheriff Adewuyi (a CAS-TWAS Postgraduate Fellow from Nigeria) for the English corrections.

Supporting Information Available: CIF files giving crystallographic data for **L2** and **C2**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM070062Z

---

[8] Sheldrick, G. M. SHELXTL-97, Program for the Refinement of Crystal Structures; University of Göttingen, Göttingen, Germany, 1997.