Fluoro-Substituted 2,6-Bis(imino)pyridyl Iron and Cobalt Complexes: High-Activity Ethylene Oligomerization Catalysts

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Six five-coordinate difluoro-substituted 2,6-bis(imino)pyridyl iron and cobalt complexes, [{2,6-(2,X-$F_2C_6H_3N{=}CCH_3)_2C_5H_3N$}$MCl_2$] ($X$ = 6, M = Fe (**1**), Co (**2**); X = 5, M = Fe (**3**), Co (**4**)); X = 4, M = Fe (**5**), Co (**6**)), were synthesized by reactions of the corresponding bis(imino)pyridyl ligands with $FeCl_2\cdot 4H_2O$ or $CoCl_2$ in tetrahydrofuran (THF). However, a reaction between 2,6-diacetylpyridinebis(2,6-difluoroanil) and $FeCl_2\cdot 4H_2O$ in CH_3CN provided the ion-pair complex $[Fe\{2,6\text{-}(2,6\text{-}F_2C_6H_3N{=}CCH_3)_2C_5H_3N\}_2]^{2+}[FeCl_4]^{2-}$ (**7**) instead of a five-coordinate complex. The molecular structures of complexes **3** and **6** were determined by X-ray diffraction. The catalytic activities of complexes **1**−**7** for ethylene oligomerization were studied using modified methylaluminoxane (MMAO) as cocatalyst. At 60 °C and 10 atm of ethylene pressure, the iron complexes **1**, **3**, and **5** show very high activities: 4.07×10^7, 9.33×10^7, and 11.1×10^7 g/((mol of cat.) h), respectively. The oligomers formed consist mainly of dimer, trimer, and tetramer, with approximately 90% of the products being in the range of C_4−C_8. The complexes **1**, **3**, and **5** also exhibit high selectivity for linear α-olefins: >98% (complex **1**) and >93% (complexes **3** and **5**). The cobalt complexes **2**, **4**, and **6** and the ion-pair iron complex **7** are inactive for ethylene oligomerization.

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Introduction

The oligomerization of ethylene is of considerable academic and industrial interest for the synthesis of α-olefins. The major use of linear α-olefins is as polyethylene comonomer surfactants and lubricants. Since Ziegler's original work on AlR_3 catalysis of ethylene oligomerization, there has been considerable sustained interest in developing new oligomerization-active catalysts. Various transition metals such as nickel, chromium, titanium, zirconium, and others have been proven to be powerful oligomerization catalysts.[1−11] Recently, iron and cobalt complexes with mono-alkyl-substituted bis(imino)pyridyl ligands were reported by Brookhart[12] and Gibson.[13,14] These iron and cobalt complexes exhibit high activity in ethylene oligomerization, and the oligomers consist of >95% linear α-olefins.

Herein, we wish to report the synthesis of a series of iron and cobalt complexes bearing 2,6-bis(imino)pyridyl ligands with fluoro substituents in different positions on the imine aryl and their reactivity in ethylene oligomerization. The iron complexes oligomerized ethylene to linear α-olefins with high activity and selectivity, and linear α-olefins obtained in these fluoro-substituted iron-complex-catalyzed ethylene oligomerizations contain much fewer high-molecular-weight products than those found in ethylene oligomerization catalyzed by the mono-alkyl-substituted iron complexes. The relation between the structures of the complexes and their activity and selectivity is also shown.

Results and Discussion

Synthesis and Structures of Complexes. 2,6-Diacetylpyridinebis(2,6-difluoroanil) (**L1**), 2,6-diacetylpyridinebis(2,5-difluoroanil) (**L2**), and 2,6-diacetylpyridinebis(2,4-difluoroanil) (**L3**) were synthesized in good yield by condensation of 2,6-diacetylpyridine with the corresponding aniline using silica−alumina catalyst support as the catalyst and molecular sieves as the water adsorbent[15] (Scheme 1). The ligands **L1**, **L2**, and

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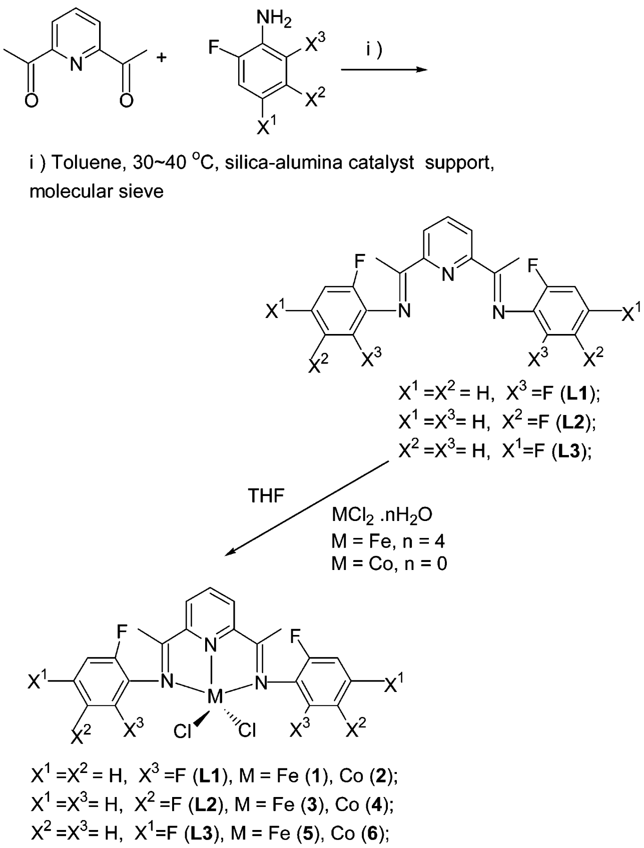
Scheme 1



L3 were characterized by elemental analysis, ^{1}H NMR, IR, and mass spectrometry.

Iron and cobalt complexes of these ligands were synthesized by dissolving $FeCl_2 \cdot 4H_2O$ or $CoCl_2$ in tetrahydrofuran (THF) (Scheme 1), followed by addition of 1 equiv of the ligand. The iron and cobalt complexes precipitated from the reaction solution. After washing with diethyl ether, the complexes **1**−**6** were obtained in good yield and high purity. The complexes were characterized by elemental analyses and IR spectroscopy. The elemental analysis results revealed that the components of all complexes were in accord with the formula $MLCl_2$, and one solvent molecule of THF was included in **5** and **6** and one molecule of H_2O in **1** and **2**. The IR spectra of the free ligands show that the C═N stretching frequencies appear at 1636−1642 cm^{-1}. In complexes **1**−**6**, the C═N stretching vibrations shift toward lower frequencies between 1616 and 1633 cm^{-1} and were greatly reduced in intensity, which indicated the coordination interaction between the imino nitrogen atoms and the metal ions.

The 2,5-difluoroanil-substituted complex **3** could also be synthesized in a strongly polar solvent, CH_3CN. However, the solvent polarity is a factor in the type of complex formed for 2,6- and 2,4-difluoroanil substitution. The reaction of 2,6-diacetylpyridinebis(2,6-difluoroanil) with $FeCl_2 \cdot 4H_2O$ in CH_3CN gave the ion-pair complex $[Fe\{2,6\text{-}(2,6\text{-}F_2C_6H_3N{=}CCH_3)_2C_5H_3N\}_2]^{2+}[FeCl_4]^{2-}$ (**7**), and the reaction of the 2,4-substituted ligand with $FeCl_2 \cdot 4H_2O$ in CH_3CN provided an unexpected ion-pair complex composed of $[Fe\{2,6\text{-}(2,4\text{-}F_2C_6H_3N{=}CCH_3)_2C_5H_3N\}_2]^{2+}$ and $[Cl_3FeOCl_3]^{2-}$.[17] The formation of these two ion-pair complexes in CH_3CN is partly due to the polarity of the organic solvent. In comparison with THF, an organic solvent of higher polarity, CH_3CN, can add further stability to the ion-pair complex.[16] Therefore, it is better to use an organic solvent of lower polarity for the synthesis of five-coordinate complexes with less bulky substituents on the imino nitrogen donors.

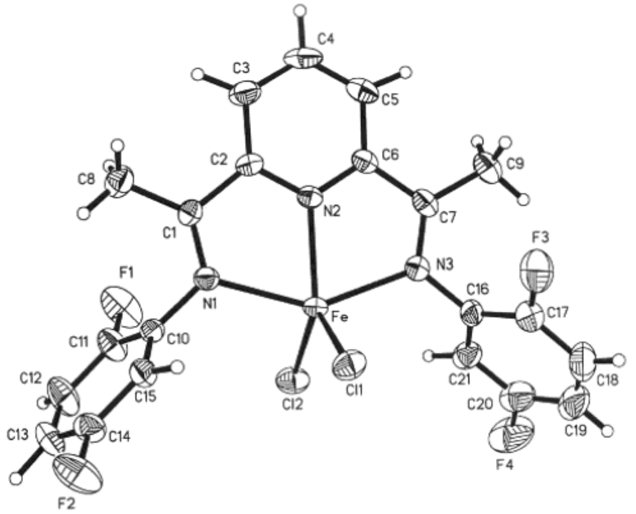


Figure 1. Molecular structure of complex **3**. Selected bond lengths (Å) and angles (deg): Fe−N(2), 2.1099(19); Fe−N(1), 2.211(2); Fe−N(3), 2.233(2); Fe−Cl(1), 2.2915(8); Fe−Cl(2), 2.2771(8); C(1)−N(1), 1.276(3); C(7)−N(3), 1.287(3); N(2)−Fe−Cl(1), 119.13(6); N(2)−Fe−Cl(2), 129.60(6); Cl(1)−Fe−Cl(2), 111.25(3); N(2)−Fe−N(1), 73.01(8); N(2)−Fe−N(3), 73.08(8); N(1)−Fe−N(3), 146.08(8); Cl(1)−Fe−N(1), 100.55(6); Cl(1)−Fe−N(3), 96.83(6); Cl(2)−Fe−N(1), 97.48(6); Cl(2)−Fe−N(3), 103.03(6).

Single crystals of complexes **3** and **6** suitable for X-ray diffraction analysis were obtained from CH_3CN solution (**3**) or from THF solution (**6**). The molecular structures of complexes **3** and **6** are shown in Figures 1 and 2, respectively.

Complex **3** displays an approximate C_2 symmetry about a plane containing the iron atom, the two chloro atoms, and the pyridyl nitrogen atom. The dihedral angles between the phenyl rings and the plane formed by three coordinated nitrogen atoms are 76.9 and 66.3°, respectively. The iron atom deviates by 0.034 Å from this coordinated plane. The coordination geometry of the central iron can be best described as distorted trigonal bipyramidal, with the pyridyl nitrogen atom and the two chloro atoms forming the equatorial plane. The equatorial angles range between 111.25(3) and 129.60(6)°, and the two axial Fe−N bonds subtend an angle of 146.08(8)°. As previously observed,[14,18] the Fe−N(imino) bonds (2.211(2) and 2.233(2) Å) are longer than the Fe−N(pyridyl) bond (2.1099(19) Å). The two imino C═N bonds have distinctive double-bond character, with C−N distances of 1.276(3) and 1.287(3) Å.

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Table 1. Results of Oligomerization of Ethylene with Complexes 1−7/MMAO

run	complex (amt (μmol))	amt of toluene (mL)	Al/M (mol/mol)	temp (°C)	pressure (atm)	time (min)	yield (g)	activity (10^7g/((mol of cat.) h)	α	linear α-olefin[a] (%)
1	**1** (0.8)	50	1250	0	1	30	0.32	0.08	0.70	>91
2	**1** (1)	150	2000	25	10	60	34.9	3.49	0.59	>98
3	**1** (1)	150	2000	40	10	60	45.1	4.51	0.49	>98
4	**1** (1)	150	2000	60	10	60	38.4	3.84	0.42	>98
5	**1** (0.6)	200	1800	60	5	15	4.8	3.20	0.44	>98
6	**1** (0.6)	200	1800	60	10	15	6.1	4.07	0.44	>98
7	**2** (1)	150	2000	40	10	60		inactive		
8	**3** (0.6)	200	1800	60	10	15	14.0	9.33	0.33	>94
9	**4** (2)	200	1800	60	10	30		inactive		
10	**5** (0.6)	200	1800	60	10	15	16.6	11.1	0.34	>93
11	**6** (2)	200	1800	60	10	30		inactive		
12	**7** (0.6)	200	1800	60	10	30		inactive		

[a] Determined by GC.

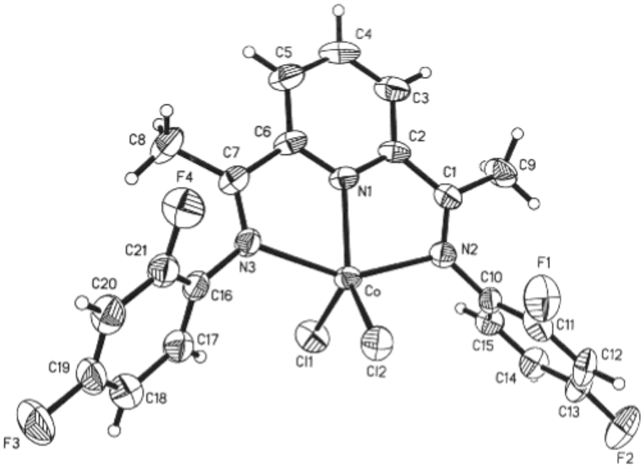

Figure 2. Molecular structure of complex **6** (one THF molecule in the lattice is not included). Selected bond lengths (Å) and angles (deg): Co−N(1), 2.045(3); Co−N(2), 2.211(3); Co−N(3), 2.225(3); Co−Cl(1), 2.2602(12); Co−Cl(2), 2.2533(11); C(1)−N(2), 1.273(4); C(7)−N(3), 1.283(4); N(1)−Co−Cl(1), 111.87(9); N(1)−Co−Cl(2), 134.75(9); Cl(1)−Co−Cl(2), 113.28(5); N(1)−Co−N(2), 75.29(13); N(1)−Co−N(3), 74.42(13); N(2)−Co−N(3), 149.54(13); Cl(1)−Co−N(2), 95.88(8); Cl(1)−Co−N(3), 98.26(9); Cl(2)−Co−N(2), 102.72 (9); Cl(2)−Co−N(3), 96.24(9).

The complex **6** possesses a structure with approximate C_s symmetry about a plane containing the cobalt atom, the two chloro atoms, and the pyridyl nitrogen atom. One difluorophenyl ring is oriented almost perpendicular (77.3°) to the plane formed by the coordinated nitrogen atoms, while the other difluorophenyl ring forms a dihedral angle of 55.7° with this plane. The cobalt atom lies on this coordinated plane. The coordination geometry at the cobalt center is also distorted trigonal bipyramidal, with the equatorial plane formed by the pyridyl nitrogen atom and the two chloro ligands, and two axial Co−N bonds. The Cl(1)−Co−Cl(2) angle is 113.28(5)°. Two N(1)-M−Cl angles are unsymmetrical: one is 134.75(9)°, while the other is 111.87(9)°. The "axial" Co−N bonds subtend an angle of 149.54(13)°. The Co−N(pyridyl) bond (2.045(3) Å) of **6** is shorter than the Fe−N(pyridyl) bond (2.1099(19) Å) of **3**, while the distances between the metal atom and the imino nitrogens in the two complexes are almost the same (2.211(2) and 2.233(2) Å in **3** and 2.211(3) and 2.225(3) Å in **6**). The two imino C═N bonds in **6** have typical double-bond character with C═N bond lengths of 1.283(4) and 1.273(4) Å.

The molecular structure of complex **7** was also determined by X-ray diffraction. It exists as an ion pair composed of $[Fe\{2,6\text{-}(2,6\text{-}F_2C_6H_3N{=}CCH_3)_2C_5H_3N\}_2]^{2+}$ and $[FeCl_4]^{2-}$. The iron center of the cation is coordinated by six nitrogen atoms from two ligands, while that in the anion is coordinated by four chloro ligands.[19] Unfortunately, the refinement results for the structure are poor, with an R value above 12%. Crystallographic data for this complex is provided in the Supporting Information.

Oligomeriztion of Ethylene. The catalytic activities of complexes **1**−**7** for the oligomerization of ethylene were evaluated employing modified methylaluminoxane (MMAO) as cocatalyst. The results are listed in Table 1. The iron complexes **1**, **3**, and **5** are highly active for the oligomerization of ethylene, under the conditions employed. At 60 °C and 10 atm of ethylene pressure, their activities are 4.07×10^7, 9.33×10^7, and 11.1×10^7 g/((mol of cat.) h), respectively. However, their cobalt analogues **2**, **4**, and **6** are inactive for the ethylene oligomerization. The distribution of oligomers obtained in **1**-, **3**-, and **5**-catalyzed ethylene oligomerization follows Schulz−Flory rules, which can be characterized by the constant α; here α represents the probability of chain propagation (α = rate of propagation/((rate of propagation) + (rate of chain transfer)) = (moles of C_{n+2})/(moles of C_n)).[20−23] The α value can be determined by the molar ratio of C_{12} and C_{14} fractions. When the complexes with fluoro groups in different positions of the aryl rings are compared, it is found that the 2,5-difluoro-substituted complex **3** and 2,4-difluoro-substituted complex **5** show much higher activity than the 2,6-difluoro-substituted complex **1**, and the activity of **5** is slightly higher than that of **3**. The α values obtained in **1**-, **3**- and **5**-catalyzed ethylene oligomerization, 0.44 (Table 1, run 6), 0.33 (Table 1, run 8), and 0.34 (Table 1, run 10), are much lower than those found in the ethylene oligomerization catalyzed by the mono-alkyl-substituted iron complexes; the alkyl-substituted iron complexes give α values of 0.70−0.85.[12,14] The small size of the fluoro group is responsible for the small α value here. The products provided by the complexes **1**, **3**, and **5** consist mainly of dimer, trimer, and tetramer, with approximately 90% of the product being in the range of

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C_4-C_8. It is also found that the 2,5-difluoro-substituted complex **3** and 2,4-difluoro-substituted complex **5** give very similar α values (0.33 and 0.34), while the 2,6-difluoro-substituted complex **1** gives a higher α value of 0.44. There are two factors which might explain the higher α value provided by **1**. One is that the fluorine atom is slightly larger than the hydrogen atom, and the other is that there might be an interaction between the fluoro group in the ortho position of the aryl ring and the β-hydrogen of the propagation chain in the active species, suppressing the β-hydrogen transfer to the iron center and favoring the chain propagation. In comparison with the 2,5-difluoro-substituted complex **3** and 2,4-difluoro-substituted complex **5**, the 2,6-difluoro-substituted complex **1** has more fluoro groups in the ortho positions of the aryl ring; therefore, **1** gives a higher α value. Recently, Fujita et al. found that such interactions also existed in the titanium complexes bearing fluorine-containing phenoxy–imine ligands and prevented β-hydrogen elimination.[24] The fluoro groups in meta or para positions of the aryl rings have little effect on the selectivity for linear α-olefins. The percentages of linear α-olefins generated in the **3-** and **5**-catalyzed ethylene oligomerizations are 94% and 93%, respectively. These values are lower than that for the 2,6-difluoro-substituted complex **1** (98%). The effects of reaction temperature on **1**-catalyzed ethylene oligomerization were also studied (Table 1, runs 2–4). The α value can be tuned by varying the reaction temperature. Decreasing the temperature results in an increase of α value, which is due to a decrease in the rate of β-hydrogen transfer relative to the rate of propagation when the temperature is lowered. In contrast to the high activity of the five-coordinate complex $[\{2,6\text{-}(2,6\text{-}F_2C_6H_3N{=}CCH_3)_2C_5H_3N\}FeCl_2]$ (**1**), the ion-pair complex $[Fe\{2,6\text{-}(2,6\text{-}F_2C_6H_3N{=}CCH_3)_2C5H_3N\}_2]^{2+}[FeCl_4]^{2-}$ (**7**) is inactive for ethylene oligomerization.

Conclusion

Reactions of the difluoro-substituted 2,6-bis(imino)pyridyl ligands $(2,X\text{-}F_2C_6H_3N{=}CCH_3)_2C_5H_3N$ (X = 6, 5, 4) with $FeCl_2 \cdot 4H_2O$ or $CoCl_2$ in THF provided the five-coordinate 2,6-bis(imino)pyridyl iron and cobalt complexes $[\{2,6\text{-}(2,X\text{-}F_2C_6H_3N{=}CCH_3)_2C_5H_3N\}MCl_2]$ (X = 6, M = Fe (**1**), Co (**2**); X = 5, M = Fe (**3**), Co (**4**); X = 4, M = Fe (**5**), Co (**6**)). Complex **3** was also obtained in a organic solvent of higher polarity, CH_3CN, while a reaction between 2,6-diacetylpyridinebis(2,6-difluoroanil) and $FeCl_2 \cdot 4H_2O$ in CH_3CN produced the ion-pair complex $[Fe\{2,6\text{-}(2,6\text{-}F_2C_6H_4N{=}CCH_3)_2C_5H_3N\}_2]^{2+}[FeCl_4]^{2-}$ (**7**). When modified methylaluminoxane (MMAO) is employed as cocatalyst, the iron complexes **1**, **3**, and **5** show very high activities for ethylene oligomerization, while the cobalt complexes **2**, **4**, and **6** and the ion-pair iron complex **7** are inactive. For the five-coordinate iron complexes $[\{2,6\text{-}(2,X\text{-}F_2C_6H_3N{=}CCH_3)_2C_5H_3N\}FeCl_2]$ (X = 6, M = Fe (**1**); X = 5, M = Fe (**3**); X = 4, M = Fe (**5**)), the activity, distribution of oligomers, and selectivity for linear α-olefins closely depend on the position of fluorine on the imine aryl. The complexes **3** and **5** show much higher activities and give much smaller Schulz–Flory α values than complex **1**, and the percentages of linear α-olefins obtained in the **3-** and **5**-catalyzed ethylene oligomerizations are lower than that found in the ethylene oligomerization catalyzed by complex **1**.

Experimental Section

All manipulations of air- and/or moisture-sensitive compounds were performed under an atmosphere of argon using standard Schlenk techniques. ^1H NMR was recorded on a Varian XL 300 MHz spectrometer. Mass spectra were carried out with a HP5989A spectrometer. IR spectra were recorded using a Nicolet AV-360 spectrometer. Elemental analyses were performed by the Analytical Laboratory of the Shanghai Institute of Organic Chemistry. Oligomer products were analyzed by Varian CP-3800 GC and Finnigan MD-800 GC-MS. The Varian CP-3800 GC was equipped with an SPB-5 capillary column (30 m × 0.32 mm) and a flame ionization detector. The analytical conditions used were as follows: injector and detector temperature, 280 °C; oven temperature program, 40 °C/6 min, 10 °C/min ramp, 250 °C/15 min. C_6 olefin isomer was used to determine the percentage of linear α-olefins. 2,4-Difluoroaniline, 2,5-difluoroaniline, and 2,6-difluoroaniline were purchased from Acros and used as received. A toluene solution of modified methylaluminoxane (MMAO) was purchased from Akzo Nobel. Silica–alumina catalyst support (grade 135) was purchased from Aldrich Chemical Co. 2,6-Diacetylpyridine was prepared according to a published procedure.[25] Tetrahydrofuran and CH_3CN were degassed to remove oxygen prior to use. Toluene used as an oligomerization solvent was distilled under argon from sodium–benzophenone.

2,6-Diacetylpyridinebis(2,6-difluoroanil) (L1). Method a. A solution of 2,6-difluoroaniline (1.61 g, 12.5 mmol), 2,6-diacetylpyridine (0.81 g, 5 mmol), and *p*-toluenesulfonic acid (0.02 g) in toluene (100 mL) was refluxed for 3 days, with azeotropic removal of water using a Dean–Stark trap. Then the reaction mixture was cooled to room temperature, and the solvent was removed in vacuo. The crude product was purified by column chromatography. **L1** was obtained as a yellow powder in 13% yield.

Method b. A solution of 2,6-diacetylpyridine (0.41 g, 2.5 mmol), 2,6-difluoroaniline (0.77 g, 6 mmol), silica–alumina catalyst support (0.2 g), and molecular sieves 4 Å (1.0 g) in toluene (8 mL) was stirred at 30–40 °C for 24 h. Then the reaction mixture was filtered, and the molecular sieves were washed with toluene several times. The toluene of the combined filtrates was removed in vacuo. Anhydrous methanol (8 mL) was added to the residue. A yellow solid was filtered off to give **L1** in 65% yield. ^1H NMR (300 MHz, $CDCl_3$): δ 8.47 (d, 2H, J = 7.8 Hz, Py H_m); 7.93 (t, 1H, J = 7.9 Hz, Py H_p); 7.07 (m , 4H, Ar H); 6.99 (t, 2H, J = 7.6 Hz, Ar H); 2.46 (s, 6H, N=CMe). IR (KBr): 1636 ($\nu_{C=N}$), 1576, 1465, 1369, 1277, 1237, 1215, 1126, 1032, 1002, 827, 789, 759 cm^{-1}. EI mass spectrum: *m/z* 385 [M^+]. Anal. Calcd for $C_{21}H_{15}N_3F_4$: C, 65.45; H, 3.92; N, 10.90. Found: C, 65.51; H, 4.08; N, 10.62.

Synthesis of 2,6-Diacetylpyridinebis(2,5-difluoroanil) (L2). Following the above procedure (**L1** method b), 2,6-diacetylpyridine (0.49 g, 3.0 mmol), 2,6-difluoroaniline (0.91 g, 7.0 mmol), silica–alumina catalyst support (0.2 g), and molecular sieves 4 Å (1.5 g) were used. **L2** was obtained as a yellow powder in 70% yield. ^1H NMR (300 MHz, $CDCl_3$): δ 8.38 (d, J = 7.9 Hz, 2H, Py H_m); 7.91 (t, J = 7.9 Hz, 1H, Py H_p); 7.07 (m , 2H, Ar H); 6.80 (m, 2H, Ar H); 6.69 (m, 2H, Ar H); 2.43 (s, 6H, N=CMe). IR (KBr): 1642 ($\nu_{C=N}$), 1617, 1578, 1492, 1367, 1323, 1268, 1245, 1196, 1142, 1098, 1080, 863, 822, 806, 760, 742, 721 cm^{-1}. EI mass spectrum: *m/z* 385 [M^+].

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Anal. Calcd for $C_{21}H_{15}N_3F_4$: C, 65.45; H, 3.92; N, 10.90. Found: C, 65.51; H, 4.12; N, 10.44.

Synthesis of 2,6-Diacetylpyridinebis(2,4-difluoroanil) (L3). Following the above procedure (**L1** method b), **L3** was obtained as a yellow powder in 72% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.38 (d, $J = 7.9$ Hz, 2H, Py H_m); 7.90 (t, $J = 7.9$ Hz, 1H, Py H_p); 6.93 (m, 6H, Ar H); 2.41 (s, 6H, N=CMe). IR (KBr): 1639 ($\nu_{C=N}$), 1596, 1575, 1497, 1426, 1366, 1322, 1261, 1199, 1140, 1094, 1080, 960, 848, 825, 778, 726 cm^{-1}. EI mass spectrum: m/z 385 [M$^+$]. Anal. Calcd for $C_{21}H_{15}N_3F_4$: C, 65.45; H, 3.92; N, 10.90. Found: C, 65.83; H, 4.14; N, 10.57.

Synthesis of [2,6-diacetylpyridinebis(2,6-difluoroanil)]-$FeCl_2 \cdot H_2O$ (1). Ligand **L1** (63 mg, 0.16 mmol) was added to a solution of $FeCl_2 \cdot 4H_2O$ (27 mg, 0.14 mmol) in THF (8 mL) at room temperature with rapid stirring. The solution turned deep blue immidiately. The dark blue product precipitated from the solution after several minutes. After it was stirred at room temperature for 12 h, the reaction volume was reduced to about 4 mL. The reaction mixture was allowed to stand at room temperature for several hours, and then the supernatant liquid was removed. The product was washed with 4 × 5 mL of Et_2O and dried in vacuo. The desired product (62 mg) was obtained as a dark blue powder in 89% yield. IR (KBr): 3422, 1616 ($\nu_{C=N}$), 1587, 1464, 1374, 1260, 1240, 1006, 784, 752 cm^{-1}. Anal. Calcd for $C_{21}H_{15}N_3F_4FeCl_2 \cdot H_2O$: C, 47.58; H, 3.23; N, 7.92. Found: C, 48.42; H, 3.36; N, 7.66.

Synthesis of [2,6-diacetylpyridinebis(2,6-difluoroanil)]-$CoCl_2 \cdot H_2O$ (2). The procedure as above, using ligand **L1** (53 mg, 0.12 mmol) and $CoCl_2$ (13 mg, 0.10 mmol), gave **2** as a golden brown powder (42 mg, 81%). IR (KBr): 3457, 1619 ($\nu_{C=N}$), 1589, 1471, 1376, 1283, 1262, 1241, 1229, 1006, 783, 751 cm^{-1}. Anal. Calcd for $C_{21}H_{15}N_3F_4CoCl_2 \cdot H_2O$: C, 47.30; H, 3.21; N, 7.88. Found: C, 47.27; H, 3.16; N, 7.68.

Synthesis of [2,6-diacetylpyridinebis(2,5-difluoroanil)]-$FeCl_2$ (3). Method a. The procedure as above, using ligand **L2** (92 mg, 0.26 mmol) and $FeCl_2 \cdot 4H_2O$ (51 mg, 0.26 mmol), gave **3** as a blue powder (100 mg, 76%). IR (KBr): 1629 ($\nu_{C=N}$), 1617, 1595, 1496, 1377, 1265, 1250, 1212, 1194, 1158, 813, 765 cm^{-1}. Anal. Calcd for $C_{21}H_{15}N_3F_4FeCl_2$: C, 49.25; H, 2.95; N, 8.20. Found: C, 49.15; H, 3.18, N, 8.16.

Method b. Ligand **L2** (68 mg, 0.17 mmol) was added to a solution of $FeCl_2 \cdot 4H_2O$ (35 mg, 0.17 mmol) in CH_3CN (7 mL) at room temperature with rapid stirring. The solution turned deep blue immidiately. After the mixture was stirred at room temperature for 2 h, the reaction volume was reduced to about 4 mL and left to stand at 0 °C for several days. Dark blue crystals of the product **3** formed and were separated from the solution (69 mg, 77%). Anal. Calcd for $C_{21}H_{15}N_3F_4FeCl_2$: C, 49.25; H, 2.95; N, 8.20. Found: C, 49.19; H, 3.10; N, 8.23.

Synthesis of [2,6-diacetylpyridinebis(2,5-difluoroanil)]-$CoCl_2$ (4). The procedure is similar to that of complex **1**, using ligand **L2** (96 mg, 0.25 mmol) and $CoCl_2$ (32 mg, 0.25 mmol) gave **4** as a yellow-green powder (98 mg, 77%). IR (KBr): 1633 ($\nu_{C=N}$), 1617, 1595, 1496, 1377, 1262, 1251, 1212, 1194, 1158, 813, 765 cm^{-1}. Anal. Calcd for $C_{21}H_{15}N_3F_4CoCl_2$: C, 48.96; H, 2.93; N, 8.16. Found: C, 48.87; H, 3.18; N, 8.06.

Synthesis of [2,6-diacetylpyridinebis(2,4-difluoroanil)]-$FeCl_2 \cdot$THF (5). The procedure as above, using ligand **L3** (103 mg, 0.27 mmol) and $FeCl_2 \cdot 4H_2O$ (53 mg, 0.27 mmol), gave **5** as a dark blue powder (108 mg, 69%). IR (KBr): 1619 ($\nu_{C=N}$), 1587, 1502, 1429, 1374, 1266, 1219, 1145, 1093, 966, 875, 806, 715 cm^{-1}. Anal. Calcd for $C_{21}H_{15}N_3F_4FeCl_2 \cdot$THF: C, 51.40; H, 3.97; N, 7.19. Found: C, 51.36; H, 4.27; N, 7.16.

Synthesis of [2,6-diacetylpyridinebis(2,4-difluoroanil)]-$CoCl_2 \cdot$THF (6). The procedure as above, using ligand **L3** (96 mg, 0.25 mmol) and $CoCl_2$ (32 mg, 0.25 mmol), gave **6** as a brown powder (107 mg, 73%). IR (KBr): 1627 ($\nu_{C=N}$), 1587, 1429, 1374, 1265, 1220, 1144, 1092, 966, 877, 808, 715 cm^{-1}. Anal. Calcd for $C_{21}H_{15}N_3F_4CoCl_2 \cdot$THF: C, 51.12; H, 3.95; N, 7.15. Found: C, 50.99; H, 4.09; N, 7.10.

Synthesis of [Fe(2,6-diacetylpyridinebis(2,6-difluoroanil))$_2$]$^{2+}$[$FeCl_4$]$^{2-}$ (7). 2,6-Diacetylpyridinebis(2,6-difluoroanil) (22 mg, 0.056 mmol) was added to a solution of $FeCl_2 \cdot 4H_2O$ (11 mg, 0.056 mmol) in CH_3CN (5 mL) at room temperature with rapid stirring. After the mixture was stirred at room temperature for 2 h, the reaction volume was reduced to about 3 mL and the mixture left to stand at 0 °C for several days. Dark blue crystals of the product formed and were separated from the solution (18 mg, 63%). Anal. Calcd for $C_{42}H_{30}N_6F_8Fe_2Cl_4$: C, 49.26; H, 2.95; N, 8.21. Found: C, 48.58; H, 3.31, N, 7.86.

General Procedure for Ethylene Oligomerization. (a) High-Pressure Oligomerization. A mechanically stirred 500 mL stainless steel reactor was heated under vacuum for at least 2 h at >85 °C and then cooled to the reaction temperature under an ethylene atmosphere. A 150 mL portion of toluene and 0.48 mmol of MMAO were charged into the reactor. The reactor was sealed, and ethylene was added (5 atm). The solution was stirred for about 10 min, during which time the desired reaction temperature was established. The ethylene pressure was then released, 10 mL of catalyst solution prepared by combination of 0.6 μmol of the complex in toluene and 0.6 mmol of MMAO was injected into the reactor, and then 40 mL of toluene was added. The reactor was then sealed and pressurized with ethylene to 10 atm. The reaction mixture was stirred under constant ethylene pressure for 15 min, after which time the reactor was resealed and the catalyst quenched with dilute hydrochloric acid. The organic layer was separated and dried over anhydrous Na_2SO_4. An aliquot of this solution was analyzed by GC. The integrated areas of the C_{12} and C_{14} oligomers were used to calculate the Schulz−Flory α constant. The standard solution containing precise known masses of 1-hexene, 1-octene, 1-decene, and 1-dodecene in toluene was prepared and chromatographed, and the mass percents of these olefins in this solution should be prepared close to those in the sample. The masses of C_6, C_8, C_{10}, and C_{12} oligomers produced can be calculated by using the formula

$$W_{C_n} = \frac{W'_{C_n} V_{C_n} V'_{Tol} W_{Tol}}{V'_{C_n} V_{Tol} W'_{Tol}}$$

where W'_{C_n} = mass of C_n in the standard solution, W'_{Tol} = mass of toluene in the standard solution, V'_{C_n} = integrated area of C_n in the standard solution, V'_{Tol} = integrated area of toluene in the standard solution, V_{C_n} = integrated area of C_n in the sample, V_{Tol} = integrated area of toluene in the sample, and W_{Tol} = mass of toluene used as the solvent in the oligomerization. The mass of C_4 was calculated by the mass of C_6 and the Schulz−Flory α constant:

$$W_{C_4} = \frac{W_{C_6}(M_w \text{ of } C_4)}{(M_w \text{ of } C_6)\alpha}$$

The masses of C_{14} and C_{16} oligomers were obtained by comparing their integrated areas with that of the C_{12} oligomer, and the mass of oligomers in the C_{18}−C_{40} range was calculated by the formula

$$W_{C_n} = \frac{W_{C_{16}}(M_w \text{ of } C_n)\alpha^{n-16/2}}{M_w \text{ of } C_{16}}$$

The total product mass was obtained by adding the mass of oligomers in the C_4−C_{40} range; therefore, the activity numbers were generated.

(b) Oligomerization at 1 atm Pressure. A 100 mL flame-dried Schlenk flask equipped with a stirrer bar was placed in an ice−water bath and purged with ethylene (1 atm), followed by charging with 40 mL of toluene and 1 mmol of MMAO. The required temperature was ensured by stirring the mixture for

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Table 2. Crystallographic Data and Refinement for Complexes 3 and 6

	3	**6**
formula	$C_{21}H_{15}N_3F_4FeCl_2$	$C_{21}H_{15}N_3F_2CoCl_2 \cdot C_4H_8O$
fw	512.11	587.29
color	dark-blue	brown
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
a, Å	10.6387(8)	12.7337(11)
b, Å	13.0812(10)	16.1664(15)
c, Å	16.3810(12)	12.8804(11)
β, deg	106.770(2)	101.808(2)
V, Å^3	2182.7(3)	2595.4(4)
Z	4	4
$D_{\text{calcd,}}$ g/cm^3	1.558	1.503
F(000)	1032	1196
μ(Mo Kα), mm^{-1}	0.983	0.919
θ range, deg	2.00−28.32	2.05−28.29
no. of rflns collected	13 195	15 696
no. of unique rflns	5119	6066
no. of obsd rflns ($I > 2\sigma(I)$)	2074	1997
no. of params	340	327
goodness of fit	0.609	0.678
final R, R_w	0.0378, 0.0487	0.0458, 0.0735
$\Delta\rho_{\text{max,min}}$/e Å^{-3}	0.419, −0.293	0.644, −0.365

about 20 min in the water bath. A 0.8 μmol amount of precatalyst in 10 mL of toluene was injected via syringe. After the reaction mixture was stirred under 1 atm of ethylene pressure for 0.5 h, the oligomerization was stopped by the injection of diluted hydrochloric acid. The oligomers were collected and worked up as described as in the oligomerization under high pressure.

X-ray Structure Determination. Data collections for complexes **3** and **6** were performed at 20 °C on a Bruker SMART diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). The SMART program package was used to determine the unit-cell parameters. A SADABS absorption correction was applied. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares techniques with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were placed at calculated positions and were included in the structure calculation without further refinement of the parameters. All calculations were carried out using the SHELXS-97 program. Crystal data and processing parameters for complexes **3** and **6** are summarized in Table 2.

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Supporting Information Available: Tables giving X-ray crystallographic data for **3**, **6**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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