ORGANOMETALLICS

Probing the Characteristics of Mono- or Bimetallic (Iron or Cobalt) Complexes Bearing 2,4-Bis(6-iminopyridin-2-yl)-3*H*-benzazepines: Synthesis, Characterization, and Ethylene Reactivity

Wen-Hua Sun,^{*,†,‡} Qifeng Xing,[†] Jiangang Yu,[†] Elena Novikova,[†] Weizhen Zhao,[†] Xiubo Tang,[†] Tongling Liang,[†] and Carl Redshaw^{*,§}

[†]Key laboratory of Engineering Plastics and Beijing National Laboratory for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, People's Republic of China

[‡]State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, People's Republic of China

[§]Department of Chemistry, University of Hull, Hull HU6 7RX, U.K.

Supporting Information

ABSTRACT: A series of 2,4-bis(6-iminopyridin-2-yl)-3*H*-benzazepines and the mono- or bimetallic (Fe²⁺ or Co²⁺) complexes thereof were synthesized and characterized. All title complexes, when activated by MAO or MMAO, exhibited high activities of up to 4.0×10^7 g (mol of Fe)⁻¹ h⁻¹ for ethylene oligomerization and polymerization. The iron(II) precatalysts generally showed higher activities and produced a wider distribution of products (including oligomers and polyethylene) than did their corresponding cobalt(II) analogues. The bimetallic precatalysts exhibited higher (almost twice) activities in comparison to their monometallic analogues. The distribution of the resulting oligomers closely resembled the Schultz–Flory rule.

INTRODUCTION

Binuclear complexes in catalysis are of interest due to potential synergistic effects.¹ Some attention has been paid to bimetallic complex precatalysts for ethylene reactivity,² and recently this was discussed in a review article.3 For reported group IVB bimetallic complexes in olefin polymerization, their use has commonly produced polymers of lower molecular weight and broader polydispersity than are observed for their monometallic analogues.^{2a,4} Other approaches have involved the combination of early and late transition metals for dual functions during ethylene oligomerization and copolymerization.⁵ Probably due to the relative stabilities of the bimetallic complexes, there are more examples of late-transition-metal systems,^{2h,j,l,6} partic-ularly of nickel and palladium binuclear complexes,^{2f,i,l,6c-g,7} which tend to produce branched polyethylenes. In contrast, iron and cobalt complex precatalysts commonly polymerize ethylene, resulting in highly linear products,⁸ including highdensity polyethylene and polyethylene waxes.⁹ A limited number of binuclear iron or cobalt complex precatalysts have been developed,^{2h,j,k} and model ligand sets using benzodiazepine to fuse the bis(imino)pyridyl and mono(imino)pyridyl frameworks provided highly efficient precatalysts,^{2j,k} in which the sp³ N of the benzodiazepine was not coordinated to the metal center. However, we recently developed a number of bidentate N[^]N ligands for iron and cobalt complexes, which revealed good activity for ethylene polymerization at elevated pressure of ethylene.¹⁰ Subsequently, our new target model



utilizes solely sp² N ligands and contains both N^N^N and N^N coordination environments. The centrally fused ring is constructed from the 3*H*-benzazepine motif instead of the benzodiazepine within 2,4-bis(6-ketiminopyridin-2-yl)-1*H*-1,5-benzodiazepines, and thus the 2,4-bis(6-acetylpyridin-2-yl)-3*H*-benzazepine ligand set was successfully prepared. The resultant mono- and bimetallic iron(II)/cobalt(II) complexes, upon activation with MAO, revealed high activities toward ethylene oligomerization and polymerization. Herein, the synthesis and characterization of the organic compounds and their metal complexes in ethylene oligomerization and polymerization is discussed.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Organic Compounds and Their Metal (Iron or Cobalt) Complexes. The reaction of 2,6-diacetylpyridine and 2-fluorobenzenamine resulted in the formation of a benzazepinyl ring,¹¹ which was exploited for connecting two acetylpyridines to afford a novel 2,4-bis(6-acetylpyridin-2-yl)-3H-benzazepine (1). This new ligand set was fully characterized, and its structure was confirmed by single-crystal X-ray diffraction. With use of the two acetyl groups of 1, further reaction with two anilines

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Scheme 1. Synthetic Procedure



afforded the corresponding compounds 2,4-bis(6-(1-aryliminoethyl)pyridin-2-yl)-3H-benzazepines (Ln; Scheme 1), all of which were fully characterized by elemental analysis and ¹H and ¹³C NMR and FT-IR spectroscopy.

With multiple coordination sites potentially available for hosting two metal ions, these compounds (Ln) were reacted with MCl_2 (M = Fe, Co), and depending on the molar ratio of metal chlorides employed, the stepwise formation of the corresponding monometallic (M1-*n*) and bimetallic complexes (M2-n) (Scheme 1) proved possible. In their IR spectra, the $\nu_{C=N}$ stretching frequencies upon coordination shifted to lower values $(1620-1632 \text{ cm}^{-1})$ in comparison to those of the free ligands (1639-1650 cm⁻¹). Notably, there are two peaks assigned to the $\nu_{\rm C=N}$ stretching frequencies for each monometallic complex, due to the presence of the two different C=N groups: viz., one coordinated to the metal and the other free. In contrast, only one peak is assigned to the $\nu_{C=N}$ stretching frequency when both C=N groups are coordinated to ions of the same metal. The metal complexes of both the monometallic LMCl₂ (M1-n) and bimetallic L(MCl₂)₂ (M2-n) forms were consistent with their elemental analytic data. In addition, the unambiguous structure of a representative monocobalt complex, Co1-1, was confirmed by single-crystal X-ray diffraction.

X-ray Crystallographic Studies. Single crystals of 2,4bis(6-acetylpyridin-2-yl)-3*H*-benzazepine and 2,4-bis(6-(1-(2,6diisopropylphenylimino)ethyl)pyridin-2-yl)-3*H*-benzazepine (L3) were grown from their respective dichloromethane solutions, while single crystals of the cobalt complex Co1-1 were obtained by laying *n*-pentane onto its tetrahydrofuran (THF) solution at room temperature. The molecular structures were confirmed by single-crystal X-ray diffraction and are shown in Figure 1 (2,4-bis(6-acetylpyridin-2-yl)-3*H*-benzazepine (1)), Figure 2 (2,4-bis(6-(1-(2,6-diisopropylphenylimino)ethyl)pyridin-2-yl)-3*H*-benzazepine (L3)) and Figure 3 (the monocobalt complex Co1-1); selected bond lengths and angles are given in Table 1.

As shown in Figures 1–3, the seven-membered rings are each constructed by C8, C9, C14–C17, and N2, individually. The C(15)-C(16) bonds have typical double-bond character with lengths of 1.334(3) (1), 1.322(3) (L3), and 1.378(8) Å (Col-1), while the C(16)-C(17) bond lengths are typical of single bonds at 1.498(3) (1), 1.494(3) (L3), and 1.507(8) Å (Col-1). The bond lengths of N(2)–C(8) are 1.296(2) (1),



Figure 1. ORTEP drawing of 2,4-bis(6-acetylpyridin-2-yl)-3*H*-benzazepine (1). Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity.

1.296(3) (L3), and 1.291(7) Å (Col-1), indicative of double-bond character. As shown in Figure 3, the monocobalt complex Col-1 possesses a pentacoordinate pseudo-squarepyramidal geometry at cobalt constructed from the three nitrogen atoms N(1), N(2), and N(4) and two chlorine atoms; the chlorides Cl(1) and Cl(2) are bonded as observed for the bis(imino)pyridylmetal chlorides.¹² The cobalt atom is almost planar to the chelating plane (N1–N2–N4) with a ca. 0.043 Å deviation, which is much less than for other $\hat{N}^{\hat{N}}N^{\hat{N}}N$ tridentate iron/cobalt complexes.¹³ The chlorides (Cl1 and Cl2) are located in trans positions relative to the chelate plane. The chelate plane and the iminophenyl plane (C18-C23) are nearly perpendicular with a dihedral angle of ca. 88.40°. Thus, the substituent R¹ will protect the active site efficiently and this is also why the steric bulk of R1 affected the catalytic performance (vide infra). However, the phenyl plane (C1-C6) from the other arm of the pyridine was not as perpendicular with the chelated plane (with a dihedral angle of ca. 55.37°). This dramatically decreases the protecting effect and thus leads to the production of oligomers rather than polymeric products. The availability of N3 and N5 for coordination of another metal can also be clearly seen from



Figure 2. ORTEP drawing of 2,4-bis(6-(1-(2,6-diisopropylphenylimino)ethyl)pyridin-2-yl)-3H-benzazepine (L3). Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity.



Figure 3. ORTEP drawing of the monocobalt complex Co1-1. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity.

the molecular structure. Despite our ability to obtain crystalline products, these compounds proved not to be suitable for singlecrystal X-ray diffraction.

Catalytic Behavior toward Ethylene. The mono-/ bimetallic Fe/Co complexes were systematically investigated for ethylene oligo-/polymerization. MAO and MMAO were evaluated as suitable cocatalysts to activate the title complexes for ethylene oligomerization/polymerization reactions. The results are summarized in Tables 2 (catalytic results for the diiron complexes), 3 (comparison of the catalytic behavior between monoiron complexes and diiron complexes), 4

Table	1. Selected	Bond	Lengths	and	Angles	for (Compo	ound	1
1, L3,	and Co1-1								

	1	L3	Co1-1
	Bond Lengths	(Å)	
N(2) - C(8)	1.296(2)	1.296(3)	1.291(7)
C(15) - C(16)	1.334(3)	1.322(3)	1.378(8)
C(16) - C(17)	1.498(3)	1.494(3)	1.507(8)
O(1) - C(2)	1.213(2)		
O(2)-C(23)	1.221(3)		
N(4) - C(2)		1.271(3)	1.261(8)
N(5)-C(23)		1.268(2)	1.233(8)
Co-N(1)			1.967(5)
Co-N(2)			2.172(5)
Co-N(4)			2.165(5)
	Bond Angles (d	leg)	
C(3)-N(1)-C(7)	117.31(15)	118.28(19)	123.3(5)
C(8) - N(2) - C(9)	122.02(17)	122.0(2)	122.2(5)
N(1)-C(3)-C(2)	116.89(17)	115.88(19)	114.8(6)
N(1)-C(7)-C(8)	115.91(16)	116.21(18)	113.2(5)
O(1) - C(2) - C(3)	120.1(2)		
O(2) - C(23) - C(22)	119.4(2)		
C(23) - N(5) - C(33)		120.44(17)	121.8(6)
C(2)-N(4)-C(25)		122.1(2)	120.5(5)
N(1)-Co-N(4)			77.67(19)
N(1)-Co-N(2)			78.05(19)
N(4)-Co-N(2)			155.65(18)
Cl(1)-Co-Cl(2)			128.22(7)

(catalytic results for the dicobalt complexes), and 5 (comparison of the catalytic behavior between monocobalt complexes and dicobalt complexes).

Ethylene Oligomerization/Polymerization Promoted by Iron Complexes. MAO and MMAO were initially used to activate complex Fe2-1 for ethylene reactivity at room temperature (entries 1 and 2, Table 2). The catalytic system activated by MMAO showed much higher activities for ethylene oligometization and polymerization with higher K values than when MAO was employed. Therefore, further catalytic studies were conducted via activation with MMAO and are given in Table 2.

Effects of Al/Fe Molar Ratio and Reaction Temperature on Catalyst Behavior. In the catalytic system Fe2-1/ MMAO, the molar radio of Al/Fe plays a significant role in the activity for ethylene oligomerization/polymerization. When the Al/Fe molar ratio was increased over the range 500-2000 (entries 2-5, Table 2), the best activity was observed with the optimized Al/Fe molar ratio of 1000. However, the K value was not affected as much and fluctuated near a value of 0.51. With the Al/Fe molar ratio fixed at 1000, the reaction temperature was varied from 0 to 80 °C (entries 2 and 6-9, Table 2). Similar to the case for other iron catalytic systems, the activity for ethylene oligomerization/polymerization decreased on increasing the reaction temperature. This is because of the instability of the active species (decomposition), together with low ethylene solubility in the reaction solution at higher temperature.¹⁵ Thus, the highest activity, as high as 2.36×10^6 g (mol of Fe)⁻¹ h⁻¹ for ethylene oligomerization and 0.41 \times 10^6 g (mol of Fe)⁻¹ h⁻¹ for ethylene polymerization, was obtained at the reaction temperature of 0 °C (entry 6, Table 2). Moreover, a higher reaction temperature always led to a higher percentage of butene and a lower K value. This indicated that chain termination is facile at elevated temperatures.¹⁶ Notably,

Tab	le 2.	Cata	lytic	Results	of	Ethy	lene	Oligo	merizati	on/l	Pol	ymerizatio	n"
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oligomer ^b											
entry	t (min)	Al/Fe	T (°C)	activity ^c	$\sum C_4 / \sum C^d$	$\sum C_6 / \sum C^d$	$\sum C_8 / \sum C^d$	α -C/ \sum C ^d	K ^e	polymer activity ^c	polymer (wt %) ^f
1^g	30	1000	20	1.06	60.6	21.1	8.23	>99	0.47	0.13	10.9
2	30	1000	20	1.95	55.7	24.8	10.5	>99	0.51	0.44	18.4
3	30	500	20	0.95	58.8	22.9	9.82	>99	0.52	0.31	24.6
4	30	1500	20	1.58	55.1	24.5	10.8	>99	0.51	0.37	19.0
5	30	2000	20	1.34	54.8	24.7	11.1	>99	0.50	0.34	20.2
6	30	1000	0	2.36	49.8	23.8	11.6	>99	0.56	0.41	14.8
7	30	1000	40	1.32	60.1	22.1	10.5	>99	0.52	0.31	19.0
8	30	1000	60	0.81	61.0	21.0	10.1	>99	0.50	0.25	23.6
9	30	1000	80	0.46	61.7	20.8	10.0	>99	0.48	0.12	20.7
10	5	1000	0	5.41	56	19.9	10	>99	0.61	1.49	21.6
11	10	1000	0	4.33	54.9	21.1	10.9	>99	0.59	1.14	20.8
12	15	1000	0	3.60	52	21.6	11.1	>99	0.60	0.89	19.8
13	20	1000	0	3.43	51.1	22.8	11.4	>99	0.56	0.81	19.1
14	40	1000	0	1.78	48	24.1	11.9	>99	0.57	0.41	18.7
15	60	1000	0	1 19	47	247	127	>00	0.58	0.27	18.5

^{*a*}General conditions: cat., 1.0 μ mol of **Fe2-1**; ethylene pressure, 1 atm; solvent, toluene (30 mL); cocatalyst, MMAO. ^{*b*}Determined by GC. ^{*c*}In units of 10⁶ g (mol of Fe)⁻¹ h⁻¹. ^{*d*} $\sum C_4$, $\sum C_6$, $\sum C_8$, and $\sum C$ denote the total amounts of butene, hexene, octene, and oligomers in mol %, respectively. ^{*e*}K = (rate of propagation)/[(rate of propagation) + (rate of chain transfer)] = (mol of C_{14})/(mol of C_{12}).¹⁴ fThe percentage of polyethylene waxes. ^{*g*}The cocatalyst is MAO.

Ta	ble	3.	Catal	ytic	Results	Based	on	Various	Iron	Comp	lexes'	Ļ
1 a	ble	3.	Catar	ytic	Results	Based	on	various	Iron	Comp	lexes	

		oligomer ^b											
entry	cat.	P (atm)	activity ^c	$\sum C_4 / \sum_{\%} C^d \pmod{mol}$	$\sum_{C_6/} C_6/$	\sum_{C_8/C^d}	${\Delta - \mathrm{C}/ \over \sum \mathrm{C}^d}$	K ^e	polymer activity ^c	$\operatorname{PE}^{f}(wt)$	${T_{\rm m}}^g$ (°C)	$M_{ m w}^{\ h}$	$M_{ m w'h}/M_{ m n}$
1	Fe1-1	1	1.51	51.2	25.0	10.6	>99	0.56	0.33	18.0			
2	Fe2-1	1	2.36	49.8	23.8	11.6	>99	0.59	0.41	14.8			
3	Fe1-2	1	1.41	50.1	23.1	11.3	>99	0.54	0.28	16.7			
4	Fe2-2	1	2.12	49.1	24.1	11.7	>99	0.57	0.38	15.1			
5	Fe1-3	1	1.05	50.5	22.9	11.2	>99	0.53	0.19	15.3			
6	Fe2-3	1	2.10	52.7	19.7	9.98	>99	0.56	0.47	18.4			
7	Fe1-4	1	1.61	55.8	18.7	10.3	>99	0.60	0.36	18.4			
8	Fe2-4	1	2.40	51.4	19.5	12.2	>99	0.63	0.49	16.9			
9	Fe1-5	1	1.55	58.2	15.6	9.51	>99	0.58	0.31	16.9			
10	Fe2-5	1	2.32	52.5	17.7	10.6	>99	0.61	0.46	16.5			
11	Fe1-1	10	29.8	57.8	23.8	9.35	>99	0.53	3.5	10.5	69.0	898	1.47
12	Fe2-1	10	34.1	51.5	24.8	10.8	>99	0.56	3.77	9.9	73.3	3145	1.74
13	Fe1-2	10	27.1	51.2	25.5	13.4	>99	0.51	4.00	12.9	129.3	17700	4.3
14	Fe2-2	10	33.9	47.1	27.9	15.1	>99	0.52	5.85	14.7	130.0	21800	6.3
15	Fe1-3	10	23.1	53.8	24.0	11.9	>99	0.49	3.31	12.5	130.2	14198	2.97
16	Fe2-3	10	29.8	46.7	25.6	14.9	>99	0.49	4.90	14.1	126.3	22554	8.9
17	Fe1-4	10	31.1	56.3	15.4	11.1	>99	0.56	4.70	13.1	124.4	1916	1.66
18	Fe2-4	10	35.1	54.1	16.6	11.9	>99	0.60	4.97	12.4	124.6	14766	1.83
19	Fe1-5	10	30.1	61.5	15.2	8.23	>99	0.55	2.79	8.5	80.9	1365	2.07
20	Fe2-5	10	34.5	55.3	20.6	15.8	>99	0.58	3.33	8.8	92.3	7417	1.48

^{*a*}General conditions: 2.0 μ mol Fe; solvent, toluene (30 mL for 1 atm and 100 mL for 10 atm); cocatalyst, MMAO (Al/Fe = 1000); reaction temperature, 0 °C; reaction time, 30 min. ^{*b*}Determined by GC. ^{*c*}In units of 10⁶ g (mol of Fe)⁻¹ h⁻¹. ^{*d*} $\sum C_4$, $\sum C_6$, $\sum C_8$, and $\sum C$ denote the total amounts of butene, hexene, octene, and oligomers in mol %, respectively. ^{*c*}K = (rate of propagation)/[(rate of propagation) + (rate of chain transfer)] = (mol of C₁₄)/(mol of C₁₂).¹⁴ ^{*f*}Percentage of polyethylene. ^{*g*}Determined by DSC. ^{*h*}Determined by GPC.

all complex precatalysts produced α -olefins with a high selectivity of over 99% (α -C/ Σ C).

Lifetime of the Catalytic System. The diiron complexes were found to deactivate over a relatively short time even at low temperature. As an example, the relationship between time and activity was studied for Fe2-1/MMAO, and the activity was found to be almost reduced by half when lengthening the reaction time from 5 to 30 min (entries 6 and 10, Table 2). After 30 min, very few oligomers and/or polymers were

produced. This indicates that the active catalytic species were deactivated in the first 30 min. However, the butene content and the K value were not as affected and proved to be quite stable over time.

Comparison of Catalytic Behavior between the Iron Complex Precatalysts Fe1-*n* and Fe2-*n* (n = 1-5). The catalytic activities of the diiron complexes are significantly affected by the bulkiness of the substituents at the imino-*N* aryl ring as well as by the coordination number of the metal. The catalytic tests of **Fe1**-*n* and **Fe2**-*n* (n = 1-5) were conducted at both 1 and 10 atm, and the results are given in Table 3. When the steric bulk of the substituent R¹ was increased, the activities decreased slightly for both the diiron and the monoiron complexes at 1 atm (entries 1–6, Table 3) and 10 atm (entries 11–16, Table 3). This is probably due to the bulky substituent inhibiting the insertion of the monomer.¹⁷ Moreover, the addition of a methyl group at the *para* position of the *N*-aryl ring also leads to a slight increase of the catalytic activity at both 1 atm (entries 1–4 and 7–10, Table 3) and 10 atm (entries 11–14 and 17–20, Table 3).

Notably, the diiron complexes are always much more active for ethylene oligomerization/polymerization with a higher Kvalue than the corresponding monoiron complexes. An example of a comparison of the product distribution is illustrated in Figure 4. It clearly shows that the diiron complexes tend to



Figure 4. Comparison of the distribution of oligomers produced by Fe1-1 and Fe2-1 (Table 3, entries 11 and 12).

produce longer-chain oligomers than do the corresponding monoiron complexes; this is attributed to the existence of synergistic effects from the dimetal complexes.

Moreover, the polyethylene samples obtained at 10 atm were evaluated (entries 11–20, Table 3), which revealed that the diiron complex precatalysts produce polyethylene with higher molecular weights and wider polydispersity than do the corresponding monoiron analogues. Higher melting points were observed for polyethylene, indicating high linearity, which was confirmed by ¹³C NMR spectroscopic measurements (in Figure 5) for the polyethylene obtained in entry 14 of Table 3.

Ethylene Oligomerization Promoted by Cobalt Complexes. In contrast to the iron catalysts, the cobalt complexes exhibited much higher activity for ethylene oligomerization/ polymerization in the presence of MAO than in the presence of MMAO (entries 1 and 2, Table 4); however, the product distribution ($C_4/\Sigma C$, $C_6/\Sigma C$, $C_8/\Sigma C$, and α -C/ ΣC) and *K* values were quite similar between the catalytic systems Co2-1/ MAO (entry 2, Table 4) and Co2-1/MMAO (entry 1, Table 4). Thus, further catalytic studies were conducted via activation with MAO, as given in Table 4.

Using MAO as the cocatalyst, the precatalyst **Co2-1** showed trends with regard to the reaction temperature, time, and Al/ Co molar ratio (entries 2–15 in Table 4) similar to those of the iron complexes. The optimized reaction conditions were found to be 20 °C and an Al/Co molar ratio of 1500 (entry 4, Table 4), for which the activity and *K* value were 1.19×10^6 g (mol of Co)⁻¹ h⁻¹ and 0.67, respectively. However, different from the iron complexes, which are active for both ethylene polymerization and oligomerization, the cobalt complexes only exhibited activity for ethylene oligomerization and no polymer was detected. Moreover, the selectivity for butene of the cobalt complexes (about 80%) was much higher than that of the iron complexes to create longer-chain products than the cobalt complexes.

The relationship between the catalytic performance of Co2-1/MAO and the reaction time was also conducted, and the results are shown in Table 4 (entries 6 and 10–15). The activity was maintained at a relatively high value (about 1.5 × 10^6 g (mol of Co)⁻¹ h⁻¹) over the first 20 min (entries 10–13), after which the activity declined linearly (entries 6, 14, and 15).

Comparison of the Catalytic Behavior between Co1-n and Co2-*n* (n = 1-5). The catalytic activities of mono-/ dicobalt complexes were also greatly affected by the sterics of the ligand set (Table 5). Interestingly, the steric bulk effect of the ligand on the activity of the monocobalt complexes versus the dicobalt complexes produced diametrically opposite trends. At both 1 and 10 atm, the activity declined slowly on increasing the bulkiness of \mathbb{R}^1 for the monocobalt complexes (entries 1, 3, 5, 11, 13, and 15, Table 5). In contrast, complexes with bulkier R¹ substituents showed higher activity for the dicobalt catalysts (entries 2, 4, 6, 12, 14, and 16, Table 5). However, the addition of a methyl group at the para position of the N-aryl ring also led to an increase of the catalytic activity, at both 1 atm (entries 1-4 and 7-10, Table 5) and 10 atm (entries 11-14 and 17-20, Table 5), similar to the case for the iron complexes. The dicobalt complexes always exhibited much higher activity than



Figure 5. ¹³C NMR spectrum of polyethylene (entry 14, Table 3).

Table 4. Catalytic Results Based on Co2-1/MAO^a

				oligomer ^ø							
entry	t (min)	Al/Co	T (°C)	activity ^c	$C_4/\sum C^d$	$C_6 / \sum C^d$	$C_8/\sum C^d$	α -C/ \sum C ^d	K^{e}		
1^{f}	30	1000	20	0.34	77	14.1	4.1	>99	0.61		
2	30	1000	20	0.84	80.0	13.2	3.83	>99	0.59		
3	30	1250	20	0.99	82.0	12.6	3.05	>99	0.64		
4	30	1500	20	1.19	83.7	11.9	2.61	>99	0.67		
5	30	1750	20	1.00	80.6	13.2	3.58	>99	0.60		
6	30	2000	20	0.99	80.1	13.2	3.45	>99	0.55		
7	30	1500	0	0.93	81.3	12.6	3.59	>99	0.58		
8	30	1500	40	0.68	84.1	11.4	3.01	>99	0.59		
9	30	1500	60	0.32	86.2	9.13	2.54	>99	0.57		
10	5	1500	20	1.81	80.6	12.4	4.86	>99	0.64		
11	10	1500	20	1.77	81.1	12.0	4.46	>99	0.59		
12	15	1500	20	1.65	82.0	11.8	3.76	>99	0.54		
13	20	1500	20	1.51	82.0	11.7	3.01	>99	0.56		
14	40	1500	20	0.90	83.6	12.0	2.65	>99	0.50		
15	60	1500	20	0.63	83.8	11.3	2.75	>99	0.49		

^{*a*}General conditions: cat., 1.0 μ mol of **Co2-1**; ethylene pressure, 1 atm; solvent, toluene (30 mL); cocatalyst, MAO. ^{*b*}Determined by GC. ^{*c*}In units of 10⁶ g (mol of Co)⁻¹ h⁻¹. ^{*d*} $\sum C_4$, $\sum C_6$, $\sum C_8$, and $\sum C$ denote the total amounts of butene, hexene, octene and oligomers in mol %, respectively. ^{*e*}K = (rate of propagation)/[(rate of propagation) + (rate of chain transfer)] = (mol of C₁₄)/(mol of C₁₂).¹⁴ f⁻The cocatalyst is MMAO.

Table 5. Catalytic Results Based on Cobalt Complexes^a

			oligomer							
entry	cat.	P (atm)	activity ^c	$\sum C_4 / \sum C^d$	$\sum C_6 / \sum C^d$	$\sum C_8 / \sum C^d$	α -C/ \sum C ^d	K ^e		
1	Co1-1	1	0.61	88.1	8.90	2.04	>99	0.40		
2	Co2-1	1	1.19	83.7	11.9	2.61	>99	0.67		
3	Co1-2	1	0.65	92.0	5.30	1.53	>99	0.49		
4	Co2-2	1	0.98	85.7	10.2	2.33	>99	0.64		
5	Co1-3	1	0.74	79.4	13.5	4.22	>99	0.52		
6	Co2-3	1	0.89	70.1	17.4	6.87	>99	0.57		
7	Co1-4	1	1.25	87.0	10.0	2.00	>99	0.56		
8	Co2-4	1	1.33	80.0	14.1	4.23	>99	0.58		
9	Co1-5	1	1.12	92.0	5.30	1.53	>99	0.49		
10	Co2-5	1	1.48	81.7	14.0	4.11	>99	0.61		
11	Co1-1	10	9.70	77.1	10.1	3.01	>99	0.49		
12	Co2-1	10	14.9	71.1	11.5	3.53	>99	0.51		
13	Co1-2	10	11.3	80.1	6.65	2.54	>99	0.47		
14	Co2-2	10	13.7	78.9	7.12	2.78	>99	0.52		
15	Co1-3	10	12.5	82.1	6.70	2.58	>99	0.49		
16	Co2-3	10	13.1	74.1	9.12	3.19	>99	0.56		
17	Co1-4	10	13.9	65.3	11.0	3.82	>99	0.57		
18	Co2-4	10	17.4	64.9	11.2	3.71	>99	0.58		
19	Co1-5	10	14.9	67.1	10.1	3.85	>99	0.52		
20	Co2-5	10	16.6	60.1	12.1	4.01	>99	0.57		

^{*a*}General conditions: cat., 2.0 μ mol of Co; solvent, toluene (30 mL for 1 atm and 100 mL for 10 atm); cocatalyst, MMAO (Al/Co = 1000); reaction temperature, 0 °C; reaction time, 30 min. ^{*b*}Determined by GC. ^{*c*}In units of 10⁶ g (mol of Co)⁻¹ h⁻¹. ^{*d*} $\sum C_4$, $\sum C_6$, $\sum C_8$, and $\sum C$ denote the total amounts of butene, hexene, octene, and oligomers in mol %, respectively. ^{*e*}K = (rate of propagation)/[(rate of propagation) + (rate of chain transfer)] = (mol of C₁₄)/(mol of C₁₂).¹⁴

the corresponding monocobalt complexes for ethylene oligomerization, which is attributed to synergistic effects.

CONCLUSION

A new series of iron/cobalt complexes ligated by 2,4-bis(6iminopyridin-2-yl)-3*H*-benzazepines have been synthesized and fully characterized. Reaction of the 2,4-bis(6-iminopyridin-2yl)-3*H*-benzazepines with iron/cobalt dichloride in 1/1 and 1/2 molar ratios afforded monometal and dimetal complexes, respectively. The free $\nu_{C=N}$ bond stretching frequency was clearly detected by FT-IR spectroscopy (around 1640 cm⁻¹) in the monometal complexes. Elemental analysis of these complexes can be used to further confirm the mono- or bimetallic nature of the complexes. All complexes have been evaluated as catalysts for ethylene oligomerization/polymerization, and the results showed that the dimetallic (both Fe and Co) complexes always exhibited much higher activity than did the corresponding monometallic complexes. Additionally, the iron complexes always showed much higher activities and higher *K* values for ethylene oligomerization than did the cobalt complexes. The activity obtained by the diiron complexes can be as high as 4.0×10^7 g (mol of Fe)⁻¹ h⁻¹ with high α -olefin

Organometallics

selectivity (>99%). Furthermore, the substituents on the *N*-aryl rings had an obvious influence on the catalytic activity as well as the distribution of products.

EXPERIMENTAL SECTION

General Considerations. All manipulations of air- and/or moisture-sensitive compounds were carried out under a nitrogen atmosphere using standard Schlenk techniques. Toluene was refluxed over sodium benzophenone and distilled under nitrogen prior to use. Methylaluminoxane (MAO, 1.46 M solution in toluene) and modified methylaluminoxane (MMAO, 1.93 M in heptane, 3A) were purchased from Akzo Nobel Corp. High-purity ethylene was purchased from Beijing Yansan Petrochemical Co. and used as received. Other reagents were purchased from Aldrich, Acros, or local suppliers. NMR spectra were recorded on a Bruker DMX 400 MHz instrument at ambient temperature using TMS as an internal standard. FT-IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer. Elemental analysis was carried out using an HPMOD 1106 microanalyzer. GC analysis was performed with a Agilent Technologies 7890A gas chromatograph equipped with a flame ionization detector and a 30 m column (0.2 mm i.d., 0.25 mm film thickness). MALDI-TOF spectroscopy was conducted on a Bruker Autoflex III instrument, using CCA as the substrate. Molecular weights (M_w) and molecular weight distributions (M_w/M_n) of polyethylenes were determined by a PL-GPC220 instrument at 150 °C with three PLgel 10 µm MIXED-B columns and 1,2,4-trichlorobenzene as the solvent. Melting points of polyethylenes were obtained from the second scanning run on a Q2000 DSC-7 instrument at a heating rate of 10 °C min⁻¹ to 150 °C.

Synthesis and Characterization of 2,4-Bis(6-acetylpyridin-2yl)-3H-benzazepine. A solution of 1 equiv of 2,6-diacetylbrydine (8.15 g, 50 mmol), 1.5 equiv of *o*-fluoroaniline (8.32 g, 75 mmol), and a catalytic amount of p-toluenesulfonic acid (0.5 g) in toluene (200 mL) was refluxed for 8 h. The solvent was evaporated at reduced pressure, and the residue was then purified by column chromatography (silica gel, petroleum ether/ethyl acetate 5/1 v/v) to afford the desired compound (yellow solid, 2.00 g, 21% yield). Mp: 138-139 °C. FT-IR (KBr disk, cm⁻¹): 1693 ($\nu_{C=0}$), 1575, 1560, 1450, 1361, 1310, 1240, 1111, 1069, 954, 896, 823, 759. ¹H NMR (400 MHz, CDCl₃): δ 8.50 $(d, J = 7.9 \text{ Hz}, 1\text{H}, \text{Py } H_{\text{m}}), 8.05 (d, J = 7.6 \text{ Hz}, 1\text{H}, \text{Py } H_{\text{m}}), 7.83 (d, J)$ = 7.8, 1H, Py $H_{\rm m}$), 7.94 (d, J = 7.6 Hz, 1H, Py $H_{\rm m}$), 7.89 (t, J = 7.8 Hz, 1H, Py H_p), 7.83 (t, J = 7.8 Hz, 1H, Py H_p), 7.73 (s, 1H, CH), 7.62 (t, J = 9.2 Hz, 2H, Ar H), 7.49 (t, J = 7.6 Hz, 1H, Ar H), 7.33 (t, J = 7.5Hz, 1H, Ar H), 3.99 (s, 2H, CH₂), 2.77 (s, 3H, CH₃), 2.60 (s, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 200.4, 199.5, 157.9, 155.9, 154.4, 153.3, 152.6, 147.1, 137.7, 134.3, 131.2, 130.0, 129.5, 128.3, 128.0, 125.1, 124.2, 122.6, 120.1, 28.9, 25.7. Anal. Calcd for C₂₄H₁₉N₃O₂ (381): C, 75.57; H, 5.02; N, 11.02. Found: C, 75.27; H, 5.15; N, 11.36.

Syntheses and Characterizations of 2,4-Bis[6-(1aryliminoethyl)pyridin-2-yl]-3H-benzazepines L1-L5. A representative synthesis is as follows: a solution of 2,4-bis(6-acetylpyridin-2yl)-3H-benzazepine (0.38 g, 1.0 mmol), 2,6-dimethylaniline (0.27 g, 2.2 mmol), and a catalytic amount of p-toluenesulfonic acid (0.03 g) were refluxed in toluene (25 mL) for 6 h. Molecular sieves (4 Å, 2 g) were added to remove water. After filtration and solvent evaporation, the crude product was purified by column chromatography (silica gel, petroleum ether/ethyl acetate 30/1 v/v). 2,4-Bis{6-[1-(2,6dimethylphenylimino)ethyl]pyridin-2-yl}-3H-benzazepine (L1) was collected and concentrated, giving a yellow solid (0.29 g, 43% yield). Mp: 140-141 °C. FT-IR (KBr disk, cm⁻¹): 3017, 2940, 2851, 1644 ($\nu_{C=N}$), 1616, 1593, 1566, 1468, 1455, 1436, 1364, 1338, 1317, 1206, 1113, 1093, 810, 761. ¹H NMR (400 MHz, $CDCl_3$): δ 8.41 (d, J = 7.9 Hz, 1H, Py H_m), 8.38 (d, J = 7.7 Hz, 1H, Py H_m), 8.27 (d, J = 7.8 Hz, 1H, Py $H_{\rm m}$), 7.91 (d, J = 7.7 Hz, 1H, Py $H_{\rm m}$), 7.87 (t, J = 7.8 Hz, 1H, Py H_p), 7.77 –7.70 (m, 2H, Py H_p + CH), 7.65 (d, J = 8.0 Hz, 1H, Ar H), 7.61 (d, J = 7.7 Hz, 1H, Ar H), 7.47 (t, J = 7.1 Hz, 1H, Ar H), 7.31 (t, J = 7.1 Hz, 1H, Ar H), 7.06 (t, J = 8.0 Hz, 4H, Ar H), 6.99-6.90 (m, 2H, Ar H), 4.01 (s, 2H); 2.21 (s, 3H, CH₃), 2.06 (s, 3H, CH₃), 1.99 (s, 6H, 2 × CH₃), 1.95 (s, 6H, 2 × CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 167.5, 167.1, 158.8, 155.8, 155.6, 155.4, 154.1, 148.9, 148.8, 147.3, 137.2, 137.1, 135.3, 131.2, 129.8, 129.4, 128.3, 128.1, 128.0, 127.7, 125.5, 124.8, 124.7, 123.3, 123.2, 122.2, 119.8, 29.4, 18.1, 18.0, 16.7, 16.6. Anal. Calcd for C₄₀H₃₇N₅ (588): C, 81.74; H, 6.35; N, 11.92. Found: C, 81.37; H, 6.15; N, 11.56.

2,4-Bis{6-[1-(2,6-diethylphenylimino)ethyl]pyridin-2-yl}-3H-benzazepine (L2). In a manner similar to that described for L1, L2 was also prepared in 49% yield as a yellow solid. Mp: 141-142 °C. FT-IR (KBr disk, cm⁻¹): 3057, 2963, 2931, 1872, 1638 ($\nu_{C=N}$), 1566, 1452, 1362, 1318, 1238, 1196, 1114, 1069, 820, 805, 762. ¹H NMR (400 MHz, CDCl₃): δ 8.41 (d, J = 7.8 Hz, 1H, Py $H_{\rm m}$), 8.37 (d, J = 7.6 Hz, 1H, Py $H_{\rm m}$), 7.93–7.84 (m, 2H, Py $H_{\rm m}$ + Py $H_{\rm p}$), 7.77–7.70 (m, 2H, Py $H_{\rm p}$ + CH), 7.65 (d, J = 8.1 Hz, 1H, Ar H), 7.60 (d, J = 7.7 Hz, 2H, Ar H), 7.47 (d, J = 7.5 Hz, 1H, Ar H), 7.30 (d, J = 7.4 Hz, 1H, Ar H), 7.10 (t, J = 8.2 Hz, 4H, Ar H), 7.07–7.00 (m, 2H, Ar H); 4.00 (s, 2H), 2.42-2.22 (m, 8H, CH₂), 2.21 (s, 3H, CH₃), 2.06 (s, 3H, CH₃), 1.10 (t, 6H, J = 7.6, 2 × CH₃), 1.03 (t, 6H, J = 7.6, 2 × CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 167.0, 166.6, 158.6, 155.6, 155.5, 155.3, 154.0, 147.8, 147.7, 147.1, 137.1, 136.9, 135.2, 131.1, 129.6, 129.3, 128.1, 127.5, 126.1, 136.0, 124.7, 124.5, 123.5, 123.3, 122.1, 119.6, 50.9, 29.3, 24.6, 1.8, 13.7. Anal. Calcd for C44H45N5 (647): C, 82.08; H, 7.04; N, 10.88. Found: C, 82.07; H, 7.15; N, 11.06.

2,4-Bis{6-[1-(2,6-biisopropylphenylimino)ethyl]pyridin-2-yl}-3Hbenzazepine (L3). In a manner similar to that described for L1, L3 was also prepared in 52% yield as a yellow solid. Mp: 234-235 °C. FT-IR (KBr disk, cm⁻¹): 3061, 2960, 2927, 2876, 1645 ($\nu_{C=N}$), 1566, 1453, 1381, 1364, 1317, 1260, 1238, 1191, 110, 1023, 868, 800, 767. ¹H NMR (400 MHz, CDCl₃): δ 8.41 (d, J = 7.7 Hz, 1H, Py H_m), 8.34 (d, J = 7.7 Hz, 1H, Py $H_{\rm m}$), 8.25 (d, J = 7.8, 1H, Py $H_{\rm m}$), 7.89–7.78 (m, 2H, Py H_m + Py H_p), 7.69 (m, 2H, Py H_p + CH), 7.62 (d, J = 8.0 Hz, 1H, Ar H), 7.7 (d, J = 7.7 Hz, 1H, Ar H), 7.43 (t, J = 7.5 Hz, 1H, Ar H), 7.26 (t, J = 7.4 Hz, 1H, Ar H), 7.12 (t, J = 6.2 Hz, 4H, Ar H), 7.09 (m, 2H, Ar H), 3.98 (s, 2H, CH_2), 2.73–2.50 (m, 4H, 4 × CH), 2.21 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 1.16–0.92 (m, 24H, 4 × CH_3). $^{13}\mathrm{C}$ NMR (100 MHz, CDCl₃): δ 166.4, 166.1, 160.0, 155.2, 154.8, 153.5, 146.6, 145.9, 136.6, 136.4, 135.2, 134.9, 130.6, 129.1, 128.8, 127.6, 127.1, 124.2, 124.1, 123.3, 123.1, 122.7, 122.5, 121.7, 119.2, 27.8, 22.7, 16.6. Anal. Calcd for C48H53N5 (700): C, 82.36; H, 7.63; N, 10.01. Found: C, 82.15; H, 7.36; N, 9.81.

2,4-Bis{6-[1-(2,4,6-trimethylphenylimino)ethyl]pyridin-2-yl}-3Hbenzazepine (L4). In a manner similar to that described for L1, L4 was also prepared in 34% yield as a yellow solid. Mp: 178-179 °C. FT-IR (KBr disk, cm⁻¹): 3051, 2963, 2941, 2913, 2855, 1642 ($\nu_{C=N}$), 1615, 1569, 1476, 1454, 1436, 1364, 1339, 1313, 1261, 1216, 1147, 1112, 1076, 1031, 1016, 852, 808, 756. ¹H NMR (400 MHz, CDCl₃): δ 8.39 (d, J = 8.0 Hz, 1H, Py H_m), 8.36 (d, J = 7.8 Hz, 1H, Py H_m), 8.25 (d, J = 7.8 Hz, 1H, Py $H_{\rm m}$), 7.90 (d, J = 7.6 Hz, 1H, Py $H_{\rm m}$), 7.86 $(t, J = 7.9 \text{ Hz}, 1\text{H}, \text{Py }H_{\text{p}}), 7.76-7.69 \text{ (m, 2H, Py }H_{\text{p}} + C\text{H}), 7.64 \text{ (d, }J$ = 8.0 Hz, 1H, Ar H), 7.60 (d, J = 7.6 Hz, 1H, Ar H), 7.47 (t, J = 7.6 Hz, 1H, Ar H), 7.30 (t, J = 7.4 Hz, 1H, Ar H), 6.89 (s, 2H, Ar H), 6.87 (s, 2H, Ar H), 3.99 (s, 2H, CH₂), 2.31 (s, 3H, CH₃), 2.29 (s, 3H, CH₃), 2.20 (s, 3H, CH₃), 2.05 (s, 3H, CH₃), 1.95 (s, 6H, 2 × CH₃), 1.92 (s, 6H, 2 × CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 167.8, 167.5, 158.8, 155.9, 155.5, 154.1, 147.3, 146.4, 146.3, 137.7, 137.2, 137.0, 135.3, 132.5, 132.4, 131.2, 129.8, 129.3, 128.8, 128.3, 127.7, 125.4, 125.3, 124.8, 125.7, 122.2, 121.8, 119.8, 29.4, 20.9, 18.0, 16.6. Anal. Calcd for C₄₂H₄₁N₅ (616): C, 81.92; H, 6.71; N, 11.37. Found: C, 82.11; H, 7.10; N, 10.99.

2,4-Bis{6-[1-(2,6-diethyl-4-methylphenylimino)ethyl]pyridin-2-yl]-3H-benzazepine (L5). In a manner similar to that described for L1, L5 was also prepared in 39% yield as a yellow solid. Mp: 188–189 °C. FT-IR (KBr disk, cm⁻¹): 3052, 2965, 2928, 2868, 2643 ($\nu_{C=N}$), 1566, 1458, 1364, 1334, 1247, 1211, 1145, 1115, 1074, 1033, 883, 813, 747, 622. ¹H NMR (400 MHz, CDCl₃): δ 8.42 (d, J = 7.7 Hz, 1H, Py H_m), 8.37 (d, J = 7.7 Hz, 1H, Py H_m), 8.27 (d, J = 7.8 Hz, 1H, Py H_m), 7.90 (d, J = 7.7 Hz, 1H, Py H_m), 7.87 (t, J = 7.8 Hz, 1H, Py H_p), 7.76–7.69 (m, 2H, Py H_p + CH), 7.65 (d, J = 8.0 Hz, 1H, Ar H), 7.61 (d, J = 7.7 Hz, 1H, Ar H), 7.47 (t, J = 7.3 Hz, 1H, Ar H), 7.31 (t, J = 7.4 Hz, 1H, Ar H), 6.93 (s, 2H, Ar H); 6.91 (s, 2H, Ar H), 4.00 (s, 2H, CH₂), 2.36 (d, *J* = 9.0 Hz, 3H, CH₃), 2.34 (s, 3H, CH₃), 2.33–2.24 (m, 8H, 4 × CH₂), 2.22 (s, 3H, CH₃), 2.07 (s, 3H, CH₃), 1.09 (t, *J* = 7.5 Hz, 6H, 2 × CH₃), 1.03 (t, *J* = 7.5 Hz, 6H, 2 × CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 167.2, 167.0, 156.0, 155.6, 154.1, 147.3, 145.3, 137.2, 137.0, 135.4, 132.7, 132.5, 131.2, 129.8, 129.3, 128.3, 127.6, 126.9, 126.8, 124.8, 124.6, 122.2, 122.1, 119.8, 29.4, 24.7, 21.2, 16.8, 14.0, 13.9. Anal. Calcd for C₄₆H₄₉N₅ (672): C, 82.23; H, 7.35; N, 10.42. Found: C, 82.11; H, 7.19; N, 10.11.

Synthesis of Complexes. Mononuclear Cobalt Complexes (Co1-n, n = 1-5). A representative synthesis of Co1-1 is as follows: a mixture of 2,4-bis{6-[1-(2,6-dimethylphenylimino)ethyl]pyridin-2-yl}-3H-benzazepine (L1); 0.10 mmol) and CoCl₂ (0.10 mmol) in THF (5 mL) was stirred for 8 h at room temperature. The precipitate was collected by filtration, washed with diethyl ether (3 × 5 mL), and then dried under vacuum to give Co1-1: yellow solid, 66.5% yield. FT-IR (KBr disk, cm⁻¹): 3422, 3065, 3018, 2960, 2915, 1646 ($\nu_{C=N}$), 1624 ($\nu_{C=N}$), 1582, 1466, 1366, 1268, 1208, 1166, 1094, 1030, 809, 770, 644. Anal. Calcd for C₄₀H₃₇Cl₂CoN₅ (716): C, 66.95; H, 5.20; N, 9.76. Found: C, 66.89; H, 5.47; N, 9.41. MS (MALDI-TOF, *m*/*z*): calcd 716.18, found 646.6 [M - 2Cl]⁺.

Co1-2: yellow solid, 70.3% yield. FT-IR (KBr disk, cm⁻¹): 3445, 3066, 2965, 2929, 2873, 1640 ($\nu_{C=N}$), 1626 ($\nu_{C=N}$), 1580, 1453, 1367, 1261, 1103, 806, 769, 665. Anal. Calcd for C₄₄H₄₅Cl₂CoN₅ (772): C, 68.30; H, 5.86; N, 9.05. Found: C, 67.94; H, 5.57; N, 9.09. MS (MALDI-TOF, *m/z*): calcd 772.24, found 702.6 [M - 2Cl]⁺.

Col-3: yellow solid, 65.5% yield. FT-IR (KBr disk, cm⁻¹): 3061, 2962, 2926, 2868, 1643 ($\nu_{C=N}$), 1631 ($\nu_{C=N}$), 1583, 1455, 1365, 1318, 1258, 1207, 1110, 800, 769, 664. Anal. Calcd for C₄₈H₅₃Cl₂CoN₅ (828): C, 69.48; H, 6.44; N, 8.44. Found: C, 65.45; H, 6.61; N, 8.21. MS (MALDI-TOF, *m*/*z*): calcd 828.30, found: 758.7 [M - 2Cl]⁺, 793.7 [M - Cl]⁺, 946.8 [M - 2Cl + CCA]⁺.

Co1-4: yellow solid, 65.1% yield. FT-IR (KBr disk, cm⁻¹): 3438, 2960, 2917, 2858, 1694, 1641 ($\nu_{C=N}$), 1630 ($\nu_{C=N}$), 1581, 1472, 1454, 1365, 1216, 1105, 1029, 855, 805, 664. Anal. Calcd for C₄₂H₄₁Cl₂CoN₅ (744): C, 67.65; H, 5.54; N, 9.39. Found: C, 67.23; H, 5.12; N, 9.50. MS (MALDI-TOF, *m*/*z*): calcd 744.21, found 674.7 [M - 2Cl]⁺.

Co1-5: yellow solid, 47.6% yield. FT-IR (KBr disk, cm⁻¹): 3443, 3057, 2965, 2928, 2873, 1644 ($\nu_{C=N}$), 1630 ($\nu_{C=N}$), 1582, 1458, 1367, 1259, 1211, 1108, 859, 808, 738, 665. Anal. Calcd. for C₄₆H₄₉Cl₂CoN₅ (800): C, 68.91; H, 6.16; N, 8.74. Found: C, 68.56; H, 6.08; N, 8.09. MS (MALDI-TOF, *m/z*): calcd 800.27, found 730.8 [M - 2Cl]⁺, 918.9 [M - 2Cl + CCA]⁺.

Dinuclear Cobalt Complexes **Co2-n** (n = 1-5). A representative synthesis of complex **Co2-1** is as follows: a mixture of 2,4-bis{6-[1-(2,6-dimethylphenylimino)ethyl]pyridin-2-yl}-3H-benzazepine (**L1**; 0.10 mmol) and 2 equiv of CoCl₂ (0.20 mmol) in THF (7 mL) was stirred for 8 h. The precipitate was collected by filtration, washed with diethyl ether (3×5 mL), and then dried under vacuum to afford **Co2-1**: blue solid, 51.5% yield. FT-IR (KBr disk, cm⁻¹): 3394, 2915, 1623 ($\nu_{C=N}$), 1584, 1465, 1560, 1465, 1428, 1365, 1256, 1207, 1097, 1028, 803, 777, 742. Anal. Calcd for C₄₀H₃₇Cl₄Co₂N₅ (847): C, 56.69; H, 4.40; N, 8.26. Found: C, 56.35; H, 4.45; N, 8.44. MS (MALDI-TOF, m/z): calcd 847.04, found 834.7 [M – 12]⁺, 681.5 [M – 12 – CCA + Cl]⁺.

Co2-2: blue solid, 60.3% yield). FT-IR (KBr disk, cm⁻¹): 3417, 3077, 2966, 2928, 2874, 1623 ($\nu_{C=N}$), 1584, 1560, 1460, 1429, 1371, 1257, 1212, 1110, 1060, 1030, 859, 813, 743, 663. Anal. Calcd for C₄₄H₄₅C₁₄Co₂N₅ (903): C, 57.62; H, 4.72; N, 8.00. Found: C, 57.43; H, 4.50; N, 7.75. MS (MALDI-TOF, *m/z*): calcd 903.11, found 891.2 [M - 12]⁺, 703.0 [M - 12 - CCA]⁺.

Co2-3: blue solid, 51.1% yield. FT-IR (KBr disk, cm⁻¹): 3421, 3065, 2964, 2925, 2866, 1621 ($\nu_{C=N}$), 1584, 1463, 1367, 1321, 1158, 1321, 1258, 1201, 1106, 801, 770, 664. Anal. Calcd for C₄₈H₅₃Cl₄Co₂N₅ (959): C, 60.08; H, 5.57; N, 7.30. Found: C, 59.90; H, 5.45; N, 7.55. MS (MALDI-TOF, *m/z*): calcd 959.17, found *m/z* 946.8 [M – 12]⁺, 793.7 [M – 12 – CCA + Cl]⁺, 758.7 [M – 12 – CCA]⁺.

Co2-4: blue solid, 56.0% yield. FT-IR (KBr disk, cm⁻¹): 3421, 3079, 3019, 2954, 2918, 2856, 1621 ($\nu_{C=N}$), 1585, 1460, 1366, 1255, 1217, 1107, 1024, 855, 806, 743, 667. Anal. Calcd for C₄₂H₄₁Cl₄Co₂N₅

(875): C, 57.62; H, 4.72; N, 8.00. Found: C, 57.59; H, 4.64; N, 8.08. MS (MALDI-TOF, m/z): calcd 875.08, found 862.7 [M – 12]⁺.

Co2-5: blue solid, 44.7% yield. FT-IR (KBr disk, cm⁻¹): 3414, 3076, 2967, 2929, 2874, 1623 ($\nu_{C=N}$), 1584, 1460, 1429, 1371, 1256, 1212, 1059, 1029, 859, 814, 744, 666. Anal. Calcd for C₄₆H₄₉Cl₄CO₂N₅ (931): C, 59.31; H, 5.30; N, 7.52. Found: C, 59.23; H, 5.19; N, 7.61. MS (MALDI-TOF, *m/z*): calcd 931.14, found 918.8 [M – 12]⁺, 765.7 [M – 12 – CCA + Cl]⁺, 730.7 [M – 12 – CCA]⁺.

Mononuclear Iron Complexes Fe1-n (n = 1-5). A representative synthesis of complex Fe1-1 is as follows: a mixture of 2,4-bis{6-[1-(2,6-dimethylphenylimino)ethyl]pyridin-2-yl}-3H-benzazepine (L1; 0.10 mmol) and FeCl₂·4H₂O (0.10 mmol) in THF (5 mL) was stirred for 8 h at room temperature. The precipitate was collected by filtration, washed with diethyl ether (3×5 mL), and then dried under vacuum to afford Fe1-1: gray solid, 58.1% yield. FT-IR (KBr disk, cm⁻¹): 3381, 3061, 3018, 2958, 2916, 2854, 1645 ($\nu_{C=N}$), 1638 ($\nu_{C=N}$), 1580, 1469, 1362, 1316, 1258, 1207, 1092, 1032, 808, 766, 664. Anal. Calcd for C₄₀H₃₇Cl₂FeN₅ (713): C, 67.24; H, 5.22; N, 9.80. Found: C, 67.11; H, 5.01; N, 9.90. MS (MALDI-TOF, *m/z*): calcd 713.18, found *m/z* 703.0 [M - 10]⁺, 891.2 [M - 10 + CCA]⁺.

Fe1-2: gray solid, 64.9% yield. FT-IR (KBr disk, cm⁻¹): 3399, 3067, 2929, 2868, 1641 ($\nu_{C=N}$), 1627 ($\nu_{C=N}$), 1585, 1463, 1284, 1175, 1102, 803, 760. Anal. Calcd for C₄₄H₄₅Cl₂FeN₅ (769): C, 68.58; H, 5.89; N, 9.09. Found: C, 68.33; H, 5.60; N, 9.42. MS (MALDI-TOF, m/z): calcd 769.24, found 887.8 [M – 2Cl + CCA]⁺, m/z 734.7 [M – Cl]⁺, 699.7 [M – 2Cl]⁺.

Fe1-3: gray solid, 65.3% yield. FT-IR (KBr disk, cm⁻¹): 3443, 3061, 2962, 2926, 2868, 1645 ($\nu_{C=N}$), 1629 ($\nu_{C=N}$), 1581, 1456, 1366, 665. Anal. Calcd for C₄₈H₅₃Cl₂FeN₅ (825): C, 69.74; H, 6.46; N, 8.47. Found: C, 70.03; H, 6.51; N, 8.59. MS (MALDI-TOF, *m/z*): calcd 825.30, found 790.7 [M - Cl]⁺.

Fe1-4: gray solid, 66.7% yield. FT-IR (KBr disk, cm⁻¹): 3389, 1704, 1644 ($\nu_{C=N}$), 1627 ($\nu_{C=N}$), 1586, 1470, 1287, 1179, 1093, 808, 773. Anal. Calcd for C₄₂H₄₁Cl₂FeN₅ (741): C, 67.93; H, 5.57; N, 9.43. Found: C, 67.68; H, 5.51; N, 9.59. MS (MALDI-TOF, *m/z*): calcd 741.21, found 705.7 [M - Cl]⁺, 894.8 [M - Cl + CCA]⁺.

Fe1-5: gray solid, 60.0% yield. FT-IR (KBr disk, cm⁻¹): 3389, 3074, 2916, 1707, 1641 ($\nu_{C=N}$), 1626 ($\nu_{C=N}$), 1583, 1474, 1282, 1200, 1166, 1025, 853, 806, 748. Anal. Calcd for C₄₆H₄₉Cl₂FeN₅ (797): C, 69.18; H, 6.18; N, 8.77. Found: C, 68.93; H, 6.23; N, 9.01. MS (MALDI-TOF, *m/z*): calcd 797.27, found 761.8 [M - Cl]⁺, 951.7 [M - Cl + CCA]⁺.

Dinuclear Iron Complexes Fe2-n (n = 1-5). A representative synthesis of complex Fe2-1 is as follows: a mixture of 2,4-bis{6-[1-(2,6-dimethylphenylimino)ethyl]pyridin-2-yl}-3H-benzazepine (L1; 0.10 mmol) and 2 equiv of FeCl₂ (0.20 mmol) in THF (7 mL) was stirred for 8 h at room temperature. The precipitate was collected by filtration, washed with diethyl ether (3×5 mL), and then dried under vacuum to afford Fe2-1: blue solid, 45.6% yield. FT-IR (KBr disk, cm⁻¹): 3417, 3069, 2959, 2919, 1623 ($\nu_{C=N}$), 1585, 1466, 1367, 1257, 1208, 1096, 1031, 806, 773, 664. Anal. Calcd for C₄₀H₃₇Cl₄Fe₂N₅ (841): C, 57.11; H, 4.43; N, 8.32. Found: C, 56.89; H, 4.23; N, 8.50. MS (MALDI-TOF, m/z): 841.05, found 831.7 [M – 10]⁺, 678.5 [M – 163(C₉H₉NO₂)]⁺.

Fe2-2: blue solid, 47.6% yield. FT-IR (KBr disk, cm⁻¹): 3389, 3069, 2966, 1706, 1627 ($\nu_{C=N}$), 1585, 1460, 1333, 1174, 1099, 809, 771. Anal. Calcd for C₄₄H₄₅Cl₄Fe₂N₅ (897): C, 58.89; H, 5.05; N, 7.80. Found: C, 59.01; H, 5.40; N, 7.64. MS (MALDI-TOF, *m/z*): calcd 897.11, found 887.7 [M - 10]⁺, 734.6 [M - 163(C₉H₉NO₂)]⁺.

Fe2-3: blue solid, 44.4% yield. FT-IR (KBr disk, cm⁻¹): 3399, 3064, 2963, 2926, 2867, 1620 ($\nu_{C=N}$), 1583, 1461, 1366, 1320, 1257, 1200, 1108, 1151, 803, 770, 665. Anal. Calcd for C₄₈H₅₃Cl₄Fe₂N₅ (953): C, 60.46; H, 5.60; N, 7.35. Found: C, 60.16; H, 5.55; N, 7.71. MS (MALDI-TOF, *m*/*z*): calcd 953.17, found 943.8 [M - 10]⁺, 790.7 [M - 163(C₉H₉NO₂)]⁺.

Fe2-4: blue solid, 50.0% yield. FT-IR (KBr disk, cm⁻¹): 3389, 3074, 2916, 1707, 1626 ($\nu_{C=N}$), 1583, 1474, 1282, 1200, 1166, 1025, 853, 806, 748. Anal. Calcd for C₄₂H₄₁Cl₄Fe₂N₅ (869): C, 58.03; H, 4.75; N, 8.06. Found: C, 58.10; H, 5.01; N, 7.83. MS (MALDI-TOF, *m/z*): calcd 869.08, found *m/z* 858.7 [M - 10]⁺, 670.5 [M - 10 - CCA]⁺.

Fe2-5: blue solid, 46.9% yield. FT-IR (KBr disk, cm⁻¹): 3389, 1705, 1626 ($\nu_{C=N}$), 1582, 1453, 1388, 1266, 1167, 1104, 1033, 811, 771. Anal. Calcd for C₄₆H₄₉Cl₄Fe₂N₅ (925): C, 59.70; H, 5.34; N, 7.57. Found: C, 60.09; H, 5.40; N, 7.65. MS (MALDI-TOF, *m/z*): calcd 925.14, found 915.0 [M - 10]⁺, 762.0 [M - 163(C₉H₉NO₂)]⁺.

General Procedure for Ethylene Oligomerization. Ethylene Oligomerization at Ambient Pressure. The precatalyst was dissolved in toluene using standard Schlenk techniques, and the reaction solution was stirred with a magnetic stir bar under an ethylene atmosphere (1 atm) with a steam bath for controlling the desired temperature. Finally, the required amount of cocatalyst (MAO, MMAO) was added by a syringe. After the reaction was carried out for the required period, a small amount of the reaction solution was collected and terminated by the addition of 10% aqueous hydrogen chloride immediately. The organic layer was analyzed by gas chromatography (GC) for monitoring the oligomers formed; the precipitated polymer was collected, washed with water and ethanol, and finally dried.

Ethylene Oligomerization at Elevated Pressure (10 atm). A 300 mL stainless steel autoclave, equipped with a mechanical stirrer and a temperature controller, was employed for the reaction. First, 50 mL of toluene (freshly distilled) was injected into the clave, which was full of ethylene. When the required temperature was reached, another 30 mL of toluene, in which the complex (2.0 μ mol of metal) was previously dissolved, the required amount of cocatalyst (MAO, MMAO), and residual toluene were added by syringe successively. The reaction mixture was intensely stirred for the desired time under the corresponding pressure of ethylene through the entire experiment. The reaction was terminated and analyzed using the same procedure as for ethylene oligomerization and polymerization.

X-ray Crystallographic Studies. Single crystals of compounds 1 and L3 suitable for X-ray diffraction analysis were recrystallized from their dichloromethane solutions, respectively; meanwhile, single crystals of complex Co1-1 suitable for X-ray diffraction analysis were obtained by layering *n*-pentane on its THF (tetrahydrofuran) solution at room temperature. With graphite-monochromated Mo K α radiation $(\lambda = 0.71073 \text{ Å})$, the single-crystal X-ray diffraction for compound 1 was performed on a Bruker SMART 1000 CCD at 273(2) K, and the single-crystal X-ray diffractions for compounds L3 at 273(2) K and Co1-1 at 173(2) K were carried out on a Rigaku Saturn724+ CCD (λ = 0.71073 Å). 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 hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXTL-97 package.¹⁸ Crystal data and refinement details are given in the Supporting Information.

ASSOCIATED CONTENT

S Supporting Information

A table giving crystal data and processing parameters for compounds 1, L3, and Co1-1 and CIF files giving X-ray crystal structure data. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*W.-H.S.: tel, +86-10-62557955; fax, +86-10-62618239; e-mail, whsun@iccas.ac.cn. C.R.: tel, +44 1482 465219; fax, +44 1482 466410; e-mail, c.redshaw@hull.ac.uk.

Notes

The authors declare no competing financial interest.

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