

Formation and Molecular Structure of an Ion Pair Iron(II) Compound Derived from 2,6-Bis-[1-(2,6-dibromophenylimino)-ethyl]pyridine and 2-Acetyl-6-[1-(2,6-dibromophenylimino)-ethyl]pyridine

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Two novel tridentate ligands of 2,6-bis-[1-(2,6-dibromophenylimino)ethyl]pyridine (L_1) and 2-acetyl-6-[1-(2,6-dibromophenylimino)ethyl]pyridine (L_2) have been synthesized. The iron(II) complex of L_1 and L_2 has been characterized with the crystal structure of $[\text{Fe}(L_1)(L_2)]^{2+}[\text{FeCl}_4]^{2-} \cdot \text{CH}_2\text{Cl}_2$ [monoclinic, $P2_1/m$ (# 11), $a = 1.0562(4)$, $b = 2.0928(4)$, $c = 1.2914(2)$ nm, $\beta = 100.12^\circ$, $V = 2.810(1)$ nm³, $D_c = 1.879$ g/cm³ and $Z = 2$].

Keywords Fe(II) complex, 2,6-bis[1-(2,6-dibromophenylimino)ethyl]pyridine, 2-acetyl-6-[1-(2,6-dibromophenylimino)-ethyl]pyridine

Introduction

In recent years, olefin polymerization catalysts derived from well-defined transition metal complexes have developed dramatically, with some of the most significant recent advances occurring for late transition metal systems. Brookhart and co-workers found that catalysts based on nickel and palladium could be used to access a range of linear and branched polyethylene.¹⁻⁴ Recently, Gibson⁵ and Brookhart⁶ have discovered the highly active iron ethylene polymerization catalysts, which incorporate tridentate pyridyl-diimine ligands bearing bulky alkyl substituents on the *ortho*-position of the phenyl ring. Previously, a series of halogen substituted 2,6-bis(imino)pyridyl iron(II) and Co(II) complexes were also

synthesized successfully, which exhibit very high activity for ethylene polymerization.⁷ In this paper, we wish to report a novel six-coordinated iron(II) complex, the structure of which is completely different from other molecular structures of the five-coordinated iron complexes developed by Gibson⁵ and Brookhart.⁶

Experimental

General procedure

All manipulations were performed using standard Schlenk techniques. ¹H NMR spectra were recorded as CDCl₃ solutions on a VXL-300 instrument. Infrared spectra were recorded on a Perkin-Elmer 983 FT-IR spectrometer as liquid forms on potassium bromide plates unless otherwise noted. Mass spectra were recorded on an HP5989A spectrometer and elemental analysis was carried out on a MOD-1106 elemental analyzer.

Preparation of 2,6-bis-[1-(2,6-dibromophenylimino)-ethyl]pyridine (L_1) and 2-acetyl-6-[1-(2,6-dibromophenylimino)ethyl]pyridine (L_2)

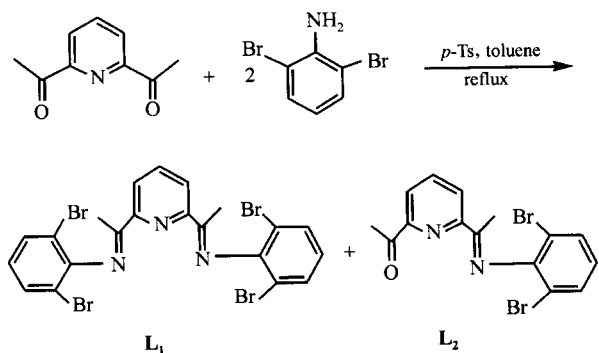
The synthetic route of the corresponding ligands of L_1 and L_2 was described as shown in Scheme 1.

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Scheme 1



A solution of 2,6-dibromoaniline (1.23 g, 5.0 mmol) and 2,6-diacetylpyridine (0.4 g, 2.5 mmol) and *p*-toluenesulfonic acid (0.020 g) in toluene (100 mL) was refluxed for 24 h, with azeotropic removal of water using a Dean-Stark trap. The mixture was cooled to room temperature and the solvent was removed under reduced pressure. The crude product was dissolved in Et₂O (100 mL) and the organic layer was washed twice with water (50 mL), once with the saturated NaCl (50 mL) and dried over MgSO₄. After the solvent was evaporated *in vacuo*, the residue was chromatographed on silica gel to afford the first product of 2,6-bis-[1-(2,6-dibromophenylimino)ethyl]pyridine (**L**₁) with 30% yields. mp 201°C. ¹H NMR (300 MHz, CDCl₃) δ_H: 8.55(d, *J* = 7.8 Hz, 2H, PyH), 7.97(t, *J* = 7.8 Hz, 1H, PyH), 7.58(d, *J* = 8.0 Hz, 4H, ArH), 6.86(t, *J* = 8.0 Hz, 2H, ArH), 2.36(s, 6H, N = CMe). MS *m/z* (%): 630(M⁺ + 1, 14), 629(M⁺ - 1, 16), 550(95), 549(76), 548(100), 468(8), 390(13), 388(14), 276(56), 235(21), 192(7), 154(7), 75(12). IR(KBr) ν: 2959, 1694, 1638, 1565, 1546, 1450, 1426, 1366, 1323, 1304, 1259, 1222, 1198, 1143, 1076, 969, 881, 822, 804, 762, 769, 652, 563, 528 cm⁻¹. Anal. C₂₁H₁₅N₃Br₄. Calcd.: C, 40.06; H, 2.38; N, 6.68. Found: C, 40.47; H, 2.73; N, 6.37.

In addition, 2-acetyl-6-[1-(2,6-dibromophenylimino)ethyl]pyridine (**L**₂) was isolated as the second product with 28% yield, mp 105°C. ¹H NMR (300 MHz, CDCl₃) δ_H: 8.59(dd, *J* = 7.9, 1.1 Hz, 1H, PyH), 8.17(dd, *J* = 7.72, 1.2 Hz, 1H, PyH), 7.97(t, *J* = 7.80, 1H, PyH), 7.58(t, *J* = 8.0 Hz, 2H, ArH), 6.87(t, *J* = 8.0 Hz, 1H, ArH), 2.80(s, 3H,

H₃CC = O), 2.35(s, 3H, N = CMe). MS *m/z* (%): 397(M⁺ + 1, 3), 396(M⁺, 7), 381(8), 317(100), 315(99), 276(44), 235(13), 193(7), 154(4), 75(7). IR(KBr) ν: 2982, 1736, 1633, 1597, 1576, 1491, 1444, 1361, 1317, 1300, 1246, 1224, 1150, 1121, 1102, 1081, 997, 957, 825, 806, 766, 751, 730, 647, 602 cm⁻¹. Anal. C₁₅H₁₂N₂OBr₂. Calcd.: C, 45.45; H, 3.03; N, 7.07. Found: C, 45.55; H, 3.12; N, 7.30.

Synthesis of [Fe(**L**₁)(**L**₂)]²⁺ [FeCl₄]²⁻ · CH₂Cl₂

Under argon, a solution of 125 mg (0.63 mmol) of FeCl₂ · 4H₂O in 15 mL of anhydrous THF was slowly added with stirring to a solution of 400 mg (0.64 mmol) of **L**₁ and 250 mg (0.63 mmol) of **L**₂ in 10 mL of anhydrous THF. The resulting deep black solution was stirred for 10 h at room temperature. Next, the volume of the solution was concentrated, and diethyl ether (20 mL) was added to precipitate the product as a black solid. Crystals of the title iron(II) complex suitable for X-ray structure determination were grown from concentrated CH₂Cl₂ solution. mp > 300°C, IR (KBr, pellet) ν: 3070, 1650, 1619, 1581, 1552, 1467, 1424, 1368, 1311, 1251, 1927, 823, 808, 778, 729, 698, 659, 618, 575 cm⁻¹. Anal. C₃₇H₂₉N₅Fe₂Cl₆Br₆O. Calcd.: C, 32.55; H, 2.13; N, 5.13. Found: C, 32.31; H, 2.08; N, 5.21.

Crystallographic structural determination

Black prismatic crystals of C₃₇H₂₉N₅Fe₂Cl₆Br₆O having approximate dimensions of 0.20 × 0.20 × 0.30 mm³ was used for X-ray diffraction analysis. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo K_α radiation and 12 kW rotating anode generator. The systematic absence in the diffraction data is uniquely consistent with the space group, *P*2₁/*m* (# 11) for [Fe(**L**₁)(**L**₂)]²⁺ [FeCl₄]²⁻ · CH₂Cl₂. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined neutral atom scattering factors were taken from Cromer and Waber. All calculations were performed using the teXsan crystallographic package of Molecular Structure Cooperation. Crystallographic

data and experimental details for structure analyses are summarized in Table 1.

Table 1 Crystallographic data and structure of refinement summary

Formula	C ₃₇ H ₂₉ N ₅ Fe ₂ Cl ₆ Br ₆ O
<i>Mr</i>	1363.51
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>m</i> (# 11)
Temp. (K)	293
<i>a</i> (nm)	1.0562(4)
<i>b</i> (nm)	2.09281(4)
<i>c</i> (nm)	1.2914(2)
α (deg.)	90.00
β (deg.)	100.12(2)
γ (deg.)	90.00
<i>V</i> (nm ³)	2.810(1)
<i>D_c</i> (g/cm ³)	1.611
<i>Z</i>	2
<i>R</i>	0.040
<i>R_w</i>	0.046
Reflections collected	4765
Independent reflections	4466
Goodness-of-fit	1.59
Max. Res. Peak (e/nm ³)	0.49 × 10 ⁻³

Results and discussion

An ORTEP drawing of the title compound is shown in Fig. 1.

The X-ray structure shows that the iron(II) compound crystallizes as an ion pair compound, [Fe(L₁)-(L₂)]²⁺ [FeCl₄]²⁻ · CH₂Cl₂, which includes a tetrachloroferrate(II) anion and a solvated CH₂Cl₂ molecule. The geometry around the Fe(II) centre can probably be best described as a distorted octahedron. It is very different from those five-coordinated iron(II) complexes with distorted square pyramidal or distorted trigonal bipyramidal geometry.^{5,6} The iron atom sits above the mean plane of the N(1), N(2), N(3) atoms and O atom. The two phenyl rings of ligand L₁ occupy symmetrically "up" and "down" the mean plane. The dihedral angle between the phenyl ring and the pyridine ring in L₁ is 90.73°. The dihedral angle between the pyridine ring in ligand L₂ and the pyridine ring in L₁ is 97.220°. Both the phenyl ring of ligand L₂ and the pyridin ring in ligand L₁ are orthogonal to the plane of the backbone. The dihedral angle between the phenyl ring in L₁ and the pyridine ring in L₂ is 8.61°, which means that these two moieties are parallel to each other.

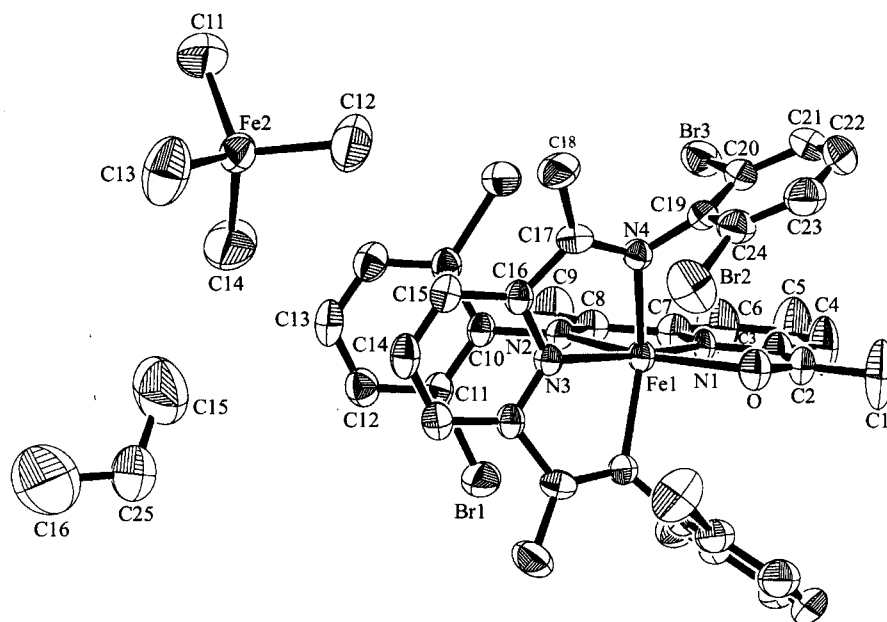


Fig. 1 Molecular structure of the titled iron(II) compound.

Selected bond distances and angles are listed in Table 2. The Fe—N(1) and Fe—N(3) bond lengths

are 0.2089(6) and 0.2067(6) nm, which are very close to the reported Fe(II)—N_{py} distance.^{5(a),8,9} As

expected, the Fe—N_{py} distance is shorter than the three Fe—N(imino) bonds (0.2368(6), 0.2189(5) and 0.2189(5) nm, respectively). The longer Fe—N(2) bond (0.2368(6) nm observed) can be attributed to the steric hindrance, in which the phenyl ring of ligand **L**₂ has to depart away from the metal center. There is no apparent delocalisation of the imino double bonds into the pyridyl ring systems. For example, N(4)—C(17) bond length is 0.1287(8) nm, which is coincident with the distance of normal N=C bond lengths being 0.1285(6) to 0.1280(6) nm reported in the litera-

ture.^{5(a)} Similarly, the C(2)—O bond length of 0.120(1) nm is also very close to the normally observed one for a C=O bond of 0.123 nm.¹⁰ In addition, the Fe—O bond distance of 0.2162 nm is much longer than the corresponding Fe—O σ bond length.^{11,12}

Due to the great strain in the five-membered ring, the N-Fe-N and N-Fe-O angles show obvious deviation from the expected value of 90°. To our knowledge, this kind of Fe(II) compound consisting of four five-membered rings has not been reported before.

Table 2 Selected bond distances ($\times 10^{-1}$ nm) and angles (deg.)

Distance			
Fe—N(1)	2.089(2)	Fe—N(2)	2.368(6)
Fe—N(3)	2.067(6)	Fe—N(4)	2.189(5)
Fe—N(4')	2.189(5)	C(2)—O	1.20(1)
Fe—O	2.162(6)	N(3)—C(16)	1.330(7)
N(1)—C(3)	1.344(10)	N(4)—C(17)	0.1287(8)
N(2)—C(8)	1.28(1)		
Angle (deg.)			
O-Fe-N(1)	74.9(2)	O-Fe-N(2)	146.5(2)
O-Fe-N(3)	127.1(2)	O-Fe-N(4)	88.6(1)
O-Fe-N(4')	88.6(1)	N(1)-Fe-N(2)	71.6(2)
N(1)-Fe-N(3)	157.9(2)	N(1)-Fe-N(4)	110.9(1)
N(2)-Fe-N(3)	86.3(2)	N(2)-Fe-N(4)	103.2(1)
N(3)-Fe-N(4')	73.4(1)	N(1)-Fe-N(3)	73.4(1)
N(4)-Fe-N(4)	135.7(2)		

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