

**Reaction of a Thienyl Schiff Base with Diiron  
Nonacarbonyl: Characterization and Structures of  
[ $\mu$ -*N*-(((2,3- $\eta^1$ : $\eta^2$ )-5-Methyl-2-thienyl)methyl)- $\eta^1$ : $\eta^1$ (*N*)-  
anilino]hexacarbonyldiiron and  
[ $\mu$ -*N*-((Anilino(2-thienyl)methyl)((2,3- $\eta^1$ : $\eta^2$ )-2-thienyl)methyl)-  
 $\eta^1$ : $\eta^1$ (*N*)-anilino]hexacarbonyldiiron**

Dong-Liang Wang and Wen-Shu Hwang\*

*Department of Chemistry, National Dong Hwa University, Hualien, Taiwan, ROC*

Lan-Chang Liang, Lien-I Wang, Liangshiu Lee, and Michael Y. Chiang

*Department of Chemistry, National Sun Yat-Sen University, Kaohsiung, Taiwan, ROC*

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When thienyl Schiff base **1** reacted with  $\text{Fe}_2(\text{CO})_9$  under very mild conditions in benzene three major products were obtained: (1) a cyclometalated ( $\mu$ - $\eta^1$ : $\eta^2$ -thienyl;  $\eta^1$ : $\eta^1$ (*N*))-hexacarbonyldiiron complex, **2**, (2) a hexacarbonyldiiron complex with an organic ligand, which is composed of two thienyl moieties derived from the original thienyl imine and coupled together by a C–C bond, **3**, and (3) a hydrogenation product of the original thienyl Schiff base. Molecular structures of compounds **2b** and **3a** have been determined by single-crystal X-ray diffraction.

### Introduction

The coordination chemistry of thiophene is currently attracting attention. However, most of the known thiophene complexes are monometallic and the binding of thiophene ligands to more than one transition metal is relatively rare. Since the late 1980s, advances have been made in understanding the coordination of thiophene in transition metal complexes.<sup>1</sup> The results have led to a more profound comprehension of the mechanisms involved in the hydrosulfurization process, as shown by the work of Angelici *et al.*<sup>2</sup> Because of the variety of binding modes between thiophene and metals, the topic is still of great interest from a structural point of view. Furthermore, development of a correlation between particular binding modes and the various patterns of reactivity is a continuing effort for many research groups.<sup>2,3</sup> The interesting aspect of sulfur atom coordination in transition metal complexes is well-demonstrated by Seyferth *et al.*<sup>4,5</sup> In their work, reagents containing the hexacarbonyldiiron moiety show many diverse reactions. We report here the preparation and characterization of complexes in which a ligand containing a thiophene group coordinates to a diiron (Fe–Fe) unit. The original ligand is a Schiff base derived from 2-thiophenecarboxaldehyde, which undergoes cyclometalation, hydrogenation, or C–C coupling during the course of its reaction with  $\text{Fe}_2(\text{CO})_9$ . The choice of a heterocyclic Schiff base also stems from their

biological interest.<sup>6</sup> The ( $\mu$ - $\eta^1$ : $\eta^2$ -thienyl;  $\eta^1$ : $\eta^1$ (*N*))hexacarbonyldiiron complexes show a unique binding mode in that the  $\beta$ -carbon and a C=C  $\pi$  bond of the bridging thiophene and the nitrogen atom all are coordinated to the diiron (Fe–Fe) unit. Of the various modes of thiophene coordination in transition metal complexes, this mode is rarely encountered. It can be regarded as the combination of an  $\eta^1$ -C-bound and an  $\eta^2$ - $\pi$ -bound mode applied on two different metal centers. This compound is very interesting in that despite the limited coordination ability of thiophene and the steric constraints of the ligand, thiophene is able to bind to both metals.

Furthermore, the coupling reactions between various types of organic ligands are important for their relevance to catalysis and organic synthesis.<sup>7</sup> The metal-mediated C–C coupling reactions are quite common.<sup>8</sup> We observe products resulting from the metal-mediated C–H activation and C–C coupling reactions in the reactions reported herein.

### Results and Discussion

The thienyl Schiff base *N*-(2-thienylmethylidene)-aniline (**1a**) reacts with diiron nonacarbonyl under very mild conditions in anhydrous benzene to give two diiron complexes, which we formulate as **2a** and **3a**, and an

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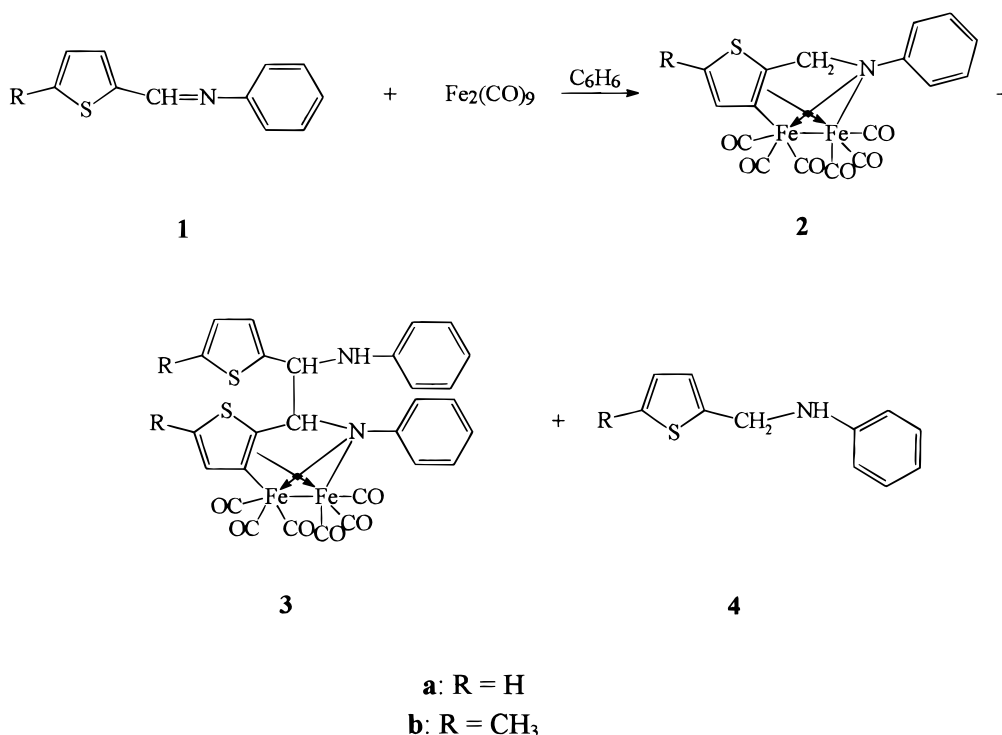
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Scheme 1



organic product, **4a**, as the major products (Scheme 1).

The presence of a NH functional group and the absence of a C=N stretching frequency in the IR spectrum indicate that compound **4a** is a product of hydrogenation of the original imine. The elemental analysis and other spectral data confirm this. The hydrogenation of a CN double bond normally requires more extreme conditions, and there is no doubt that compound **4a** arises as a result of coordination of **1a** to an iron carbonyl. The hydrogenation reaction was also observed when the reaction medium was anhydrous THF (*vide infra*) or deuterated benzene.

The cyclometalated product **2a** is a red oil. The  $^1\text{H}$  NMR spectrum of **2a** shows the absence of the methine proton (resonance at 8.72 ppm in **1a**), and a singlet methylene resonance appears at 4.42 ppm. In the aromatic region, two doublet thiophene protons appear at  $\delta$  7.81 and 7.45 ppm with a coupling constant  $J_{\text{H-H}} = 5.1$  Hz. The integrated intensities clearly show that only seven aromatic protons are left. In its IR spectrum, while the C=N stretching is absent, there are three sharp and intense C=O stretches appearing at 2069, 2032, and 1995  $\text{cm}^{-1}$ . This result could be interpreted by assuming that coordination of the imine nitrogen of the thienyl Schiff base to one of the iron centers, a cyclometalation occurs at a  $\beta$ -carbon of the thienyl ring and the methine group becomes a methylene group by accepting the hydrogen that was removed from the  $\beta$ -carbon. The mass spectrum of this product shows the complete loss of six CO ligands in a sequential manner, in accordance with the formulated structure.

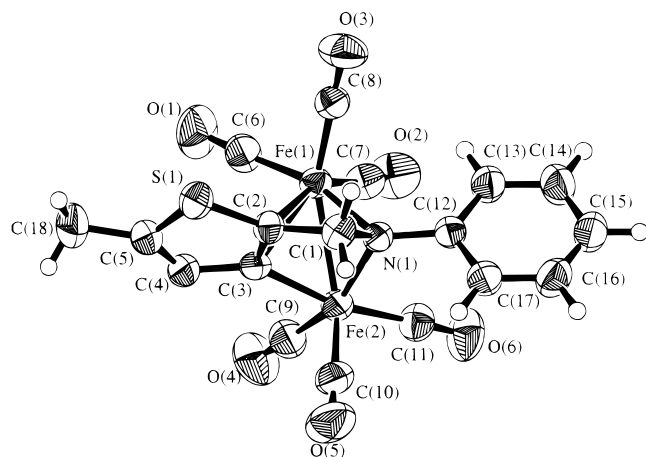
In order to have a better understanding of the coordination mode and to confirm the structure of compound **2a**, a methyl-substituted thienyl Schiff base *N*-(5-methyl-2-thienylmethylidene)aniline (**1b**) was reacted with diiron nonacarbonyl under the same conditions. Similar results were obtained, and products **2b**, **3b**, and **4b** were isolated and characterized. Com-

Table 1. Crystal and Data Collection Parameters for Compounds **2b** and **3a**

compd	<b>2b</b>	<b>3a</b>
formula	$\text{C}_{18}\text{H}_{18}\text{Fe}_2\text{NO}_6\text{S}$	$\text{C}_{28}\text{H}_{18}\text{Fe}_2\text{NO}_6\text{S}_2$
fw	481	655
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
<i>a</i> (Å)	8.314(2)	10.358(2)
<i>b</i> (Å)	9.302(1)	8.991(3)
<i>c</i> (Å)	13.382(3)	30.871(2)
$\alpha$ (deg)	84.65(2)	
$\beta$ (deg)	74.59(2)	95.04(1)
$\gamma$ (deg)	81.35(2)	
<i>V</i> (Å <sup>3</sup> )	984.8(8)	2863.8(9)
<i>Z</i>	2	4
<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )	1.622	1.52
cryst size (mm)	0.16 × 0.33 × 0.50	0.25 × 0.33 × 0.38
temp (K)	297	297
2 $\theta$ <sub>max</sub> (deg)	50.0	50.0
scan type	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$
no. of reflns measd:	3689, 3456	5726, 5409
total, unique		
no. of obsd reflns	2897	3262
(1 > 3.00 $\sigma$ (1))		
no. of variables	253	361
<i>F</i> <sub>000</sub>	484.00	1328.00
$\mu$ , (Mo K $\alpha$ ) (cm <sup>-1</sup> )	16.07	12.02
<i>R</i>	0.039	0.039
<i>R</i> <sub>w</sub>	0.049	0.044

pounds **2b**, **3b**, and **4b** exhibit spectral data that very closely resemble those of **2a**, **3a**, and **4a**, as shown in the Experimental Section.

A red prism crystal of **2b** was subjected to a single-crystal X-ray analysis. Crystal and data collection parameters are shown in Table 1. An ORTEP diagram of one rotamer is shown in Figure 1. Selected bond distances and bond angles are tabulated in Table 2. It is readily seen that C3 of the thienyl ring is  $\sigma$  bonded to Fe2 with a bond distance of 1.959(4) Å. C3 and C2 are bonded to Fe1 with bond distances of 2.156(4) and 2.251(4) Å, respectively. Hence, Fe1 is bonded to thiophene by the  $\pi$  bond between C2 and C3, and the bond distance between C2 and C3 is lengthened to



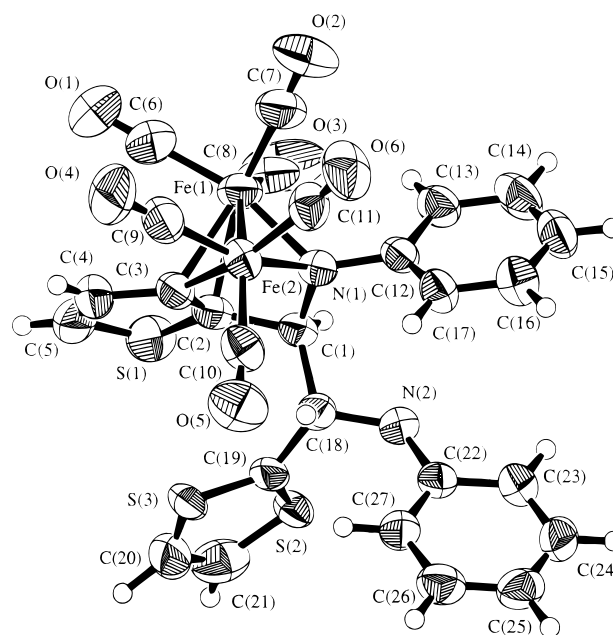
**Figure 1.** ORTEP diagram of compound **2b** at the 30% probability level.

**Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) of Compound 2b**

Fe(1)–Fe(2)	2.4617(9)	Fe(1)–C(2)	2.251(4)
Fe(1)–C(3)	2.156(4)	Fe(1)–N(1)	1.981(3)
Fe(2)–C(3)	1.959(4)	Fe(2)–N(1)	2.002(3)
C(2)–C(3)	1.406(5)	C(1)–N(1)	1.491(4)
Fe(1)–N(1)–Fe(2)	76.3(1)	Fe(1)–C(3)–Fe(2)	73.3(1)

1.406(5) Å. This binding involving  $\pi$  electrons of a thienyl ring has been reported.<sup>1</sup> We conclude, therefore, that the thienyl group in the organic ligand serves as a three-electron donor and bridges the two iron centers. The bond distance between C1 and N1, 1.491(4) Å, is in the single bond range, while the bond distance between N1 and Fe1 and N1 and Fe2 is 1.981(3) and 2.002(3) Å, respectively. A 36-electron structure can be rationalized on the supposition that the nitrogen atom acts as another three-electron bridge in **2b**. An iron–iron distance of 2.4617(9) Å is shorter than usual for diiron complexes<sup>9</sup> but is in accordance with other nitrogen-bridged diiron complexes.<sup>10,11</sup> The Fe1–N–Fe2 angle is 76.3(1)° and Fe1–C3–Fe2 is 73.3(1)°. The compression of these two angles from the tetrahedral value is a result of the ligand constraints of double bridging, which also brings about the shorter metal–metal distance. The structure of **2b** is analogous to that of the nitrogen-containing organometallic complexes reported by Baikie and Mills.<sup>10</sup> The ferrocyclopentadiene and ferraindene complexes reported by Braye and Hübeler<sup>12</sup> are similar to **2b** structurally. In both cases, a phenyl group acts as bridge instead of a thiophene. Complex **2b** also bears some resemblance to  $\text{Fe}_2(\text{CO})_6$  complexes with bridging  $\eta^1:\eta^2$ -vinyl, furyl, and thienyl ligands reported by Seyferth.<sup>4,5</sup>

The molecular structure of compound **3a**, determined by a single-crystal X-ray diffraction study, is shown in Figure 2. Crystal and data collection parameters are tabulated in Table 1. Selected bond distance and bond angles are reported in Table 3. There are two thienyl moieties derived from the original thienyl imine coupled together by a C–C single bond between C1 and C18 (1.552(5) Å). The moiety (L) that coordinates to diiron



**Figure 2.** ORTEP diagram of compound **3a** at the 30% probability level. S2 and S3 indicate the packing disorder of the second thiophene group.

**Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) of Compound 3a**

Fe(1)–Fe(2)	2.444(1)	Fe(1)–C(2)	2.207(4)
Fe(1)–C(3)	2.181(4)	Fe(1)–N(1)	1.980(3)
Fe(2)–C(3)	1.947(4)	Fe(2)–N(1)	2.007(3)
C(2)–C(3)	1.389(6)	C(1)–N(1)	1.493(5)
C(1)–C(18)	1.552(5)	C(18)–N(2)	1.456(5)
Fe(1)–N(1)–Fe(2)	75.6(1)	Fe(1)–C(3)–Fe(2)	72.4(1)
N(1)–C(1)–C(2)	97.2(3)	N(1)–C(1)–C(18)	115.6(3)
C(2)–C(1)–C(18)	114.7(3)	C(1)–C(18)–C(19)	113.7(3)

is a  $\mu\text{-}\eta^1:\eta^2$ -thienyl;  $\eta^1:\eta^1(\text{N})$  bridge, and structural parameters are similar to those of **2b**. Another moiety (L') is fairly free from metal interaction. For example, a 50:50 packing disorder (50% occupancy factor is assigned to both S2 and S3) is observed for the thienyl group that does not bind to either one of the iron centers. Spectral data of complex **3a** are self explanatory and in accordance with X-ray analysis. Both homonuclear ( $^1\text{H}$ – $^1\text{H}$ ) and heteronuclear ( $^1\text{H}$ – $^{13}\text{C}$ ) COSY experiments were performed to assist the assignments of the NMR spectra. Figure 3 shows the  $^1\text{H}$ – $^1\text{H}$  COSY spectrum of **3a** with assignments on the top of the figure. Protons numbered with primes are those attached to the thienyl moiety L'. Notably, proton 1' ( $\delta$  4.38 ppm) appears more upfield than proton 1 ( $\delta$  5.05 ppm), an indication that the aliphatic C–H unit in L is polarized by metal interactions. In addition, steric constraints from the hexacarbonyldiiron portion of the complex causes the phenyl and thienyl groups on L' to bend to the same side of C18 (Figure 2). The situation places proton 7' in the shielding core of the thienyl ring. Therefore, it has the lowest chemical shift ( $\delta$  6.04 ppm) among all the aromatic protons.

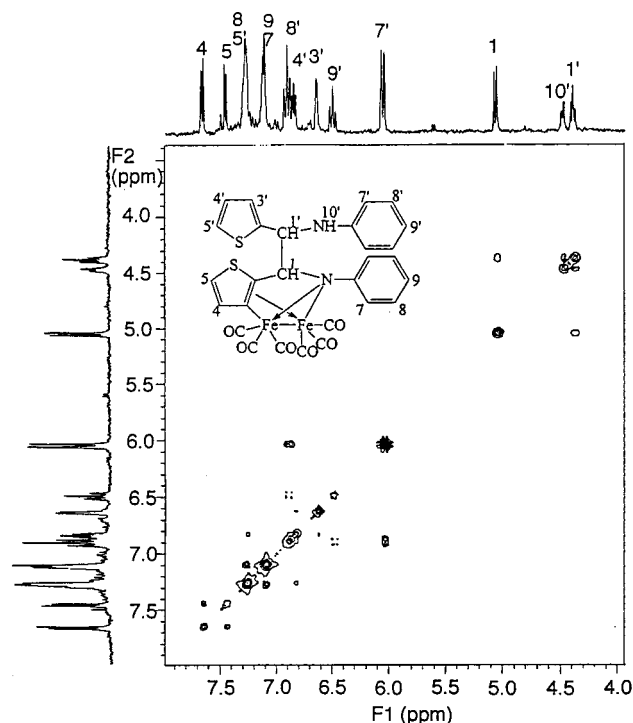
When the reaction medium is THF, the reaction is for the most part parallel to that in benzene. The most striking difference is the substantial reduction in yield of the products. The decrease in polarity of the solvent seems to increase the stability or encourage the formation of compounds **2** and **3**. In fact, a complex similar to **3** is not obtained in the case of a reaction carried out

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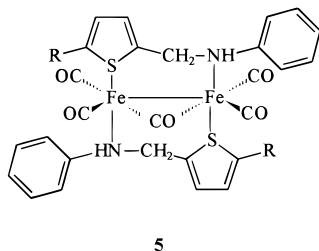
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**Figure 3.**  $^1\text{H}$ – $^1\text{H}$  COSY spectrum of compound **3a** in acetone- $d_6$ .

in THF. However, trace amounts of pentacarbonyldiiron complex **5** were isolated. Although complex **5** is



very unstable, we were able to deduce its structure, as shown above, by its  $^1\text{H}$  NMR, IR, and mass spectra. It contains a bridging carbonyl between the two iron centers. The bridging carbonyl has a stretching frequency of  $1732\text{ cm}^{-1}$ . The broad and intense absorption at  $3416\text{ cm}^{-1}$  indicates the presence of the  $-\text{NH}$  group. The mass spectrum shows the complete loss of five COs successively, and the molecular ion peak at  $m/z$  630/658 suggests that two organic ligands **4a/4b** are incorporated. The simplicity of the  $^1\text{H}$  NMR spectrum suggests that the two organic ligands are arranged more or less symmetrically. Since S-bound thiophene in transition metal complexes had been reported in many occasions,<sup>13</sup> we suggest that such a possibility also exists in **5**. We suggest that complex **5** is an intermediate in the formation of the hydrogenation product **4**.

### Experimental Section

Diiron nonacarbonyl was prepared by photolysis of iron pentacarbonyl (Aldrich) in glacial acetic acid.<sup>14</sup> Solvents were

dried (sodium/benzophenone,  $\text{P}_4\text{O}_{10}$ ) and distilled under nitrogen prior to use. All other chemicals were reagent grade and used without purification. The NMR spectra were recorded on either a Varian EM-390 or Varian VXR-300 NMR spectrometer ( $^1\text{H}$ , 299.95 MHz;  $^{13}\text{C}$ , 75.43 MHz). Chemical shifts were referenced to TMS, and deuterated acetone (Janssen) was used as a solvent and as a secondary reference. Mass spectra were obtained on a VG-Biotect Quattro 5022 spectrometer. IR spectra were recorded on a Bio-Rad FTS-40 spectrometer. Elemental analyses were performed using a Heraeus CHNO rapid analyzer. Crystals for X-ray diffraction were obtained by sublimation. A single crystal was mounted on a glass fiber, and the X-ray diffraction intensity data were measured on a Rigaku AFC7S diffraction at room temperature.

**Synthesis of *N*-(2-Thienylmethylidene)aniline (**1a**) and *N*-(5-Methyl-2-thienylmethylidene)aniline (**1b**).** The synthesis of the Schiff base employed the usual approach of condensation in alcohol solution.<sup>15</sup> Equimolar quantities of 2-thiophenecarboxaldehyde (Aldrich, 3.8 mL, 40 mmol) or 5-methyl-2-thiophenecarboxaldehyde (Aldrich, 4.3 mL, 40 mmol) and aniline (Merck, 3.6 mL, 40 mmol) were heated at reflux in methanol (Merck, 65 mL) for 12 h. The solvent was removed under vacuum. The residue was distilled with a Kugelrohr distillation apparatus under reduced pressure (0.1 mmHg). The orange-red compound **1a** was obtained (7.02 g; 94% yield) at  $175\text{ }^\circ\text{C}$ .  $^1\text{H}$  NMR:  $\delta$  8.72 (s, 1H), 7.69 (d,  $J$  = 5.1 Hz, 1H), 7.60 (d,  $J$  = 3.6 Hz, 1H), 7.40 (m, 2H), 7.25 (m, 3H), 7.19 (dd,  $J$  = 3.6, 5.1 Hz, 1H).  $^{13}\text{C}$  NMR:  $\delta$  153.9, 152.2, 143.9, 133.6, 131.2, 129.9, 128.6, 126.7, 121.7. IR ( $\text{CHCl}_3$ )  $\nu_{\text{C}=\text{N}}$ :  $1617\text{ cm}^{-1}$ . MS (EI):  $m/z$  187 ( $\text{M}^+$ ). Anal. Calcd for  $\text{C}_{11}\text{H}_9\text{NS}$ : C, 70.55; H, 4.86; N, 7.48. Found: C, 70.40; H, 4.89; N, 7.51. The orange-red compound **1b** was obtained (7.40 g; 92% yield) at  $185\text{ }^\circ\text{C}$ .  $^1\text{H}$  NMR:  $\delta$  8.60 (s, 1H), 7.42 (d,  $J$  = 3.9 Hz, 1H), 7.37 (m, 2H), 7.21 (m, 3H), 6.87 (d,  $J$  = 3.9 Hz, 1H), 2.52 (s, 3H).  $^{13}\text{C}$  NMR:  $\delta$  153.8, 152.4, 146.3, 141.9, 134.1, 129.9, 127.2, 126.5, 121.7, 16.7. IR ( $\text{CHCl}_3$ )  $\nu_{\text{C}=\text{N}}$ :  $1614\text{ cm}^{-1}$ . MS (EI):  $m/z$  201 ( $\text{M}^+$ ), 200 ( $\text{M}^+ - \text{H}$ ). Anal. Calcd for  $\text{C}_{12}\text{H}_{11}\text{NS}$ : C, 71.60; H, 5.51; N, 6.96. Found: C, 71.61, H, 5.52; N, 6.95.

**Reaction of **1** with  $\text{Fe}_2(\text{CO})_9$  in Benzene To Give  $[\mu\text{-}N\text{-}((2,3\text{-}\eta^1\text{-}\eta^2)\text{-}2\text{-Thienyl)methyl-}\eta^1\text{-}\eta^1(N\text{-anilino})\text{hexacarbonyldiiron (2a)}/[\mu\text{-}N\text{-}((2,3\text{-}\eta^1\text{-}\eta^2)\text{-}5\text{-Methyl-2-thienyl)methyl-}\eta^1\text{-}\eta^1(N\text{-anilino})\text{hexacarbonyldiiron (2b)}, [\mu\text{-}N\text{-}((\text{Anilino}(2\text{-thienyl)methyl)((2,3\text{-}\eta^1\text{-}\eta^2)\text{-}2\text{-thienyl)methyl-}\eta^1\text{-}\eta^1(N\text{-anilino})\text{hexacarbonyldiiron (3a)}/[\mu\text{-}N\text{-}((\text{Anilino}(5\text{-Methyl-2-thienyl)methyl)((2,3\text{-}\eta^1\text{-}\eta^2)\text{-}5\text{-methyl-2-thienyl)methyl-}\eta^1\text{-}\eta^1(N\text{-anilino})\text{hexacarbonyldiiron (3b)}, \text{and } N\text{-}((2\text{-Thienyl)methyl)aniline (4a)}/N\text{-}((5\text{-Methyl-2-thienyl)methyl)aniline (4b)}$ .** Eight millimoles of compound **1** in 30 mL of anhydrous benzene was added gradually to 70 mL of anhydrous benzene solution containing 6.0 mmol of  $\text{Fe}_2(\text{CO})_9$  in the dark under nitrogen, and the reaction mixture was stirred for 40 h at  $15\text{ }^\circ\text{C}$ . The residue was filtered, and the solvent was removed under reduced pressure. The residue was separated by a  $3.5\text{ cm} \times 40\text{ cm}$  column (230–400 mesh ASTM silica gel (Merck)) with ethyl acetate/chloroform/*n*-hexane (1:5:20) as eluent. The red band gave a crude product that was further treated by column chromatography (*vide infra*). The orange band produced 135 mg of **4a** (11.9% yield) and 169 mg of **4b** (13.9% yield). Compound **4a**:  $^1\text{H}$  NMR  $\delta$  7.28 (d, 1H), 7.08 (m, 3H), 6.95 (1H), 6.72 (m, 2H), 6.63 (m, 1H), 5.42 (br, 1H), 4.53 (d,  $J$  = 4.8 Hz, 2H).  $^{13}\text{C}$  NMR:  $\delta$  149.2, 145.1, 129.7, 127.4, 125.4, 124.9, 117.7, 113.7, 43.4. MS (EI):  $m/z$  189 ( $\text{M}^+$ ). Anal. Calcd for  $\text{C}_{11}\text{H}_{11}\text{NS}$ : C, 69.80; H, 5.86; N, 7.40. Found: C, 69.15; H, 5.88; N, 7.43. Compound **4b**:  $^1\text{H}$  NMR  $\delta$  7.10 (m, 2H), 6.80 (1H), 6.71 (m, 2H), 6.62 (m, 2H), 5.32 (br, 1H), 4.43 (d,  $J$  = 4.8 Hz, 2H), 2.39 (s, 3H).  $^{13}\text{C}$  NMR:

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$\delta$  149.3, 142.6, 139.0, 129.7, 125.5, 125.3, 117.6, 113.7, 43.4, 15.2. MS (EI):  $m/z$  203 ( $\text{M}^+$ ). Anal. Calcd for  $\text{C}_{12}\text{H}_{13}\text{NS}$ : C, 70.89; H, 6.44; N, 6.89. Found: C, 70.78; H, 6.44; N, 6.85. Substantial amounts of  $\text{Fe}_3(\text{CO})_{12}$  also were collected.

The crude product of the red band was purified further by column chromatography with ethyl acetate/chloroform/*n*-hexane (1:35:50) as eluent. A red oil, **2a** (399 mg, 14.2% yield)/red solid, **2b** (710 mg, 24.6% yield) and a red solid, **3a** (123 mg, 3.1% yield)/red solid, **3b** (113 mg, 2.8% yield) were isolated. Compound **2a**:  $^1\text{H}$  NMR  $\delta$  7.81 (d,  $J = 5.1$  Hz, 1H), 7.45 (d,  $J = 5.1$  Hz, 1H), 7.30 (m, 2H), 7.15 (m, 3H), 4.42 (s, 2H).  $^{13}\text{C}$  NMR:  $\delta$  159.3, 158.5, 140.1, 133.3, 129.9, 127.6, 126.7, 124.3, 73.7. IR ( $\text{CHCl}_3$ ):  $\nu_{\text{CO}}$ : 2069, 2032, 1995  $\text{cm}^{-1}$ . UV-vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  465.6 ( $\epsilon = 4900 \text{ M}^{-1} \text{ cm}^{-1}$ ), 336 ( $\epsilon = 1500 \text{ M}^{-1} \text{ cm}^{-1}$ ) nm. MS (EI):  $m/z$  467 ( $\text{M}^+$ ), 439 ( $\text{M}^+ - \text{CO}$ ), 411 ( $\text{M}^+ - 2\text{CO}$ ), 383 ( $\text{M}^+ - 3\text{CO}$ ), 355 ( $\text{M}^+ - 4\text{CO}$ ), 327 ( $\text{M}^+ - 5\text{CO}$ ), 299 ( $\text{M}^+ - 6\text{CO}$ ), 187 ( $\text{L}^+$ ). Anal. Calcd for  $\text{Fe}_2\text{C}_{17}\text{H}_9\text{NSO}_6$ : C, 43.68; H, 1.93; N, 3.00. Found: C, 43.78; H, 1.95; N, 2.98. Compound **2b**:  $^1\text{H}$  NMR  $\delta$  7.30 (m, 2H), 7.14 (m, 4H), 4.33 (s, 2H), 2.50 (s, 3H).  $^{13}\text{C}$  NMR:  $\delta$  159.3, 148.6, 138.2, 137.4, 129.1, 126.6, 126.0, 124.2, 74.0, 15.8. IR ( $\text{CHCl}_3$ ):  $\nu_{\text{CO}}$ : 2068, 2030, 1993  $\text{cm}^{-1}$ . UV-vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  465.6 ( $\epsilon = 3000 \text{ M}^{-1} \text{ cm}^{-1}$ ), 336 ( $\epsilon = 9000 \text{ M}^{-1} \text{ cm}^{-1}$ ) nm. MS (EI):  $m/z$  481 ( $\text{M}^+$ ), 453 ( $\text{M}^+ - \text{CO}$ ), 425 ( $\text{M}^+ - 2\text{CO}$ ), 397 ( $\text{M}^+ - 3\text{CO}$ ), 369 ( $\text{M}^+ - 4\text{CO}$ ), 341 ( $\text{M}^+ - 5\text{CO}$ ), 313 ( $\text{M}^+ - 6\text{CO}$ ), 201 ( $\text{L}^+$ ). Anal. Calcd for  $\text{Fe}_2\text{C}_{18}\text{H}_{11}\text{NSO}_6$ : C, 44.91; H, 2.28; N, 2.91. Found: C, 45.01; H, 2.31; N, 2.89. Compound **3a**:  $^1\text{H}$  NMR  $\delta$  7.65 (d,  $J = 5.1$  Hz, 1H), 7.45 (d,  $J = 5.1$  Hz, 1H), 7.27 (m, 3H), 7.11 (m, 3H), 6.90 (dd, 2H), 6.83 (dd, 1H), 6.63 (d,  $J = 3.9$  Hz, 1H), 6.49 (dd, 1H), 6.04 (d, 2H), 5.05 (d,  $J = 6.2$  Hz, 1H), 4.46 (d,  $J = 5.7$  Hz, 1H), 4.38 (dd, 1H).  $^{13}\text{C}$  NMR:  $\delta$  159.4, 157.9, 146.9, 144.9, 138.6, 135.2, 129.9, 129.4, 129.0, 128.3, 127.3, 126.4, 125.5, 117.9, 113.6, 86.8, 63.2. IR ( $\text{CHCl}_3$ ):  $\nu_{\text{CO}}$ : 2067, 2026, 1996, 1960  $\text{cm}^{-1}$ ;  $\nu_{\text{NH}}$  3403  $\text{cm}^{-1}$ . UV-vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  443.6 ( $\epsilon = 2500 \text{ M}^{-1} \text{ cm}^{-1}$ ), 343.2 ( $\epsilon = 8800 \text{ M}^{-1} \text{ cm}^{-1}$ ) nm. MS (EI):  $m/z$  655 ( $\text{M}^+ + 1$ ), 626 ( $\text{M}^+ - \text{CO}$ ), 598 ( $\text{M}^+ - 2\text{CO}$ ), 570 ( $\text{M}^+ - 3\text{CO}$ ), 542 ( $\text{M}^+ - 4\text{CO}$ ), 514 ( $\text{M}^+ - 5\text{CO}$ ), 486 ( $\text{M}^+ - 6\text{CO}$ ), 466 ( $\text{M}^+ - \text{L}^+$ ), 188 ( $\text{L}^+$ ), 186 ( $\text{L}^+$ ). Anal. Calcd for  $\text{Fe}_2\text{C}_{28}\text{H}_{18}\text{N}_2\text{S}_2\text{O}_6$ : C, 51.38; H, 2.75; N, 4.28; O, 14.68. Found: C, 51.63; H, 2.78; N, 4.26; O, 14.78. Compound **3b**:  $^1\text{H}$  NMR  $\delta$  7.23

(m, 2H), 7.09 (m, 4H), 6.90 (dd, 2H), 6.49 (m, 3H), 6.05 (d, 2H), 4.86 (d,  $J = 6.3$  Hz, 1H), 4.36 (d,  $J = 6.3$  Hz, 1H), 4.26 (dd, 1H), 2.35 (s, 6H).  $^{13}\text{C}$  NMR:  $\delta$  163.4, 157.9, 150.7, 147.0, 142.4, 140.6, 136.0, 129.9, 129.3, 128.9, 127.2, 126.3, 125.3, 117.8, 113.6, 87.2, 63.4, 15.6, 15.3. IR ( $\text{CHCl}_3$ ):  $\nu_{\text{CO}}$  2067, 2026, 1996, 1960  $\text{cm}^{-1}$ ;  $\nu_{\text{NH}}$  3407  $\text{cm}^{-1}$ . UV-vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  436.0 ( $\epsilon = 5900 \text{ M}^{-1} \text{ cm}^{-1}$ ), 340.0 ( $\epsilon = 19\,200 \text{ M}^{-1} \text{ cm}^{-1}$ ) nm. MS (EI):  $m/z$  683 ( $\text{M}^+ + 1$ ), 654 ( $\text{M}^+ - \text{CO}$ ), 626 ( $\text{M}^+ - 2\text{CO}$ ), 598 ( $\text{M}^+ - 3\text{CO}$ ), 570 ( $\text{M}^+ - 4\text{CO}$ ), 542 ( $\text{M}^+ - 5\text{CO}$ ), 514 ( $\text{M}^+ - 6\text{CO}$ ), 202 ( $\text{L}^+$ ). Anal. Calcd for  $\text{Fe}_2\text{C}_{30}\text{H}_{22}\text{N}_2\text{S}_2\text{O}_6$ : C, 52.79; H, 3.23; N, 4.10; O, 14.08. Found: C, 53.01; H, 3.21; N, 4.12; O, 14.15.

**Reaction of 1 with  $\text{Fe}_2(\text{CO})_9$  in THF.** The reaction under the same condition as performed in benzene gave much lower yields of products **2a/2b** (0.6%/0.9%) and **4a/4b** (4.4%/6.9%). A complex similar to **3a/3b** was not obtained. However, trace amount of compound **5a/5b** was isolated, and a substantial amount of  $\text{Fe}_3(\text{CO})_{12}$  (~30%) was collected. Compound **5a**:  $^1\text{H}$  NMR  $\delta$  7.61 (1H), 7.45 (1H), 7.29 (1H), 7.12 (2H), 6.84 (1H), 6.73 (2H), 6.08 (1H), 4.78 (2H). IR ( $\text{CHCl}_3$ ):  $\nu_{\text{CO}}$  2068, 2030, 1997, 1986, 1732  $\text{cm}^{-1}$ ;  $\nu_{\text{NH}}$  3416  $\text{cm}^{-1}$ . MS (EI):  $m/z$  630 ( $\text{M}^+$ ), 602 ( $\text{M}^+ - \text{CO}$ ), 574 ( $\text{M}^+ - 2\text{CO}$ ), 546 ( $\text{M}^+ - 3\text{CO}$ ), 518 ( $\text{M}^+ - 4\text{CO}$ ), 490 ( $\text{M}^+ - 5\text{CO}$ ), 189 (**4a** $^+$ ). Compound **5b**:  $^1\text{H}$  NMR  $\delta$  7.37 (1H), 7.24 (1H), 7.12 (2H), 6.71 (2H), 6.63 (1H), 6.08 (1H), 4.64 (2H), 2.60 (3H). IR ( $\text{CHCl}_3$ ):  $\nu_{\text{CO}}$  2068, 2028, 1996, 1981, 1732  $\text{cm}^{-1}$ ;  $\nu_{\text{NH}}$  3416  $\text{cm}^{-1}$ . MS (EI):  $m/z$  658 ( $\text{M}^+$ ), 630 ( $\text{M}^+ - \text{CO}$ ), 602 ( $\text{M}^+ - 2\text{CO}$ ), 546 ( $\text{M}^+ - 4\text{CO}$ ), 518 ( $\text{M}^+ - 5\text{CO}$ ), 203 (**4b** $^+$ ).

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**Supporting Information Available:** Text of the X-ray crystal structure experimental details, tables of the experimental details, atomic coordinates, anisotropic displacement parameters, and bond distances and angles, and ORTEP diagrams of **2b** and **3a** (33 pages). Ordering information is given on any current masthead page.

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