2118 *Organometallics* **2010,** *29,* 2118–2125
DOI: 10.1021/om9010356

An Unsymmetrical Iron(II) Bis(imino)pyridyl Catalyst for Ethylene Polymerization: Effect of a Bulky Ortho Substituent on the Thermostability and Molecular Weight of Polyethylene

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Received December 1, 2009

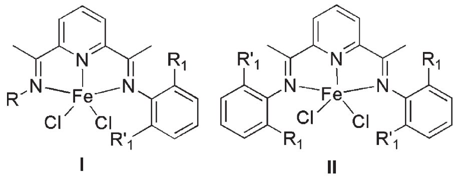
Three new iron(II) 2,6-bis(imino)pyridyl complexes bearing bulky and unsymmetrical substituted aniline groups, $[2\text{-}(CH(CH_3)(C_6H_5))\text{-}4\text{-}R_1\text{-}6\text{-}R_2\text{-}C_6H_2N{=}C(CH_3)]_2C_5H_3NFeCl_2$ (**1**, R_1 = H, R_2 = methyl; **2**, R_1 = methyl, R_2 = methyl; **3**, R_1 = H, R_2 = methoxy), were synthesized. The unsymmetrical bis(imino)pyridyl ligand **L2** contains three isomers that can be detected by ^{1}H NMR and ^{13}C NMR spectroscopy. However, the corresponding complex **2** exhibits only one isomer in solution. X-ray diffraction of **2** confirms that the iron complex adopts a C_s configuration. These complexes activated by methylaluminoxane (MAO) have high catalytic activities for ethylene polymerization and produce linear polyethylenes with bimodal or broad molecular weight distribution. The steric and electronic effects of the ortho substituents on the aniline moiety distinctly affect the molecular weight of the obtained polyethylene. In comparison with **1** and **3**, having a single ortho substituent on the aryl rings, and the typical complex **4**, containing *o*-diisopropyl substitution, complex **2** has better thermal stability and produces much higher molecular weight polyethylene. Even at 70 °C, the **2**/MAO system still keeps high activity and relatively stable kinetics.

Introduction

Important progress in the area of late-transition-metal catalysts using iron(II) bis(imino)pyridyl for ethylene polymerization has been achieved in the past few decades.[1] In contrast to the nickel and palladium α-diimine catalysts, which typically produced highly or moderately branched polyethylene,[2] tridentate iron(II) bis(imino)pyridyl catalysts, in spite of their higher activity, produced highly linear polyethylene with low molecular weight and broad molecular weight distribution.

Since the initial studies by Brookhart[1a] and Gibson,[1b,c] a great deal of research has been involved in the design of new ligands,[1d,e] especially on changes of the backbone substituents on the carbon atoms of imine groups and replacement of the aniline moiety and the resultant influence on ethylene polymerization. Generally, bulkiness on imine carbon can increase catalytic activity for ethylene polymerization and the molecular weight of the polyethylenes (Fe/ketimine > Fe/aldimine),[1a,3b] while the steric hindrance of the 2,6-substitution on the aniline moiety can decrease catalytic activity (Me > Et > *i*-Pr) but give an obvious increase in the molecular weight of the products (Me < Et < *i*-Pr).[1a−c,3] Iron(II) catalysts lacking ortho alkyl substituents only produced oligomers or trace polymer.[3b,4b,e] One drawback of these

Scheme 1



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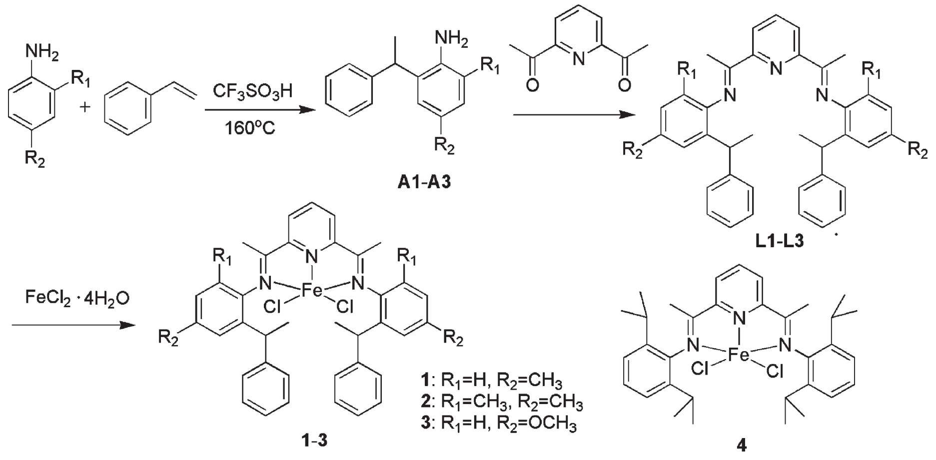
Scheme 2. Synthesis of Bis(imino)pyridyl Ligands and Corresponding Iron Complexes



catalysts is their poor thermal stability. The activity and molecular weight dropped rapidly as the reaction temperature increased.[1] A bulky macrocyclic iron(II) bis(imino)pyridyl complex can restrain the catalytically active iron center from deactivation and produce higher molecular weight polymers.[5]

Moreover, a great deal of work has been focused on unsymmetrical catalyst precursors as follows: a change of substituents at the ketimine nitrogen atoms (**I**)[6] and a change in the alkylphenyl moiety in the 2,6-positions (**II**) (Scheme 1).[1a,c,f,g,3b,4] Catalysts derived from such Fe complexes **I** with the alkyl group R were still very active but typically gave ethylene oligomers.[6b] The complexes **II** with unsymmetric ortho substitution of various alkyl/aryl groups on aniline produced highly linear polymers after activation by MAO. Despite all this, modification of the ligand of iron bis(imino)pyridyl catalysts to improve their thermostability and produce higher molecular weight polyethylene remains a challenge.

Previous studies have shown that a bulky α-diimine complex with *sec*-phenethyl substituents on the aniline moiety adopts a C_2-symmetric configuration and can effectively shield the axial space.[4d,f] The objective of the present study is to synthesize new iron(II) 2,6-bis(imino)pyridyl complexes bearing unsymmetrical and bulky *o*-*sec*-phenethyl-substituted aryl groups and to obtain high-molecular-weight polyethylenes at elevated temperature. The syntheses of three new iron(II) complexes containing *o*-*sec*-phenethylaniline groups and their catalytic properties in ethylene polymerization are reported herein. It was found that an appropriate ortho substitution on aniline moieties can promote the thermostability of the catalyst and the control of molecular weight more efficiently than typical iron(II) *o*-diisopropyl-substituted bis(imino)pyridyl analogues.

Results and Discussion

Syntheses and Characterization of Ligands and Complexes. The procedures in the preparation of ligands and complexes are shown in Scheme 2. Reaction of the 2,4-disubstituted anilines with styrene at elevated temperature (160 °C) in the presence of CF_3SO_3H catalyst resulted in the corresponding *o*-*sec*-phenethylanilines *rac*-**A1**−**A3**. The tridentate 2,6-bis(imino)pyridine ligands **L1**−**L3** were synthesized by the Schiff base condensation of 2,6-diacetylpyridine with 2 equiv of the *o*-*sec*-phenethylanilines in toluene at 80−110 °C using *p*-toluenesulfonic acid (*p*-TsOH) as catalyst and molecular sieves as the water adsorbent[7] and were verified by elemental analysis, ^{1}H NMR, and ^{13}C NMR.

The ^{1}H NMR spectrum of ligand **L2** at 20 °C shows the presence of three isomers in the ratio 5.6/2.3/1. As shown in Figure 1, three quartets at 4.08, 4.03, and 3.74 ppm are clearly observed, corresponding to methine protons of the *o*-*sec*-phenethyl substituents. The origin of the isomers may be *S,S*, *S,R*, and *R,R* diastereomers of chiral carbon[8] or *E,Z*, *Z,Z*, and *E,E* configurations of the C=N double bond of imine.[9] *rac*/*meso* diastereoisomers can be safely ruled out, because the ratio of these three isomers is temperature dependent. The ratio of peak intensities of the three isomers changes from 5.6/2.3/1 to 6.4/3/1 with an increase in temperature from 20 to 60 °C. Therefore, there are many possibilities for *E,Z*, *Z,Z*, and *E,E* configurational isomers for the ligand. Previous reports have also noted that the *E*/*Z* isomerization is reversible via an inversion at the imine nitrogen.[9c,d]

Treatments of metal salt with the ligands **L1**−**L3** in THF for 8 h afforded the complexes **1**−**3**. It has been reported[3f,10] that the C=N stretching frequencies of the analoguous free ligands appeared at 1638−1645 cm^{-1} in FTIR spectra. For complexes **1**−**3**, the C=N stretching vibrations are shifted to

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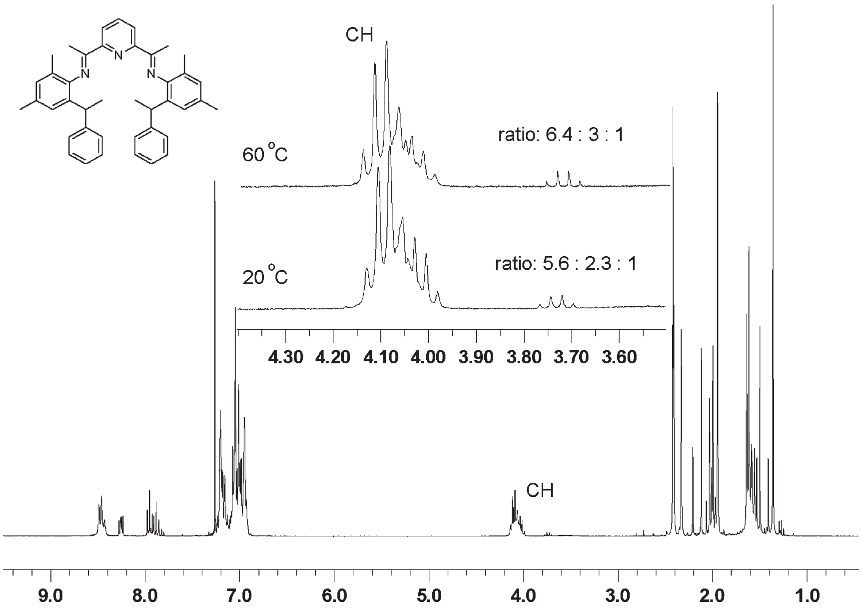

Figure 1. ^{1}H NMR spectra of ligand **L2** measured at 20 and 60 °C.

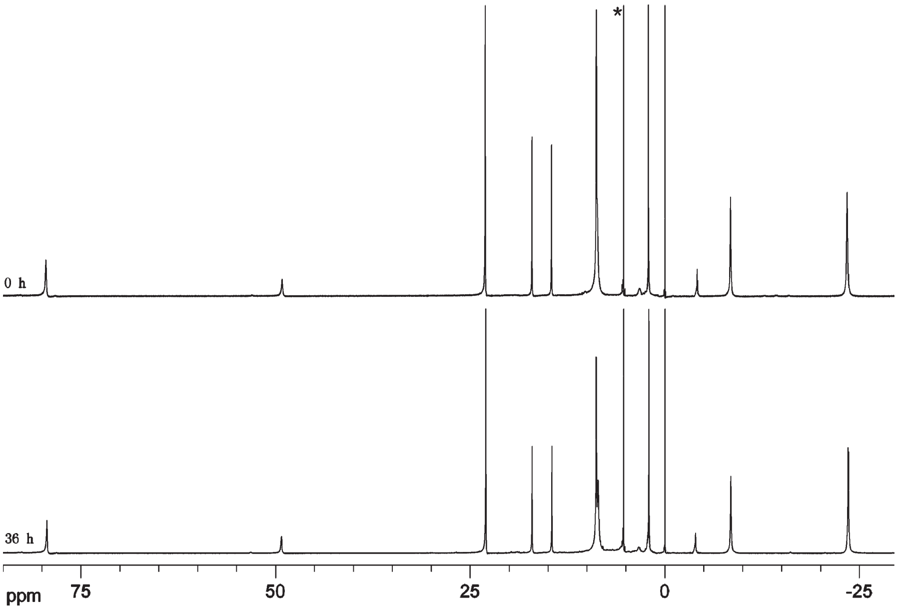

Figure 2. ^{1}H NMR spectra of complex **2** at 25 °C at different times (500 MHz, CD_2Cl_2 (peak indicated by an asterisk), 20 °C): (0 h) determined immediately after fresh solution was prepared from the precipitated solid; (36 h) determined after the solution was stored for 36 h.

lower frequencies around 1602−1620 cm^{-1}, indicating an efficacious coordination interaction between the imino nitrogen atoms and the metal ions. The synthesis of the typical complex **4** was performed according to the literature method.[1a−c]

^{1}H NMR spectra showed that the iron(II) bis(imino)pyridyl complexes individually exhibit only one isomer. A fresh powder sample of complex **2** was typically chosen to study time dependence by ^{1}H NMR analysis in CD_2Cl_2. Figure 2 clearly shows only one set of signals corresponding to a variety of 12 hydrogen atoms of complex **2** and no changes in the spectra can be observed within 36 h, revealing that no isomerization occurs on the NMR time scale.[4a,11] This result also further confirms that the isomers of ligand **L2** cannot come from chiral carbons. Reyes[12] previously reported that there is an equilibrium between the C_s and C_2 diastereoisomers of a iron(II) bis(imino)pyridyl complex with unsymmetrical 2-methyl-6-isopropyl substitution on aniline. In contrast, iron complexes **1**−**3** have a single isomer in solution. This obvious difference is a result of the more bulky *o-sec*-phenethyl substituen, which can effectively prohibit the rotations of C−N bonds. An observation that the conversion rate of the isomers depends on the steric bulkiness of ortho substituents has been reported by Pellecchia.[11]

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Table 1. Results of Ethylene Polymerizations Catalyzed by 1-4/MAO at 30 °C[a]

entry	complex	yield (g)	activity (10^5g/((mol of Fe) h))	M_w[b] (kg/mol)	PDI[c]	M_{pk1}/M_{pk2}[d] (kg/mol)	T_m[e] (°C)
1	**1**	2.21	7.37	9.3	2.8	4.3	125.0
2	**2**	2.50	8.33	1190.5	167.6	969.8/2.7	135.4
3	**3**	1.86	6.20	108.9	21.5	30.1/1.7	130.1
4	**4**	2.55	8.50	553.1	88.5	608.6/2.7	132.2

[a] General conditions: 3 μmol of iron complex; Al/Fe = 1500; 30 °C; 30 mL of toluene; 60 min; 1 bar of ethylene pressure. [b] Weight-average molecular weight based on the whole GPC trace. [c] Based on the whole polymer sample. [d] Molecular weight of the peaks in the GPC trace. [e] Determined by DSC.

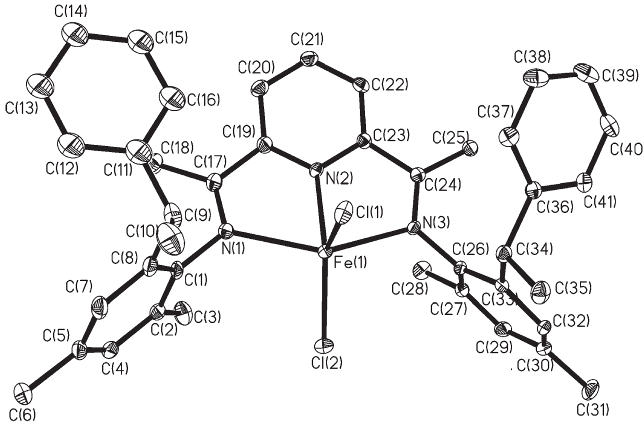

Figure 3. Molecular structure of complex **2**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe(1)−N(1), 2.284(3); Fe(1)−N(2), 2.083(3); Fe(1)−N(3), 2.248(3); Fe(1)−Cl(1), 2.3275(14); Fe(1)−Cl(2), 2.2597(13); Cl(2)−Fe(1)−Cl(1), 128.14(5); N(1)−Fe(1)−Cl(1), 95.90(10); N(3)−Fe(1)−Cl(1), 94.61(9); N(2)−Fe(1)−Cl(1), 95.50(10); N(2)−Fe(1)−Cl(2), 136.34(11); N(3)−Fe(1)−N(1), 146.71(12); N(2)−Fe(1)−N(1) 73.55(13).

A single crystal suitable for X-ray diffraction analysis was obtained by slow diffusion of hexane into a dichloromethane solution of complex **2**. Fortunately, a crystal of pure complex **2** could be obtained and the ORTEP diagram is shown in Figure 3. Unlike the unsymmetrical bulky α-diimine Ni(II) complexes which typically adopt a C_2 configuration,[4a,d,13,14] iron complex **2** possesses a near C_s-symmetric configuration, and both *sec*-phenethyl groups are oriented above the bis(imino)pyridyl plane. The origin of this structural difference is that the iron complex has more open steric space due to its N−N−N coordination geometry, as compared to α-diimine nickel complexes with N−N coordination geometry. Therefore, it is reasonably concluded that the iron complexes have a single isomer with a C_s-symmetric configuration both in the solid state and in solution. The phenyl rings attached on imine groups are nearly perpendicular to the coordination plane, with the dihedral angles being 84.36° for the ring bonded to N(1) and 82.19° for the ring bonded to N(3) for **2**, respectively. The axial sites for the metal center are almost blocked by the *o*-sec-phenethyl substituents, which will play a critical role in maintaining high activity and obtaining high-molecular-weight polymers at elevated temperatures.

Ethylene Polymerization. Effect of Ligand Structure. The results from ethylene polymerizations conducted at 30 °C and 1 bar by using complexes **1**−**4** as catalyst precursors in the presence of MAO are shown in Table 1. A striking feature observed in the data is that the complexes with only one ortho substituent on the aniline moieties do not yield high-M_{pk} polymer even though the substituent is bulky. Among the *o*-*sec*-phenethyl substitution analogues **1**−**3**, complex **2**, containing methyl substituted for H on another ortho position, exhibits slightly better catalytic activity and produces much higher molecular weight polymer than the single-ortho-substituent analogues **1** and **3**. As shown in Figure 4, the polymers produced by the catalysts exhibit broad or bimodal molecular weight distributions that are in accordance with the previous observation from other iron bis(imino)pyridyl catalysts.[1] The broad or bimodal molecular weight distributions can be attributed to the coexistence of two chain-transfer processes in the polymerizations: β-H transfer to monomer or metal and chain transfer to alkylaluminum.[1a,c] The results obtained herein indicate that the

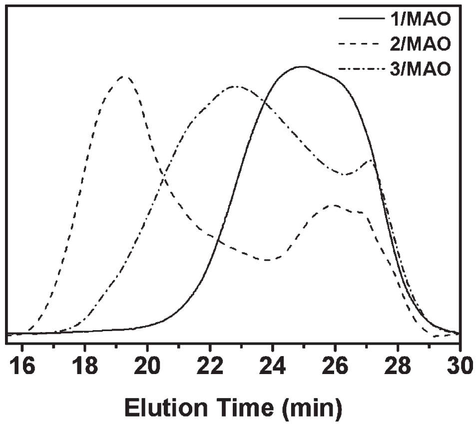

Figure 4. GPC curves of the polyethylenes prepared by **1**−**3**/MAO at 30 °C.

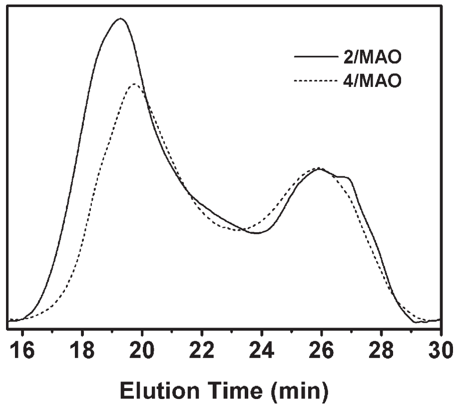

Figure 5. GPC curves of the polyethylenes prepared by **2**/MAO and **4**/MAO at 30 °C.

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Table 2. Results of Ethylene Polymerizations under Various Conditions[a]

entry	complex	temp (°C)	Al/Fe (mol/mol)	yield (g)	activity (10^5g/((mol of Fe) h))	M_w[b] (kg/mol)	PDI[c]	M_{pk1}/M_{pk2}[d] (kg/mol)	T_m[e] (°C)
5	**1**	0	1500	2.31	7.70	38.6	9.3	8.8	127.8
1	**1**	30	1500	2.21	7.37	9.3	2.8	4.3	125.0
6	**1**	50	1500	2.15	7.17	6.3	2.2	2.6	122.8
7	**1**	70	1500	0.94	3.13	2.8	[f]	2.0	106.4
8	**2**	0	1500	2.25	7.50	855.8	140.2	905.2/3.7	134.6
2	**2**	30	1500	2.50	8.33	1190.5	167.6	969.8/2.7	135.4
9	**2**	50	1500	3.31	11.03	1121.6	131.7	796.5/2.5	134.7
10	**2**	70	1500	2.74	9.13	23.3	5.7	9.0	127.2
11	**2**	30	1000	1.03	0.34	1499.2	155.8	1222.2/3.1	136.1
12	**2**	30	2000	3.59	11.97	1054.1	257.1	1122.1/1.6	135.7
13	**3**	0	1500	2.32	7.73	152.3	26.0	45.0/1.9	131.6
3	**3**	30	1500	1.86	6.20	108.9	21.5	30.1/1.7	130.1
14	**3**	50	1500	2.31	7.70	28.2	8.5	5.6	125.5
15	**3**	70	1500	1.27	4.23	6.5	2.7	4.5	123.0
16	**4**	0	1500	1.50	5.00	483.1	64.2	723.5/3.2	131.7
4	**4**	30	1500	2.55	8.50	553.1	88.5	608.6/2.7	132.2
17	**4**	50	1500	2.03	6.77	269.1	26.5	321.3/2.5	131.2
18	**4**	70	1500	1.04	3.48	8.6	4.3	3.8	124.5

[a] General conditions: 3 μmol of iron complex; 30 mL of toluene; 60 min; ethylene pressure 1 bar. [b] Weight-average molecular weight based on the whole GPC trace. [c] Based on the whole polymer sample. [d] Molecular weight of the peaks in the GPC trace. [e] Determined by DSC. [f] The molecular weight is too low to get a correct PDI value.

bulky ortho disubstitution on the aniline can efficiently suppress the chain transfer reactions, especially for β-H transfer.

For the catalysts with a single ortho substituent, a change of para substituent from methyl (**1**) to the more strongly electron-donating methoxy (**3**) results in a slight decrease of catalytic activity from 7.37 × 10^5 to 6.20 × 10^5 g/((mol of Fe) h) but a significant increase of M_{pk1} of the obtained polymer from 4.3 to 30.1 kg/mol (Table 1, entries 1 and 3). The result suggests that the electron-donating effect on para substitution can also decrease the rate of chain transfer relative to the rate of chain propagation, although the electron-donating effect may not be so strong, as compared with the steric hindrance on ortho substitution as mentioned above.

In particular, in contrast to the case for the typical complex **4**, which contains *o*-diisopropyl sbustituents on the aniline moiety, complex **2** affords ca. 1.5-fold increased M_{pk1} value for polyethylene with a higher melting point. As shown in Figure 5, by using complexes **2** and **4**, both polyethylenes display similar bimodal molecular weight distributions. However, the high-molecular-weight fraction of the polymer obtained by complex **2** accounts for 58% more than that by complex **4** (46%).

As investigated by Brookhart[1a] and Gibson,[1c] the low-molecular-weight fraction is a result of chain transfer to alkylaluminum while the high-molecular-weight fraction is produced mainly by β-H transfer. When all of the above results are combined, it is clear that the bulky *o*-*sec*-phenethyl substituent is a crucial factor in protecting the metal center and increasing the molecular weight of the polymer. Ortho disubstitutions, just as in complex **2**, can provide adequate steric hindrance for the metal center and significantly reduce β-H transfer reaction; thus, high-M_{pk1} polyethylenes and even superhigh-molecular-weight polymers can be obtained. Due to the chain transfer to alkylaluminum by formation of Fe–Al heterobimetallic species,[15] the low-molecular-weight fraction is inevitable but can be decreased by the adequate steric hindrance of the ligands.

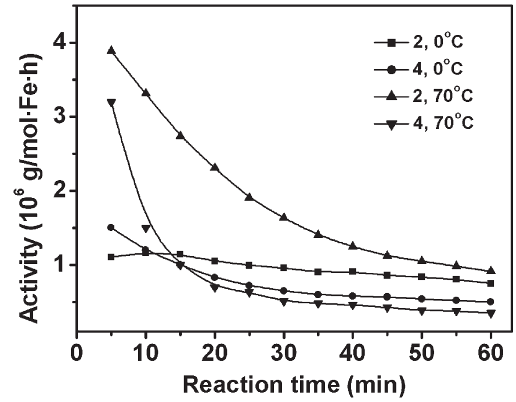

Figure 6. Time dependences of the catalytic activities of complexes **2** and **4** at 0 and 70 °C. Polymerization conditions: ethylene pressure 1 bar; Al/Fe = 1500.

Effect of Reaction Conditions. The polymerization results under various conditions are summarized in Table 2. These complexes have different sensitivities to polymerization temperature. With elevated temperature, the catalytic activities of complexes **1** and **3** containing single *o*-*sec*-phenethyl substitution on the aniline moiety are practically constant from 0 to 50 °C and then drop rapidly at 70 °C and the M_{pk} values of the obtained polymer decrease continuously. Complex **4**, containing *o*-diisopropyl substitution on the aniline, exhibits a maximum activity of 8.5 × 10^5 g/((mol of Fe) h) and produces the highest molecular weight polymer (M_{pk1} = 608.6 kg/mol) at 30 °C. It is worth noting that complex **2**, containing 2-*sec*-phenethyl-6-methylaniline, reaches its maximum activity of 11 × 10^5 g/((mol of Fe) h) at 50 °C and still retains a high activity of 9.1 × 10^5 g/((mol of Fe) h) at 70 °C and affords superhigh-molecular-weight polymers (M_{pk1} = 797–970 kg/mol) at 30–50 °C. It is quite evident that complex **2** has better thermostable properties for ethylene polymerization than do its analogues.

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Table 3. Results of Ethylene Polymerizations under 10 bar of Ethylene Pressure[a]

entry	complex	temp (°C)	yield (g)	activity (10^5g/((mol of Fe) h))	M_w[b] (kg/mol)	PDI[c]	M_{pk}[d] (kg/mol)	T_m[e] (°C)
19	**2**	0	3.46	138	nd[f]	nd	nd	136.6
20	**2**	30	3.52	141	nd	nd	nd	136.3
21	**2**	50	4.12	165	nd	nd	nd	136.5
22	**2**	70	10.9	436	nd	nd	nd	136.3
23	**4**	0	2.86	114	nd	nd	nd	134.8
24	**4**	30	2.95	118	828.5	5.8	617.3	135.4
25	**4**	50	3.38	135	566.6	4.1	226.2	134.7
26	**4**	70	2.75	110	16.0	2.8	10.1	127.2

[a] General conditions: 0.5 μmol of iron complex; Al/Fe = 1500; 250 mL of toluene; 30 min. [b] Weight-average molecular weight based on the whole polymer sample. [c] Based on the whole polymer sample. [d] Molecular weight of the peaks in the GPC trace. [e] Determined by DSC. [f] Not determined due to insolubility of the polymers.

Figure 6 shows the time dependences of catalytic activities of complex **2** and **4** for ethylene polymerizations at 0 and 70 °C. For these two complexes, with elevating polymerization temperature, catalytic activities increase but the rate profiles exhibit decay kinetics. Though the rate profile of complex **2** exhibits decay kinetics as the temperature increased, it still displays higher activity and slower decay at 70 °C relative to that of complex **4**. The half-lifetime of the catalytic activity of complex **4** at 70 °C is only 10 min, while the half-lifetime of complex **2** is much longer: up to 25 min at the same temperature. The result indicates that the bulky and unsymmetrical substituted ligand can restrain the catalytically active iron centers from deactivation and effectively prolong the catalyst lifetime.

To further examine the thermal stability of the complexes, we carried out ethylene polymerizations by using **2** and **4** activated with MAO under 10 bar of pressure. High ethylene pressure significantly increases the catalytic activities and molecular weights of the products. The catalytic activity of **2** increases consistently on an increase in temperature from 0 to 70 °C under 10 bar of pressure (entries 19–22 in Table 3), and very high activity up to 4.4×10^7 g/((mol of Fe) h) can be achieved at 70 °C. The obtained products are linear PEs having high melting points ($T_m \approx 136$ °C) and are insoluble in TCB. Therefore, it is difficult to determine their molecular weight by GPC using TCB. The superhigh molecular weight is the only possible explanation for the insolubility of these PEs. Although **4** also shows an increased activity under 10 bar of pressure, it exhibits the maximun activity (1.3×10^7 g/((mol of Fe) h)) at 50 °C. Therefore, the results further confirm the better thermal stability of complex **2** for ethylene polymerization.

As mentioned above, the coexistence of two chain transfer pathways results in a bimodal molecular weight distribution for iron 2,6-bis(imino)pyridyl catalysts; thus, the influence of Al/Fe ratio on these two chain-transfer processes is obvious. Complex **2** was chosen to examine the effect of Al/Fe ratio, and the results are shown in Table 2 (entries 2, 11, and 12). On raising the Al/Fe ratio from 1000 to 2000, an increase in catalytic activity and PDI of the whole polymer sample and a decrease in the peak value of the low-molecular-weight fraction (M_{pk2}) can be observed. As shown in Figure 7, with an increase of Al/Fe ratio, the high-molecular-weight fraction is essentially unchanged in the GPC traces, while the low-molecular-weight fraction increases and M_{pk2} moves to lower molecular weight in the GPC traces. The percentage of the low-molecular-weight fraction in the whole polymer mass increases from 39% to 53% as the Al/Fe ratio increases from 1000 to 2000. The results further demonstrate that β-H transfer is restrained by the bulky steric hindrance of complex **2**, so that the rate of β-H transfer is relatively reduced and the chain transfer to alkylaluminum can become competitive or even dominant at a high Al/Fe ratio.

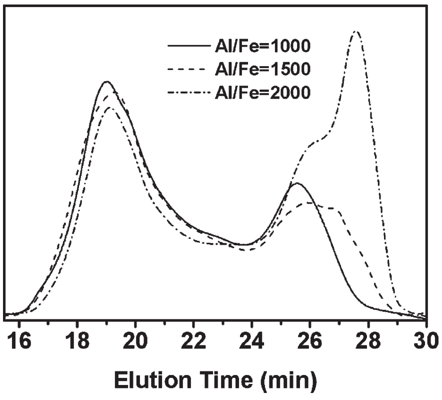

Figure 7. GPC curves of the polyethylenes prepared by **2**/MAO at different Al/Fe ratios.

Conclusion

In summary, three new unsymmetrical iron(II) bis(imino)pyridyl complexes with bulky *o*-*sec*-phenethyl-substituted aryl groups have been successfully synthesized and characterized. Though the bis(imino)pyridyl ligands may contain *E* and *Z*configuration, all the iron complexes exhibit only one isomer in the solid state and solution. The substituent of the ortho positions on the aniline moiety plays a crucial role in promoting the thermal stability of the catalyst and control of molecular weight of polymer for ethylene polymerization. Complex **2**, containing 2-methyl-6-*sec*-phenethyl substituents on the aniline moiety, exhibits a better activity and produces much higher molecular weight polyethylene as compared to the singly ortho-substituted analogues **1** and **3** and the typical *o*-diisopropyl-substituted complex **4**. Even at 70 °C, catalyst **2** still maintains a high activity and relatively stable kinetics. The polymers obtained by the unsymmetrical and bulky alkyl-substituted catalysts appear as a bimodal molecular weight distribution due to the coexistence of two chain transfer pathways, and the content of the low-molecular-weight fraction increases with an increase in the Al/Fe ratio.

Experimental Section

General Considerations. All manipulations of air- and/or moisture-sensitive compounds were performed by means of standard high-vacuum Schlenk and cannula techniques under a N_2 atmosphere. Toluene, hexane, and THF were refluxed over metallic sodium for 48 h and distilled under a nitrogen atmosphere before use. Dichloromethane was distilled from P_2O_5. MAO was prepared by the controlled reaction of trimethylaluminum (TMA) with H_2O from $Al_2 (SO_4)_3 \cdot 18H_2O$ dispersed in toluene at 0−60 °C for several hours. The initial $[H_2O]/[TMA]$ molar ratio was 1.3. CF_3SO_3H was used from a freshly opened ampule. Other commercially available reagents were purchased and used without purification.

Synthesis of 4-Methyl-2-(*sec*-phenethyl)aniline (A1). A1 was prepared according to the literature procedure.[16]

Synthesis of 4,6-Dimethyl-2-(*sec*-phenethyl)aniline (A2). 2,4-Dimethylaniline (15 mL, 0.12 mol), styrene (20 mL, 0.17 mol), and CF_3SO_3H (3 mL, 0.034 mol) in 25 mL of xylenes were heated in a sealed tube at 160 °C for 30 h. Volatile materials were then removed by rotary evaporation, and the residue was recrystallized in a petroleum ether/ethyl acetate (9/1) mixed solvent to give pure **A2** as white crystals with a yield of 8.43 g (31%). ^1H NMR (300 MHz, $CDCl_3$, δ (ppm)): 7.16−7.30 (m, 5H, J = 6.9 Hz, aryl-*H*), 6.99 (s, 1H, aryl-*H*), 6.84 (s, 1H, aryl-*H*), 4.12 (q, 1H, J = 6.9 Hz, C*H*CH$_3$), 2.30 (s, 3H, *p*-CH_3), 2.13 (s, 3H, *o*-CH_3), 1.62 (d, 3H, J = 6.9 Hz, CHCH_3). EI-MS (*m*/*z*): 226.2 $[M]^+$.

Synthesis of 4-Methoxy-2-(*sec*-phenethyl)aniline (A3). 4-Methoxyaniline (15.7 g, 0.11 mol), styrene (13 mL, 0.11 mol), and CF_3SO_3H (2 mL, 0.023 mol) in 25 mL of xylenes were heated in a sealed tube at 160 °C for 30 h. Volatile materials were then removed by rotary evaporation, and the residue was typically purified by chromatography on silica gel (petroleum ether/ ethyl acetate 5/1) to give the desired product as a light red oil. The oil was recrystallized in a petroleum ether/ethyl acetate (9/1) mixed solvent to produce pure **A3** as white crystals with a yield of 3.19 g (11%). ^1H NMR (300 MHz, $CDCl_3$, δ (ppm)): 7.18−7.30 (m, 5H, aryl-*H*), 6.91 (s, 1H, aryl-*H*), 6.58−6.69 (m, 2H, aryl-*H*), 4.11 (q, 1H, J = 7.2 Hz, C*H*CH$_3$), 3.80 (s, 3H, *p*-OCH_3), 3.18 (2H, NH_2), 1.61 (d, 3H, J = 7.2 Hz, CHCH_3). EI-MS (*m*/*z*): 228.5 $[M]^+$.

Synthesis of ArN=C(C_5H_3N)C=NAr (L1; Ar = 4-Methyl-2-(*sec*-phenethyl)phenyl). A solution of 2,6-diacetylpyridine (1.05 g, 6.44 mmol), aniline **A1** (3.12 g, 14.8 mmol), *p*-toluenesulfonic acid (0.20 g), and molecular sieves 4 Å (3.0 g) in toluene (40 mL) was stirred at 80−110 °C for 24 h. Then the reaction mixture was filtered, and the molecular sieves were washed with CH_2Cl_2 several times. The solvents of the combined filtrates were removed under vacuum. Anhydrous ethanol (30 mL) was added to the residue. A yellow solid was filtered off to give **L1** in a 45% yield (1.50 g). ^1H NMR (300 MHz, $CDCl_3$, δ (ppm)): 8.30 (d, 2H, J = 7.8 Hz, Py-H_m), 7.87 (t, 1H, J = 7.5 Hz, Py-H_p), 7.02−7.23 (m, 14H, aryl-*H*), 6.53 (d, 2H, J = 7.5 Hz, aryl-*H*), 4.21 (q, 2H, J = 6.9 Hz, C*H*CH$_3$), 2.40 (s, 6H, *p*-CH_3), 1.84 (d, 6H, J = 7.5 Hz, CHCH_3), 1.63 (d, 6H, J = 6.9 Hz, N=C*Me*). ^{13}C NMR ($CDCl_3$, δ (ppm)): 167.55, 155.57, 147.11, 146.70, 136.74, 135.73, 133.25, 128.34, 128.07, 127.85, 127.50, 125.79, 122.25, 118.69, 40.59, 21.82, 21.68, 16.31. Anal. Calcd for $C_{39}H_{39}N_3$: C, 85.21; H, 7.15; N, 7.64. Found: C, 84.74; H, 7.15; N, 7.64. EI-MS (*m*/*z*): 551.1 $[M]^+$.

Synthesis of ArN=C(C_5H_3N)C=NAr (L2; Ar = 4,6-Dimethyl-2-(*sec*-phenethyl)phenyl). A solution of 2,6-diacetylpyridine (1.15 g, 7.05 mmol), aniline **A2** (4.27 g, 18.9 mmol), *p*-toluenesulfonic acid (0.25 g), and molecular sieves 4 Å (3.0 g) in toluene (40 mL) was stirred at 80−110 °C for 24 h. Then the reaction mixture was filtered, and the molecular sieves were washed with CH_2Cl_2 several times. The solvents of the combined filtrates were removed under vacuum. Anhydrous ethanol (30 mL) was added to the residue. A yellow solid was filtered off to give **L2** in 47% yield (1.86 g). ^1H NMR (300 MHz, $CDCl_3$, δ (ppm)): 8.43−8.48 (m, 2H, Py-H_m), 8.23−8.27 (m, 1H, Py-H_p), 6.94−7.97 (m, 14H, aryl-*H*), 3.69−4.13 (m, 2H, C*H*CH$_3$), 2.20−2.41 (m, 6H, aryl-*p*-CH_3), 1.93−2.11 (m, 6H, aryl-*o*-CH_3), 1.52−1.63 (m, 6H, CHCH_3), 1.35−1.48 (m, 6H, N=C*Me*). ^{13}C NMR ($CDCl_3$, δ (ppm)): 168.77, 167.63, 167.44, 155.14, 155.02, 154.91, 146.89, 146.74, 145.95, 145.73, 145.51 136.55, 133.92, 133.76, 133.63, 129.01, 128.14, 127.99, 127.94, 127.64, 125.86, 125.59, 125.43, 124.95, 124.90, 124.77, 122.12, 121.97, 121.85, 40.66, 40.56, 39.63, 22.48, 22.29, 21.16, 21.01, 20.56, 18.02, 17.73, 17.66, 16.61, 16.15, 16.01. Anal. Calcd for $C_{41}H_{43}N_3$: C, 85.23; H, 7.50; N, 7.27. Found: C, 84.48; H, 7.41; N, 7.01. EI-MS (*m*/*z*): 578.9 $[M]^+$.

Synthesis of ArN=C(C_5H_3N)C=NAr (L3; Ar = 4-Methoxy-2-(*sec*-phenethyl)phenyl). A solution of 2,6-diacetylpyridine (0.24 g, 1.47 mmol), aniline **A3** (0.68 g, 2.99 mmol), *p*-toluenesulfonic acid (0.10 g), and molecular sieves 4 Å (3.0 g) in toluene (30 mL) was stirred at 80−110 °C for 24 h. Then the reaction mixture was filtered, and the molecular sieves were washed with CH_2Cl_2 several times. The solvents of the combined filtrates were removed under vacuum. Anhydrous ethanol (30 mL) was added to the residue. A yellow solid was filtered off to give **L3** with a yield of 0.425 g (51%). ^1H NMR (300 MHz, $CDCl_3$, δ (ppm)): 8.33 (d, 2H, J = 7.8 Hz, Py-H_m), 7.87 (t, 1H, J = 7.5 Hz, Py-H_p), 7.01−7.10 (m, 12H, aryl-*H*), 6.77 (d, 2H, J = 8.4 Hz, aryl-*H*), 6.58 (d, 2H, J = 8.4 Hz, aryl-*H*), 4.28 (q, 2H, J = 6.9 Hz, C*H*CH$_3$), 3.85 (s, 6H, *p*-OCH_3), 1.88 (d, 6H, J = 8.1 Hz, CHCH_3), 1.63 (d, 6H, J = 6.9 Hz, N=C*Me*). ^{13}C NMR ($CDCl_3$, δ (ppm)): 167.80, 156.54, 155.59, 146.26, 142.87, 137.73, 136.65, 128.92, 128.29, 127.95, 127.66, 125.81, 122.12, 119.50, 113.77, 111.19, 55.78, 40.64, 21.65, 16.26. Anal. Calcd for $C_{39}H_{39}N_3O_2$: C, 80.52; H, 6.76; N, 7.22. Found: C, 80.65; H, 7.12; N, 6.77. EI-MS (*m*/*z*): 582.8 $[M]^+$.

Synthesis of (ArN=C(C_5H_3N)C=NAr)FeCl_2 (1; Ar = 4-Methyl-2-(*sec*-phenethyl)phenyl). L1 (0.56 g, 1.02 mmol) was added to a solution of $FeCl_2 \cdot 4H_2O$ (0.19 g, 0.96 mmol) in THF (35 mL) at room temperature with violent stirring. The solution turned deep blue immediately, and the blue product precipitated from the solution after several minutes. After the mixture was stirred for 8 h at room temperature, the supernatant liquid was removed and the product was washed three times with 3 × 5 mL of Et_2O and dried under vacuum. The desired product was isolated as a light blue powder in 84% yield (0.58 g). ^1H NMR (500 MHz, CD_2Cl_2, δ (ppm)): 76.65 (s, 2H, Py-H_m), 37.3 (s, 1H, Py-H_p), 22.93 (s, 4H, Ar-H_o), 21.56 (s, 2H, aryl-H_o), 20.83 (s, 2H, aryl-H_m), 16.81 (s, 4H, Ar-H_p), 11.01 (s, 2H, aryl-H_m), 9.42 (s, 6H, *p*-CH_3), −3.82 (s, 2H, Ar-H_p), −5.52 (s, 6H, CHCH_3), −16.09 (s, 2H, C*H*CH$_3$), −24.41 (s, 6H, N=C*Me*). Anal. Calcd for $C_{39}H_{39}Cl_2FeN_3$: C, 69.24; H, 5.81; N, 6.21. Found: C, 68.84; H, 5.68; N, 5.99. IR (KBr, cm^{-1}): 1620 ($\nu_{C=N}$), 1586, 1451, 1371, 1266, 1217, 1029, 817, 763. FAB-MS (*m*/*z*): 675 $[M]^+$.

Synthesis of (ArN=C(C_5H_3N)C=NAr)FeCl_2 (2; Ar = 4,6-Dimethyl-2-(*sec*-phenethyl)phenyl). By the above procedure, **2** was isolated as a deep blue powder in 67% yield. ^1H NMR (500 MHz, CD_2Cl_2, δ (ppm)): 79.48 (s, 2H, Py-H_m), 49.16 (s, 1H, Py-H_p), 23.07 (s, 4H, Ar-H_o), 17.07, 14.54 (s, 4H, aryl-H_m), 8.80 (s, 6H, aryl-*o*-CH_3), 8.66 (s, 4H, Ar-H_m), 3.24 (s, 2H, C*H*CH$_3$), 2.15 (s, 6H, aryl-*p*-CH_3), −4.05 (s, 2H, Ar-H_p), −8.46 (s, 6H, CHCH_3), −23.41 (s, 6H, N=C*Me*). Anal. Calcd for $C_{41}H_{43}Cl_2FeN_3$: C, 69.89; H, 6.15; N, 5.96. Found: C, 69.52; H, 6.45; N, 5.77. IR (KBr, cm^{-1}): 1616 ($\nu_{C=N}$), 1581, 1470, 1371, 1261, 1214, 1028, 817, 764. FAB-MS (*m*/*z*): 703 $[M]^+$.

Synthesis of (ArN=C(C_5H_3N)C=NAr)FeCl_2 (3; Ar = 4-Methoxy-2-(*sec*-phenethyl)phenyl). By the above procedure, **3** was isolated as a light brown powder in 91% yield. ^1H NMR (500 MHz, CD_2Cl_2, δ (ppm)): 81.62 (s, 2H, Py-H_m), 60.1 (s, 1H, Py-H_p), 23.74 (s, 4H, Ar-H_o), 18.35 (s, 4H, Ar-H_m), 16.02 (s, 2H, aryl-H_o), 15.45, 11.39 (s, 4H, aryl-H_m), 5.96 (s, 6H, *p*-OCH_3), −1.07 (s, 4H, Ar-H_p), −3.87 (s, 6H, CHCH_3), −6.13 (s, 2H, C*H*CH$_3$), −18.60 (s, 6H, N=C*Me*). Anal. Calcd for $C_{39}H_{39}Cl_2FeN_3O_2$: C, 66.11; H, 5.55; N, 5.93. Found: C, 65.92; H, 5.71; N, 5.67. IR (KBr, cm^{-1}): 1602 ($\nu_{C=N}$), 1480, 1372, 1289, 1214, 1029, 806, 773. FAB-MS (*m*/*z*): 707 $[M]^+$.

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Synthesis of (ArN=C(C_5H_3N)C=NAr)$FeCl_2$ (4; Ar = 2,6-Diisopropylphenyl). Complex **4** was prepared according to a published procedure.[1a−c]

Polymerization of Ethylene under 1 bar of Pressure. The polymerization runs were carried out under an extra-pure-grade nitrogen atmosphere in a 100 mL glass flask equipped with a magnetic stirrer. MAO in toluene (30 mL) was injected into the reactor, and then the solution was saturated under 1 bar of ethylene pressure. The solution of iron(II) complex in toluene was added into the reactor. After 1 h, the polymerizations were stopped by quenching with ethanol containing 10% HCl. The resulting polymer was separated by filtration and dried under vacuum at 50 °C to constant weight.

Polymerization of Ethylene under 10 bar of Ethylene Pressure. A mechanically stirred 500 mL Parr reactor was heated overnight to 150 °C under vacuum and then cooled to room temperature. The autoclave was pressurized to 10 bar of ethylene and vented three times. The autoclave was then charged with 240 mL of a solution of MAO in toluene under 1 bar of ethylene at initialization temperature. The system was maintained by continuous stirring for 30 min, and then 10 mL of a solution of the iron complex in toluene was charged into the autoclave under 1 atm of ethylene. The ethylene pressure was raised to the specified value (10 bar), and the reaction was carried out for a certain time. Polymerization was terminated by addition of acidic ethanol after releasing ethylene pressure. The resulting precipitated polymers were collected and treated by filtering, washing with ethanol several times, and drying under vacuum at 50 °C to a constant weight.

Measurements. Elemental analyses were performed on a Vario EL microanalyzer. Mass spectra were obtained using either fast atom bombardment (FAB) LCQ DECA XP or electron impact (EI) LCMS-2010A. ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded in $CDCl_3$ on a Varian Unity Inova 300 spectrometer for the ligands, and ^1H NMR spectra were carried out on an INOVA 500 MHz spectrometer in CD_2Cl_2 solution for the complexes. ^1H and ^{13}C NMR chemical shifts were referenced to TMS and to the ^{13}C NMR signals of the deuterated solvents, respectively. IR spectra were recorded on a Nicolet NEXUS-670 FT-IR spectrometer. DSC analysis was conducted with a PerkinElmer DCS-7 system. The DSC curves were recorded at a heating rate of 10 °C/min to 160 °C. The cooling rate was 10 °C/min. Gel permeation chromatography (GPC) analyses of the molecular weight and molecular weight distribution of the polymers were performed on a Waters 135C instrument using standard polystyrene as reference and with 1,2,4-trichlorobenzene (TCB) as the solvent at a flow rate of 1.0 mL/min. The samples were obtained by removing the aluminum cocatalyst through the addition of HCl-acidified ethanol and subsequent filtration of the polymerization products.

Crystal Structure Determination. Crystals were mounted on glass fibers using the oil drop scan method.[17] Data obtained with the $\omega-2\theta$ scan mode was collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) at 293 K. The structures were solved using direct methods, while further refinement with full-matrix least squares on F^2 was obtained with the SHELXTL program package.[18,19] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms.

Acknowledgment. Financial support by the NSFC (Projects 20734004, 20974125, and 20674097), NSFG (Project 8251027501000018), and the Ministry of Education of China (Foundation for Ph.D. Training) are gratefully acknowledged.

Supporting Information Available: A CIF file and a table giving details of the crystallographic data of complex **2** and figures giving NMR spectra of ligands **L1**−**L3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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