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Polyhedron 20 (2001) 353-362



# Ironcarbonyl complexes from N-(2-thienylmethylidene)benzylamines: *endo* as well as *exo* cyclometalation and alkyl exchange

Wen-Shu Hwang<sup>a,\*</sup>, Tzu-Shiuan Tzeng<sup>a</sup>, Dong-Liang Wang<sup>b</sup>, Michael Y. Chiang<sup>c</sup>

<sup>a</sup> Department of Chemistry, National Dong Hwa University, Hualien, Taiwan, ROC

<sup>b</sup> Department of Cosmetic Science, Chia Nan College of Pharmacy and Science, Tainan, Taiwan, ROC

<sup>c</sup> Department of Chemistry, National Sun Yat-Sen University, Kaohsiung, Taiwan, ROC

Received 8 September 2000; accepted 13 November 2000

#### Abstract

The reaction of methyl substituted *N*-(2-thienylmethylidene)benzylamine (1) with Fe<sub>2</sub>(CO)<sub>9</sub> in benzene gives *endo* cyclometalated ( $\mu$ - $\eta^1$ : $\eta^2$ -thienyl;  $\eta^1$ : $\eta^1(N)$ )hexacarbonyldiiron complexes (2 and 5), *exo* cyclometalated ( $\mu$ - $\eta^1$ : $\eta^2$ -phenyl;  $\eta^1$ : $\eta^1(N)$ )hexacarbonyldiiron complexes (3 and 6) and/or imidoyl triironnonacarbonyl cluster (4), in accordance with the position of methyl substituent(s). In complex 3, the thienyl unit of the original Schiff base has been replaced by a phenyl group, which comes from the same Schiff base. The X-ray structure analyses were carried out on complexes 2a, 2b, 2c and 3a. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: N-(2-Thienylmethylidene)benzylamine; Diironhexacarbonyl complexes; endo Cyclometalation; exo Cyclometalation; 1,3-Hydrogen shift; 1,5-Hydrogen shift

# 1. Introduction

In the past decades, transition metal mediate activation of C–H bond remains one of the most prominent challenges in organometallic chemistry. Cyclometalation is one of the classical ways used to activate C–H bond in hetero-substituted organic molecules [1].

It is well-known that N-donor ligands have a strong tendency to give five-membered metallacycle [2]. In systems where there is a possibility of choice between several modes of metalation, five-membered metallacycle complexes are always the major compounds obtained [3]. It is also known that Schiff bases have a strong tendency to give *endo* cyclometalated derivatives [4]. Only a few *exo* metallcycles of Schiff bases were obtained by C–H activation. They are derivatives of 2,6-disubstituted *N*-benzylideneamines, which contain substituents on the *ortho* positions of the benzal ring

[1f,i,j,4b]. Usually, the tendency to proceed *endo* cyclometalation is so strong that, in the presence of  $Pd(AcO)_2$ , an aliphatic C–H bond of N-(2,4,6-trimethylbenzylidene)benzylamine is activated in preference to the activation of an aromatic C–H bond and results with the formation of a six-membered *endo* metallacycle as the sole product rather than a five-membered *exo* metallacycle [5]. Evidence for a regiospecific *endo* cyclometalation was therefore observed.

We report here the interesting results from the action of diiron nonacarbonyl on *N*-(5-methyl-2-thienylmethylidene)benzylamines (**1a**-**c**) and *N*-(3-methyl-2thienylmethylidene)benzylamines (**1d**-**f**). Schiff bases **1d**-**f** have a methyl substituent block at the  $\beta$ -position of the thienyl ring, which would otherwise be a site where an *endo* cyclometalation might occur. During the course of reactions, we observe products resulting from *endo* cyclometalation followed by 1,3-hydrogen shift, *exo* cyclometalation induced methyl migration and hydrogen shift, and substitution of the thienylmethyl group of *exo* cyclometalated intermediate by a benzyl group.

<sup>\*</sup> Corresponding author. Tel.: + 886-3-866-2769; fax: + 886-3-866-770.

E-mail address: hws@mail.ndhu.edu.tw (W.-S. Hwang).

#### 2. Results and discussion

The thienyl Schiff bases 1a-f are prepared by normal procedure of condensation of thienyl-2-carboxaldehyde with the corresponding amines.

The thienyl Schiff base N-(5-methyl-2-thienylmethylidene)benzylamine (1a) reacts with diiron nonacarbonyl in anhydrous benzene for 5 h at 45°C to give *endo* and *exo* cyclometalated diironhexacarbonyl complexes, which we formulate as 2a and 3a, respectively (Scheme 1).

The <sup>1</sup>H NMR spectrum of 2a shows the absence of a methine proton (resonance at  $\delta$  8.48 ppm in **1a**) and the addition of a pair of methylene resonances at  $\delta$  3.97 and 3.83 ppm. In the aromatic region, the integrated intensities clearly shows only six protons left, of which one is a thienyl proton that appears at  $\delta$  7.04 ppm. In the corresponding IR spectrum, while a C=N stretching mode is absent, there are three sharp and intense C=O stretches appearing at 2068, 2024, and 1984 cm $^{-1}$ . This result was interpreted as coordination of the imine nitrogen of the thienyl Schiff base on one of the iron centers, a C–H activation occurs at the  $\beta$ -carbon of the thienyl ring to form a five-membered endo metallacycle, and the methine group becomes a methylene by accepting the hydrogen originated from the  $\beta$ -carbon. This transformation follows the sequential route, coordination, endo cyclometalation, and 1,3-hydrogen shift. The mass spectrum of the product contains a signal for the molecular ion and six peaks corresponding to sequential CO loss products.

A red prism crystal of **2a** was subjected to a singlecrystal X-ray analysis. Crystal and data collection parameters are shown in Table 1. An ORTEP diagram of **2a** is shown in Fig. 1. It is readily seen that C(3) of the thienyl ring is  $\sigma$  bonded to Fe(1) with a bond distance of 1.971(6) Å. C(2) and C(3) are  $\pi$  bonded to Fe(2) with

bond distances of 2.304(7) and 2.167(6) Å, respectively, and the bond distance between C(2) and C(3) is lengthened to 1.395(8). The thienyl ring serves as a three-electron donor and bridges the two irons centers. The bond distance from N(1) to C(1), 1.495(7) Å, is in the single bond range and is comparable to that of N(1)-C(12)distance, 1.503(8) Å. The nitrogen atom acts as another three-electron donor bridge and the bond distances to Fe(1) and Fe(2) are 1.992(5) and 1.968(5) Å, respectively. An iron-iron distance of 2.440(1) Å is shorter than usual for diiron complexes [6] but is in accordance with other nitrogen-bridged diiron complexes [7]. The Fe(1)-N-Fe(2) angle is 76.1(2)° and Fe(1)-C(3)-Fe(2) angle is 72.1(2)°. The compression of these two angles from the tetrahedral value is a result of the ligand constrains of double bridging, which also brings about the shorter iron-iron distance.

Competitive with the formation of **2a**, **3a** is observed. The <sup>1</sup>H NMR spectrum of **3a** also shows the absence of a methine proton and the addition of a pair of methylene resonances at  $\delta$  4.09 and 3.98 ppm. There are nine protons in the aromatic region, of which four benzene protons down field shift to  $\delta$  8.07 and 7.65 ppm with a coupling constant  $J_{\text{H-H}} = 8.7$  Hz, and no thienyl proton is observed. In the corresponding IR spectrum, there are three sharp and intense C=O stretching absorption at 2068, 2028, and 1982 cm<sup>-1</sup> instead of the original C=N stretching mode. The mass spectrum of the product contains a signal for the molecular ion at m/z465 and six peaks corresponding to sequential CO loss products, in accordance with the formulated structure.

The molecular structure of complex **3a**, determined by a single-crystal X-ray diffraction analysis, is shown in Fig. 2. Crystal and data collection parameters are listed in Table 1. The molecular structure clearly shows that C(3) of the phenyl ring is  $\sigma$  bonded to Fe(2) with a bond distance of 1.992(7) Å. C(3) and C(2) are  $\pi$ 



Scheme 1.

Table 1							
Crystal and d	ata collection	parameters f	or compounds	2a, 2	2b, 2	2c and	3a

	2a	2b	2c	3a
Formula	C <sub>19</sub> H <sub>13</sub> Fe <sub>2</sub> NO <sub>6</sub> S	C <sub>20</sub> H <sub>15</sub> Fe <sub>2</sub> NO <sub>6</sub> S	C <sub>20</sub> H <sub>15</sub> Fe <sub>2</sub> NO <sub>6</sub> S	$C_{20}H_{13}Fe_2NO_6$
$f_{\mathbf{w}}$	495.07	509.10	509.10	475.02
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/n$ (no. 14)	<i>P</i> 1 (no. 2)	$P2_1$ (no. 4)	$P2_1/c$ (no. 14)
a (Å)	10.556(2)	8.054(9)	8.544(2)	13.138(3)
b (Å)	14.184(2)	11.459(2)	9.011(3)	7.258(3)
<i>c</i> (Å)	14.528(2)	13.029(2)	14.172(4)	21.290(2)
α (°)		64.08(1)		
β (°)	111.36(1)	89.97(1)	100.75(3)	94.64(1)
γ (°)		80.43(1)		
$V(Å^3)$	2025.8(6)	1066.3(3)	1071.9(4)	2023.6(6)
Z	4	2	2	4
$D_{\text{calc}} (\text{g cm}^{-3})$	1.623	1.586	1.677	1.559
Crystal size (mm)	$0.22 \times 0.35 \times 0.40$	0.28  imes 0.40  imes 0.48	0.38  imes 0.40  imes 0.60	0.33  imes 0.41  imes 0.44
<i>T</i> (K)	296	296	293	296
$2\theta_{\max}$ (°)	50.2	50.0	55.0	50.1
Scan type	$\omega - 2\theta$	$\omega - 2\theta$	$\omega - 2\theta$	$\omega - 2\theta$
Reflections measured: total, unique	3978, 3762	3989, 3770	2789, 2620	4081, 3902
Observed reflections $[I > 3\sigma(I)]$	2004	2673	2407	2130
Variables	262	271	269	262
$F_{000}$	1000.00	516.00	516.00	960.00
$\mu$ (Mo K $\alpha$ ) (cm <sup>-1</sup> )	15.69	14.93	14.85	14.68
R	0.039	0.036	0.024	0.058
R <sub>w</sub>	0.038	0.023	0.018	0.046

bonded to Fe(1) with bond distances of 2.186(8) and 2.359(8) Å, respectively, and the bond distance between C(3) and C(2) is lengthened to 1.392(10) Å. The phenyl ring acts as a three-electron donor and bridges the two iron centers. The bond distances from N(1) to C(1) and from N(1) to C(14) are 1.476(9) and 1.498(9) Å, respectively, are in the single bond range. The nitrogen atom serves as another bridge and the bond distances to Fe(1) and Fe(2) are 1.949(6) and 1.990(6) Å, respeciron-iron distance, 2.454(2)tively. The А, Fe(1)-N-Fe(2)bond angle. 77.0(2)°, and Fe(1)-C(3)-F(2) angle, 71.8(3)°, are very closely resemble that of complex 2a described above. Fig. 2 also shows that the 5-methylthienyl group of the original Schiff base has been substituted with a phenyl ring.

Complex **3a** is an unexpected product. Although the original Schiff base contained a thienyl unit, it is missing in **3a**. The Schiff base has therefore undergone a chemical transformation. It seems that, after the coordination of the imine nitrogen to one of the iron centers, a C-H activation occurs at one of the  $\beta$ -carbon of the phenyl ring to form a five-membered metallacycle and then the methine carbon adopts the hydrogen originated from the  $\beta$ -carbon of the phenyl ring to form an intermediate that is similar to the complex **6** in Scheme 2 (vide infra). This is a consecutive process of coordination, *exo* cyclometalation, and 1,5-hydrogen shift. However, the complex thus formed might undergo a chemical transformation, the substitution of the thienyl unit with a phenyl group, to form product **3a**.

Similar result was found from the reaction of 1b with diiron nonacarbonyl. Two cyclometalated complexes 2b and 3b were isolated as shown in Scheme 1. Complexes 2b and 3b were characterized spectrally and identified to be structurally similar to that of complexes 2a and 3a, respectively. The crystal structure of complex 2b is shown in Fig. 3. For complex 3b, it shows that the



Fig. 1. ORTEP diagram of complex **2a** at the 50% probability level. Selected bond lengths (Å): Fe(1)-Fe(2) 2.440(1), Fe(1)-N 1.992(5), Fe(2)-N 1.968(5), Fe(1)-C(3) 1.971(6), Fe(2)-C(2), 2.304(7), Fe(2)-C(3) 2.167(6), C(2)-C(3) 1.359(8), N-C(1) 1.495(7), N-C(12) 1.503(8). Bond angles (°): Fe(1)-N-Fe(2) 76.1(2), Fe(1)-C(3)-Fe(2) 72.1(2), Fe(2)-N-C(1) 99.5(4), Fe(2)-N-C(12) 125.5(4), Fe(1)-N-C(1) 113.2(4), Fe(1)-N-C(12) 125.3(4), C(1)-N-C(12) 111.1(5), N-C(12)-C(13) 114.0(5).



Fig. 2. ORTEP diagram of complex **3a** at the 50% probability level. Selected bond lengths (Å): Fe(1)–Fe(2) 2.454(2), Fe(1)–N 1.949(6), Fe(2)–N 1.990(6), Fe(2)–C(3) 1.992(7), Fe(1)–C(2), 2.359(8), Fe(1)–C(3) 2.186(8), C(2)–C(3) 1.392(10), N–C(1) 1.476(9), N–C(114) 1.498(9). Bond angles (°): Fe(1)–N–Fe(2) 77.0(2), Fe(1)–C(3)–Fe(2) 71.8(3), Fe(2)–N–C(1) 111.5(5), Fe(2)–N–C(14) 120.3(5), Fe(1)–N–C(1) 99.7(4), Fe(1)–N–C(14) 129.4(5), C(1)–N–C(14) 111.5(5), N–C(14)–C(15) 115.1(6).

5-methyl-2-thienyl group disappeared from its original Schiff base **1b** and a tolyl group took its place to finalize the product. Obviously, a C–N bond cleavage or a C–C bond cleavage must be involved in the course of complex formation. In terms of bond energies of C=N, C–N, and C–C bonds, it is most likely that a



Fig. 3. ORTEP diagram of complex **2b** at the 50% probability level. Selected bond lengths (Å): Fe(1)–Fe(2) 2.4569(8), Fe(1)–N 1.989(3), Fe(2)–N 1.967(3), Fe(1)–C(3) 1.965(4), Fe(1)–C(4), 2.299(4), Fe(1)–C(3) 2.173(4), C(3)–C(4) 1.393(5), N–C(6) 1.477(4), N–C(7) 1.480(4). Bond angles (°): Fe(1)–N–Fe(2) 76.8(1), Fe(1)–C(3)–Fe(2) 72.6(1), Fe(1)–N–C(6) 98.4(2), Fe(1)–N–C(7) 130.2(2), Fe(2)–N–C(6) 112.3(2), Fe(2)–N–C(7) 120.8(2), C(6)–N–C(7) 112.8(3), N–C(7)–C(8) 116.5(3).

C-N bond cleavage occurred on 1a-1b or 2a-2b. The 5-methyl-2-thienylmethyl group of the *exo*-cyclometa-lated product might be substituted by a benzyl-xylyl



Scheme 2.

group that was cleaved from 1a-1b or 2a-2b to form complex 3a-3b.

In order to have a better understanding of the formation of complex 3, the Schiff base 1c was prepared and reacted with diiron nonacarbonyl under exactly the same reaction condition. Two complexes, 2c and 4c, were isolated after the reaction. Unfortunately, there was no complex in the form similar to complex 3 found. The structure feature of complex 2c, as shown in Fig. 4, closely resembles that of complexes 2a and 2b, as explicated above. While no direct structure evidence is available for complex 4c, we are able to deduce its structure by its NMR, IR, and mass spectra as well as elemental analyses. It is an imidoyl triironnonacarbonyl cluster with the imidovl group (-C=N-) atop on the three-iron plane and triply bridging to the iron triangle via two  $\sigma$  and one  $\pi$  bonding, and a hydrogen atom bridging on two irons. The fact that the disappearance of the methine proton resonance and the appearance of a singlet resonance at  $\delta - 26.2$  ppm in the <sup>1</sup>H NMR spectrum of complex 4c indicates that the hydrogen is removed from the methine group and a bridging metal hydride is formed. In its IR spectrum, the C–N stretching frequency of 1348 cm $^{-1}$  (relative to the corresponding band at 1632  $\text{cm}^{-1}$  in the free Schiff base 1c) indicating a partial double bond feature of a coordinated imidoyl group [8d,e]. The significant shift to the lower frequency is attributed to the two  $\sigma$  and one  $\pi$ donation and back  $\pi$  accepting of the highly conjugated imidoyl ligand. There are also four sharp and intense C-O stretches appearing at 2088, 2052, 2016, and 1972  $cm^{-1}$ . The mass spectrum shows the entirely loss of nine COs successively, and the molecular ion peak at



Fig. 4. ORTEP diagram of complex **2c** at the 50% probability level. Selected bond lengths (Å): Fe(1)-Fe(2) 2.4454(5), Fe(1)-N 1.977(3), Fe(2)-N 1.998(3), Fe(2)-C(3) 1.956(4), Fe(1)-C(4), 2.246(4), Fe(1)-C(3) 2.188(4), C(3)-C(4) 1.404(4), N-C(6) 1.498(4), N-C(7) 1.492(4). Bond angles (°): Fe(1)-N-Fe(2) 75.94(10), Fe(1)-C(3)-Fe(2) 72.1(1), Fe(1)-N-C(6) 97.8(2), Fe(1)-N-C(7) 128.4(2), Fe(2)-N-C(6) 111.9(2), Fe(2)-N-C(7) 122.8(2), C(6)-N-C(7) 113.4(5), N-C(7)-C(8) 110.6(3).

m/z 649 consists with the formulated structure. The structure of **4b** is analogous to that of literature reported trimetalnonacarbonyl complexes with a triply bridging imidoyl ligand and an  $\eta^2$ -hydride [8].

Reactions of N-(3-methyl-2-thienylmethylidene)benzylamine derivatives, **1d**, **1e** and **1f**, in which the  $\beta$ -position of the thienyl ring is blocked with a methyl substituent in order to favor the *exo* cyclometalation to occur, with diiron nonacarbonyl were conducted under the same reaction condition and all complexes thus formed were outlined in Scheme 2.

The reaction of Schiff base 1d-1e leads to the formation of three isomeric complexes, 2a-2b, 5d-5e and 6d-6e, and complex 3a-3b. Isomeric complexes 2 and 5 are different only in the location of the methyl substitutent on the thienyl ring. The methyl group had been migrated from its original  $\beta$ -position to the  $\alpha'$ - and  $\beta'$ -position of the thienvl ring during the course of *endo* cyclometalation to form complexes 2 and 5, respectively. On the other hand, complex 6 is formed as the result of the consecutive process of imine coordination, exo cyclometalation, and 1,5-hydrogen shift. Another exo cyclometalated product, complex 3, which is also found from the reaction of 1a-1b (Scheme 1) is similar to complex 6 but with a phenyl-p-xylyl group substitutes the 3-methyl-2-thienyl group. However, the reaction of Schiff base 1f leads to the formation of an imidoyl triironnonacarbonyl cluster 4f and an exo cyclometalated complex 6f only.

Since the free Schiff base itself was stable to the reaction condition, the iron center must be responsible for the methyl migration and the formation of products 2 and 5. A plausible explanation can be suggested as the following. Upon coordination of the methine nitrogen of the 3-methylthienyl Schiff base to one of the iron centers, an endo cyclometalation induced carbon-carbon bond cleavage occurs between the methyl group and the  $\beta$ -carbon of the thienyl ring to form a stable five-membered metalacycle. The cleaved methyl group attacks the  $\beta'$ - or  $\alpha'$ -carbon of the thienyl ring and leads to the activation of the  $\beta'$ - or  $\alpha'$ -hydrogen. Finally, the methine carbon becomes a methylene group by adopting the hydrogen originated from the  $\beta'$ - or  $\alpha'$ -carbon and the nitrogen coordinates to another iron center concomitantly to give the product 2 or 5. The methyl migration process might be similar to the iridium catalyzed ethyl migration reaction of 1,1-diethylcyclopentadiene reported by Crabtree et al. [9]. In their case, the driving force is the formation of an ethylcyclopentadienyl-iridium-ethyl intermediate. Further investigation of the mechanism concerning the methyl migration is in progress.

It is interesting to find that if the reaction time of ligand 1d-1e was prolonged from 5 to 8 h at 45°C in benzene, only 3a-3b and 6d-6e two complex products were isolated. The yield of product 3a-3b increases

about 4% and the yield of 6a-6e decreases about 4%. This amount is about the sum of products 2a-2b and 5d-5e that disappeared during the prolonged reaction. On the other hand, if the reaction was stopped after 3 h of reaction under the same reaction condition, ca. 8% of complex 2a-2b and ca. 9% of complex 5d-5e were obtained accompanying with ca. 5% of complex 3a-3band ca. 20% of complex 5d-6e. Therefore, the formation of benzyl-*p*-xylyl substituted product 3 might be suggested to follow the underlying process:



A reaction of equimolar quantities of complex 2a-2band complex 6d-6e was conducted under exactly the same reaction condition. More than 90% of complex 3a-3b, 82% of 2,3-dimethylthiophene, and 70% of 5methyl-2-(aminomethyl)thiophene were obtained and no any thienyl-contained complex was found, confirming the substitution process suggested.

There are two potential sites, the  $\beta$ -position of thienyl ring and the  $\beta$ -position of phenyl ring, in the Schiff base 1 that might involve in the cyclometalation and leads to the formation of endo and/or exo fivemembered metalacycle. In the case of 1a-1b, The products and yields distribution, as shown in Scheme 1, clearly shows that the C-H activation that occurs at the  $\beta$ -position of thienyl ring is relatively more favorable than that of phenyl ring (with ca. 44-17% ratio). The minor exo cyclometalated intermediate 6 thus formed might react with excess amount of endo cyclometalated product 2 and leads to the formation of net products 2 and 3. In the case of 1d-1e, because a methyl group has blocked the  $\beta$ -position of thienyl ring, the C–H activation that occurs at the  $\beta$ -position of the phenyl ring becomes the favorite one (31% for 1d and 37% for 1e). Although certain amount of endo cyclometalated complexes 2 and 5 could be formed via an endo cyclometalation induced methyl migration process (ca. 26%), they were eventually converted to the final complex 3 in the presence of complex 6. The result is completely different from that of the action of Pd(II) on N-(2,4,6trimethylbenzylidene)benzylamines reported by Albert et al. [5]. In their case, activation of a C-H bond of ortho-methyl group with the formation of a six-membered endo metallcycle takes place in preference to the activation of an aromatic C–H bond to form a fivemembered *exo* metallacycle. In our case, although the activation of the thienyl-methyl bond with the formation of a five-membered *endo* metallacycle is observed due to the *endo* effect, an activation of a phenyl C–H bond with the formation of a five-membered *exo* metallacycle is found to be more favorable.

It is noteworthy that with a methyl substituent added on the benzylic carbon of the ligand, the reaction of 1c-1f gives no product in the form similar to complex

3. Instead, an imidoyl triiron cluster is formed due to the electronic effect in both 1c and 1f cases with about the equal amount. The activation of C–H bond takes place only at the  $\beta$ -carbon of the thienyl ring (*endo* cyclometalation) in the case of 1c. However, if a methyl group blocked the  $\beta$ -carbon of the thienyl ring, it takes place only at the  $\beta$ -carbon of the phenyl ring (*exo* cyclometalation). The behavior of these two ligands toward the regioselective cyclometalation is not clear at this stage. The impact of the various substituents on the benzylic carbon of the ligand will be further investigated.

#### 3. Experimental

Diiron nonacarbonyl was prepared by photolysis of iron pentacarbonyl (Aldrich) in glacial acetic acid [10]. Solvents were dried (sodium-benzophenone,  $P_4O_{10}$ ) and distilled under nitrogen prior to use. All other chemicals were reagent grade and without further purification. The NMR spectra were recorded on a Varian VXR-300 NMR spectrometer (<sup>1</sup>H, 299.95 MHz; <sup>13</sup>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 from a VG-Biotech Quattro 5022 spectrometer. IR spectra were recorded from 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 (2a) or from *n*-hexane solution (3a, 2b and 2c). A single crystal was mounted on a glass fiber and the X-ray diffraction

intensity data were measured on a Rigaku AFC7S diffractometer at room temperature.

3.1. Synthesis of N-(5-methyl-2-thienylmethylidene)benzylamine (**1a**), N-(5-methyl-2-thienylmethylidene)p-xylylamine (**1b**), N-(5-methyl-2-thienylmethylidene)-1-phenylethylamine (**1c**), N-(3-methyl-2-thienylmethylidene)benzylamine (**1d**), N-(3-methyl-2-thienylmethylidene)-p-xylylamine (**1e**) and N-(3-methyl-2thienylmethylidene)-1-phenylethylamine (**1f**)

The synthesis of Schiff base employed the usual approach of condensation in alcohol solution [11]. Equimolar quantities of 5-methyl-2-thiophenecarboxaldehyde or 3-methyl-2-thiophenecarboxaldehyde (Aldrich, 4.3 ml, 40 mmol) and amine (E. Merck, benzylamine 4.25 g, *p*-methylbenzylamine 4.81 g, or 1-phenylethylamine 4.81 g, 40 mmol) were heated at reflux in 95% ethanol (E. Merck, 100 ml) for 24 h. The solvent was removed in vacuo. The residue was distilled with a Kugelrohr distillation apparatus under reduced pressure (0.1 mmHg). A pale yellow Schiff base was obtained.

#### 3.1.1. Compound 1a

Yield 95%, 8.07 g. <sup>1</sup>H NMR:  $\delta$  8.48 (s, 1H), 7.32 (m, 4H), 7.23 (m, 2H), 6.80 (d, J = 3.3 Hz, 1H), 4.71 (s, 2H), 2.48 (s, 3H). <sup>13</sup>C NMR:  $\delta$  155.5, 144.3, 141.3, 140.5, 131.8, 128.8, 128.4, 127.2, 126.4, 64.5, 15.5. IR (CHCl<sub>3</sub>)  $v_{C=N}$ : 1630 cm<sup>-1</sup>. MS (EI): m/z 215 ( $M^+$ ). Anal. Calc. for C<sub>13</sub>H<sub>13</sub>NS: C, 72.56; H, 6.05; N, 6.51. Found: C, 72.66; H, 6.01; N, 6.52%.

#### 3.1.2. Compound 1b

Yield 91%, 8.27 g. <sup>1</sup>H NMR:  $\delta$  8.39 (s, 1H), 7.26 (m, 2H), 7.18 (m, 3H), 6.78 (d, J = 3.3 Hz, 1H), 4.70 (s, 2H), 2.45 (s, 3H), 2.33 (s, 3H). <sup>13</sup>C NMR:  $\delta$  155.2, 144.2, 141.4, 137.4, 136.5, 131.7, 129.5, 128.4, 126.4, 64.4, 21.0, 15.5. IR (CHCl<sub>3</sub>)  $v_{C=N}$ : 1630 cm<sup>-1</sup>. MS (EI): m/z 229 ( $M^+$ ). Anal. Calc. for C<sub>14</sub>H<sub>15</sub>NS: C, 73.36; H, 6.55; N, 6.11. Found: C, 73.46; H, 6.58; N, 6.09%.

#### 3.1.3. Compound 1c

Yield 93%, 8.45 g. <sup>1</sup>H NMR:  $\delta$  8.42 (s, 1H), 7.43 (d, J = 7.5 Hz, 2H), 7.33 (t, J = 7.5 Hz, 2H), 7.25 (d, J = 7.5 Hz, 1H), 7.19 (d, J = 3.3 Hz, 1H), 6.77 (d, J = 3.3 Hz, 1H), 4.50 (q, J = 6.6 Hz, 1H), 2.46 (s, 3H), 1.50 (d, J = 6.6 Hz, 3H). <sup>13</sup>C NMR:  $\delta$  153.2, 146.1, 144.1, 141.4, 131.6, 128.7, 127.0, 126.9, 126.3, 69.4, 25.2, 15.4. IR (CHCl<sub>3</sub>)  $v_{C=N}$ : 1624 cm<sup>-1</sup>. MS (FAB): m/z 229 ( $M^+$ ). Anal. Calc. for C<sub>14</sub>H<sub>15</sub>NS: C, 73.36; H, 6.55; N, 6.11. Found: C, 73.46; H, 6.58; N, 6.08%.

# 3.1.4. Compound 1d

Yield 93%, 7.92 g. <sup>1</sup>H NMR:  $\delta$  8.69 (s, 1H), 7.44 (d, J = 5.1 Hz, 1H), 7.32 (m, 4H), 7.23 (m, 1H), 6.92 (d,

 $J = 5.1 \text{ Hz}, 1\text{H}, 4.76 \text{ (s, 2H)}, 2.41 \text{ (s, 3H)}. {}^{13}\text{C NMR: } \delta$ 154.8, 141.3, 141.1, 137.0, 131.7, 129.2, 129.0, 128.8, 121.6, 65.2, 13.9. IR (CHCl<sub>3</sub>)  $v_{\text{C=N}}$ : 1632 cm<sup>-1</sup>. MS (EI): m/z 215( $M^+$ ). Anal. Calc. for C<sub>13</sub>H<sub>13</sub>NS: C, 72.56; H, 6.05; N, 6.51. Found: C, 72.56; H, 6.08; N, 6.55%.

#### 3.1.5. Compound 1e

Yield 95%, 9.07 g. <sup>1</sup>H NMR:  $\delta$  8.63 (s, 1H), 7.39(d, J = 5.1 Hz, 1H), 7.26 (d, J = 7.8 Hz, 2H), 7.15 (d, J = 7.8 Hz, 2H), 6.90 ( d, J = 5.1 Hz, 1H), 4.73 (s, 2H), 2.39 (s, 3H), 2.32 (s, 3H). <sup>13</sup>C NMR:  $\delta$  154.0, 140.6, 137.5, 136.7, 136.5, 131.2, 129.4, 128.5, 128.4, 64.7, 21.0, 13.7. IR (CHCl<sub>3</sub>)  $v_{C=N}$ : 1626 cm<sup>-1</sup>. MS (FAB): m/z 229 ( $M^+$ ). Anal. Calc. for C<sub>14</sub>H<sub>15</sub>NS: C, 73.36; H, 6.55; N, 6.11. Found: C, 73.26; H, 6.62; N, 6.09%.

#### 3.1.6. Compound 1f

Yield 94%, 8.98 g. <sup>1</sup>H NMR:  $\delta$  8.65 (s, 1H), 7.47 (d, J = 7.5 Hz, 2H), 7.40 (d, J = 5.1 Hz, 1H), 7.34 (t, J = 7.5 Hz, 2H), 7.23 (t, J = 7.2 Hz, 1H), 6.90 (d, J = 5.1 Hz, 1H), 4.56 (q, J = 6.6 Hz, 1H), 2.38 (s, 3H), 1.54 (d, J = 6.6 Hz, 3H). <sup>13</sup>C NMR:  $\delta$  152.0, 146.2, 140.7, 136.6, 131.2, 128.7, 128.5, 127.1, 127.0, 69.8, 25.4, 13.6. IR (CHCl<sub>3</sub>)  $v_{C=N}$ : 1617 cm<sup>-1</sup>. MS (FAB): m/z 229 ( $M^+$ ). Anal. Calc. for C<sub>14</sub>H<sub>15</sub>NS: C, 73.36; H, 6.55; N, 6.11. Found: C, 73.38; H, 6.67; N, 6.11%.

# 3.2. Reaction of Schiff base 1 with $Fe_2(CO)_9$ in benzene

In a typical reaction, 8.0 mmol of compound 1 in 30 ml of anhydrous benzene was added dropwise to a 70 ml of anhydrous benzene solution containing 16.0 mmol of Fe<sub>2</sub>(CO)<sub>9</sub> in the dark under nitrogen and the reaction mixture was heated at 45°C for 5 h. The reaction mixture was filtered through Celite 545 and the solvent was removed under reduced pressure. The residue was chromatographed on a silica gel column with ethyl acetate-chloroform-*n*-hexane (1:5:20) as eluent. Substantial amount of Fe<sub>3</sub>(CO)<sub>9</sub>, dimethylthiophene, and methyl-2-(aminomethyl)thiophene were also collected accompany with the complex products.

3.2.1. Reaction of **1a** with  $Fe_2(CO)_9$  to give  $[\mu-N-(((2,3-\eta^1:\eta^2)-5-methyl-2-thienyl)methyl)-\eta^1:\eta^1-(N)-benzylamino]hexacarbonyldiiron ($ **2a** $) and <math>[\mu-N-(((1,2-\eta^1:\eta^2)-phenyl)methyl)-\eta^1:\eta^1-(N)-benzylamino]hexacarbonyldiiron ($ **3a**)

Complex **2a** (28.8% yield): <sup>1</sup>H NMR:  $\delta$  7.43 (m, 5H), 7.04 (s, 1H), 3.97 (s, 2H), 3.83 (s, 2H), 2.43 (s, 3H). <sup>13</sup>C NMR:  $\delta$  211.6, 160.4, 147.9, 138.4, 137.4, 130.9, 129.4, 129.3, 114.9, 72.2, 68.8, 15.8. IR (CHCl<sub>3</sub>)  $v_{CO}$ : 2068, 2024, 1984 cm<sup>-1</sup>. MS (EI): m/z 495 ( $M^+$ ), 467 ( $M^+ -$ CO), 439 ( $M^+ -$  2CO), 411 ( $M^+ -$  3CO), 383 ( $M^+ -$ 4CO), 355 ( $M^+ -$  5CO), 327 ( $M^+ -$  6CO), 215 (L<sup>+</sup>). *Anal.* Calc. For Fe<sub>2</sub>C<sub>19</sub>H<sub>13</sub>NSO<sub>6</sub>: C, 46.06; H, 2.63; N, 2.83. Found: C, 46.05; H, 2.73; N, 2.86%. Complex **3a**  (15.6% yield): <sup>1</sup>H NMR:  $\delta$  8.07 (d, J = 8.7 Hz, 1H), 7.65 (d, J = 8.7 Hz, 1H), 7.42 (m, 6H), 7.14 (t, J = 7.8 Hz, 1H), 4.09 (s, 2H), 3.98 (s, 2H). <sup>13</sup>C NMR:  $\delta$  211.4, 151.4, 146.9, 138.5, 131.7, 131.0, 129.8, 129.5, 129.3, 126.9, 126.6, 72.6, 71.6. IR (CHCl<sub>3</sub>)  $v_{\rm CO}$ : 2068, 2028, 1982 cm<sup>-1</sup>. MS (EI): m/z 475 ( $M^+$ ), 447 ( $M^+ -$  CO), 419 ( $M^+ -$  2CO), 391 ( $M^+ -$  3CO), 363 ( $M^+ -$  4CO), 335 ( $M^+ -$  5CO), 307 ( $M^+ -$  6CO), 195 (L<sup>+</sup>). Anal. Calc. For Fe<sub>2</sub>C<sub>20</sub>H<sub>13</sub>NO<sub>6</sub>: C, 50.50; H, 2.74; N, 2.95. Found: C, 50.38; H, 2.83; N, 2.95%.

3.2.2. Reaction of **1b** with  $Fe_2(CO)_9$  to give  $[\mu-N-(((2,3-\eta^1:\eta^2)-5-methyl-2-thienyl)methyl)-\eta^1:\eta^1-(N)-p-xylylamino]hexacarbonyldiiron ($ **2b** $) and <math>[\mu-N-(((1,2-\eta^1:\eta^2)-p-tolyl)methyl)-\eta^1:\eta^1-(N)-p-xylylamino]hexacarbonyldiiron ($ **3b**)

Complex **2b** (25.2% yield): <sup>1</sup>H NMR:  $\delta$  7.28 (d, J = 8.1 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 7.04 (s, 1H), 3.92 (s, 2H), 3.82 (s, 2H), 2.43 (s, 3H), 2.33 (s, 3H). <sup>13</sup>C NMR:  $\delta$  211.1, 159.8, 147.3, 138.4, 136.9, 135.0, 130.2, 129.4, 114.4, 71.4, 68.2, 20.7, 15.2. IR (CHCl<sub>3</sub>)  $v_{\rm CO}$ : 2061, 2021, 1976 cm<sup>-1</sup>. MS (FAB): m/z 509  $(M^+)$ , 481  $(M^+ - CO)$ , 453  $(M^+ - 2CO)$ , 425  $(M^+ -$ 3CO), 397  $(M^+ - 4CO)$ , 369  $(M^+ - 5CO)$ , 341  $(M^+$ -6CO), 229 (L<sup>+</sup>). Anal. Calc. For Fe<sub>2</sub>C<sub>20</sub>H<sub>15</sub>NO<sub>6</sub>S: C, 47.15; H, 2.95; N, 2.75. Found: C, 47.28; H, 2.91; N, 2.78%. Complex **3b** (18.5% yield): <sup>1</sup>H NMR:  $\delta$  7.84 (s, 1H), 7.57 (d, J = 8.1 Hz, 1H), 7.32 (d, J = 8.1 Hz, 2H), 7.22 (m, 3H), 4.02 (s, 2H), 3.90 (s, 2H), 2.33 (s, 3H), 2.29 (s, 3H). <sup>13</sup>C NMR:  $\delta$  211.4, 149.3, 148.0, 138.4, 136.0, 135.1, 133.0, 130.3, 129.4, 129.3, 121.4, 71.7, 70.7, 20.7, 20.6. IR (CHCl<sub>3</sub>)  $v_{CO}$ : 2047, 2018, 1992 cm<sup>-1</sup>. MS (FAB): m/z 503 ( $M^+$ ), 475 ( $M^+$  – CO), 447  $(M^+ - 2CO)$ , 419  $(M^+ - 3CO)$ , 391  $(M^+ - 3CO)$ 4CO), 363  $(M^+ - 5CO)$ , 335  $(M^+ - 6CO)$ , 223  $(L^+)$ . Anal. Calc. For Fe<sub>2</sub>C<sub>22</sub>H<sub>17</sub>NO<sub>6</sub>: C, 52.49; H, 3.38; N, 2.78. Found: C, 52.60; H, 3.41; N, 2.72%.

3.2.3. Reaction of **1c** with  $Fe_2(CO)_9$  to give  $[\mu-N-(((2,3-\eta^1:\eta^2)-5-methyl-2-thienyl)methyl)-\eta^1:\eta^1-(N)-1-phenylethylamino]hexacarbonyldiiron ($ **2c** $) and <math>[\mu_3-((N-1-\eta)-1-phenylethyl-(5-methyl-2-thienyl)-formidoyl-N,C)]nonacarbonyl-<math>\mu$ -hydrido-triangulo-triiron (**4c**)

Complex **2c** (26.8% yield): <sup>1</sup>H NMR:  $\delta$  7.44 (m, 5H), 7.04 (s, 1H), 3.92 (d, J = 15 Hz, 1H), 3.87 (d, J = 15 Hz, 1H), 3.70 (q, J = 6.9 Hz, 1H), 2.42 (s, 3H), 1.57 (s, 3H). <sup>13</sup>C NMR:  $\delta$  160.1, 147.4, 142.4, 136.7, 129.1, 128.8, 128.7, 113.5, 73.4, 61.4, 20.7, 15.3. IR (CHCl<sub>3</sub>)  $v_{\rm CO}$ : 2070, 2030, 1991 cm<sup>-1</sup>. MS (FAB): m/z 509 ( $M^+$ ), 481 ( $M^+ -$  CO), 453 ( $M^+ -$  2CO), 425 ( $M^+ -$  3CO), 397 ( $M^+ -$  4CO), 369 ( $M^+ -$  5CO), 341 ( $M^+ -$  6CO), 229 (L<sup>+</sup>). Anal. Calc. For

Fe<sub>2</sub>C<sub>20</sub>H<sub>15</sub>NO<sub>6</sub>S: C, 47.15; H, 2.95; N, 2.75. Found: C, 47.21; H, 2.92; N, 2.79%. Complex 4c (16.6% yield): <sup>1</sup>H NMR:  $\delta$  7.40 (m, 5H), 7.12 (d, J = 3.6 Hz, 1 H), 6.86 (d, J = 3.6 Hz, 1 H), 5.60 (q, J = 6.6 Hz, 1H), 2.52 (s, 3H), 1.59 (d, J = 6.6 Hz, 3H), -26.2 (s, 1H). <sup>13</sup>C NMR:  $\delta$  211.1, 162.2, 155.6, 137.8, 134.6, 128.2, 126.6, 126.5, 125.0, 123.4, 64.4, 19.5, 11.8. IR (CHCl<sub>3</sub>)  $v_{\rm CO}$ : 2081, 2047, 2012 cm<sup>-1</sup>,  $v_{\rm CN}$ : 1343 cm<sup>-1</sup>. MS (FAB): m/z 649 ( $M^+$ ), 565 ( $M^+ - 3$ CO), 509 ( $M^+ -$ 3CO-Fe), 453  $(M^+ - 5CO-Fe)$ , 425  $(M^+ - 6CO-Fe)$ , 397  $(M^+ - 7\text{CO}-\text{Fe})$ , 369  $(M^+ - 8\text{CO}-\text{Fe})$ , 341  $(M^+$ – 9CO–Fe), 228  $(L^+ - 1)$ . Anal. Calc. For Fe<sub>3</sub>C<sub>23</sub>H<sub>15</sub>NO<sub>9</sub>S: C, 42.53; H, 2.31; N, 2.16. Found: C, 42.38; H, 2.28; N, 2.19%.

3.2.4. Reaction of **1d** with  $Fe_2(CO)_9$  to give  $[\mu-N-(((2,3-\eta^1:\eta^2)-5-methyl-2-thienyl)methyl) \eta^1:\eta^1-(N)$ -benzylamino]hexacarbonyldiiron (**2a**),  $[\mu-N-(((1,2-\eta^1:\eta^2)-phenyl)methyl)-\eta^1:\eta^1-(N)$ benzylamino]hexacarbonyldiiron (**3a**),  $[\mu-N-(((2,3-\eta^1:\eta^2)-4-methyl-2-thienyl)methyl) \eta^1:\eta^1-(N)$ -benzylamino]hexacarbonyldiiron (**5d**) and  $[\mu-N-(((1,2-\eta^1:\eta^2)-phenyl)methyl)-\eta^1:\eta^1-(N)-3$ methyl-2-thienylmethylamino]hexacarbonyldiiron (**6d**)

Complex 2a, 3.2% yield. Complex 3a, 18.0% yield. Complex 5d (3.4% yield): <sup>1</sup>H NMR:  $\delta$  7.43. (m, 5H), 7.25 (s, 1H), 4.05 (s, 2H), 3.88 (s, 2H), 2.40 (s, 3H). <sup>13</sup>C NMR: δ 211.4, 152.0, 146.2, 140.6, 136.6, 131.1, 128.7, 128.4, 127.1, 126.9, 72.1, 68.7, 13.4. IR (CHCl<sub>3</sub>)  $v_{\rm CO}$ : 2067, 2022, 1982 cm<sup>-1</sup>. MS (EI): m/z 495 ( $M^+$ ), 467  $(M^+ - CO)$ , 439  $(M^+ - 2CO)$ , 411  $(M^+ - 3CO)$ , 383  $(M^+ - 4CO)$ , 355  $(M^+ - 5CO)$ , 327  $(M^+ - 6CO)$ , 215 (L<sup>+</sup>). Anal. Calc. For C<sub>19</sub>H<sub>13</sub>Fe<sub>2</sub>NO<sub>6</sub>S: C, 46.06; H, 2.63; N, 2.83. Found: C, 46.07; H, 2.71; N, 2.81%. Complex 6d (12.8% yield): <sup>1</sup>H NMR:  $\delta$  8.06 (d, J = 8.1Hz, 1H), 7.68 (d, J = 8.1 Hz, 1H), 7.42 (d, J = 5.1 Hz, 1H), 7.37 (m, 1H), 7.15 (m, 1H), 6.87 (d, J = 5.1 Hz, 1H), 4.22 (s, 2H), 3.93 (s, 2H), 2.37 (s, 3H). <sup>13</sup>C NMR: δ 211.4, 149.5, 147.7, 136.8, 136.0, 131.0, 129.8, 129.6, 128.8, 126.4, 125.2, 71.2, 64.3, 20.6, 14.0. IR (CHCl<sub>3</sub>)  $v_{CO}$ : 2068, 2026, 1984 cm<sup>-1</sup>. MS (EI): m/z495  $(M^+)$ , 467  $(M^+ - CO)$ , 439  $(M^+ - 2CO)$ , 411  $(M^+ - 3CO)$ , 383  $(M^+ - 4CO)$ , 355  $(M^+ - 5CO)$ , 327  $(M^+ - 6 \text{CO}),$ 215  $(L^{+}).$ Anal. Calc. For C<sub>19</sub>H<sub>13</sub>Fe<sub>2</sub>NO<sub>6</sub>S: C, 46.06; H, 2.63; N, 2.83. Found: C, 46.18; H, 2.67; N, 2.81%.

If the reaction was proceeded for 8 h under the same condition, only two complexes, 3a (22.8% yield) and 6d (8.9% yield), were obtained.

If the reaction was stopped after 3 h of reaction, 8.0% of **2a**, 5.2% of **3a**, 9.2% of **5d**, and 19.8% of **6d** were isolated.

3.2.5. Reaction of **1e** with  $Fe_2(CO)_9$  to give  $[\mu-N-(((2,3-\eta^1:\eta^2)-5-methyl-2-thienyl)methyl)-\eta^1:\eta^1-(N)-p-xylylamino]hexacarbonyldiiron ($ **2b**), $<math>[\mu-N-(((1,2-\eta^1:\eta^2)-p-tolyl)methyl)-\eta^1:\eta^1-(N)-p-xylylamino]hexacarbonyldiiron ($ **3b** $), <math>[\mu-N-(((2,3-\eta^1:\eta^2)-4-methyl-2-thienyl)methyl)-\eta^1:\eta^1-(N)-p-xylylamino]-hexacarbonyldiiron ($ **5e** $) and <math>[\mu-N-(((1,2-\eta^1:\eta^2)-p-tolyl)methyl)-\eta^1:\eta^1-(N)-3-methyl-2-t$ hienylmethylamino]hexacarbonyldiiron (**6e**)

Complex 2b, 2.3% yield. Complex 3b, 22.4% yield. Complex 5e (2.2% yield): <sup>1</sup>H NMR:  $\delta$  7.30 (d, J = 8.1Hz, 2H), 7.26 (s, 1H), 7.21 (d, J = 8.1 Hz, 2H), 4.00 (s, 2H), 3.90 (s, 2H), 2.42 (s, 3H), 2.35 (s, 3H). <sup>13</sup>C NMR: δ 211.3, 156.2, 145.8, 137.7, 136.5, 133.3, 129.7, 128.8, 127.6, 71.3, 68.0, 20.5, 13.1. IR (CHCl<sub>3</sub>)  $v_{CO}$ : 2060, 2018, 1974 cm<sup>-1</sup>. MS (FAB): m/z 509 ( $M^+$ ), 481  $(M^+ - CO), 453 (M^+ - 2CO), 425 (M^+ - 3CO), 397$  $(M^+ - 4CO)$ , 369  $(M^+ - 5CO)$ , 341  $(M^+ - 6CO)$ , 229 (L<sup>+</sup>). Anal. Calc. For C<sub>20</sub>H<sub>15</sub>Fe<sub>2</sub>NO<sub>6</sub>S: C, 47.15; H, 2.95; N, 2.75. Found: C, 47.06; H, 2.98; N, 2.74%. Complex **6e** (14.6% yield): <sup>1</sup>H NMR:  $\delta$  7.84 (s, 1H), 7.61 (d, J = 8.1 Hz, 1H), 7.39 (d, J = 5.1 Hz, 1H), 7.25 (d, J = 8.1 Hz, 1H), 6.86 (d, J = 5.1 Hz, 1H), 4.20 (s, 2H), 3.92 (s, 2H), 2.39 (s, 3H), 2.30 (s, 3H). <sup>13</sup>C NMR:  $\delta$  211.3, 149.6, 146.9, 137.1, 136.1, 133.6, 133.2, 129.9, 129.2, 124.8, 122.5, 70.9, 63.8, 20.6, 13.9. IR (CHCl<sub>3</sub>)  $v_{\rm CO}$ : 2061, 2020, 1973 cm<sup>-1</sup>. MS (FAB): m/z 509 ( $M^+$ ), 481  $(M^+ - CO)$ , 453  $(M^+ - 2CO)$ , 425  $(M^+ - 3CO)$ , 397  $(M^+ - 4CO)$ , 369  $(M^+ - 5CO)$ , 341  $(M^+ - 6CO)$ , 229 (L<sup>+</sup>). Anal. Calc. For C<sub>20</sub>H<sub>15</sub>Fe<sub>2</sub>NO<sub>6</sub>S: C, 47.15; H, 2.95; N, 2.75. Found: C, 47.18; H, 2.98; N, 2.73%.

If the reaction was proceeded for 8 h under the same condition, only two complexes, **3b** (26.6% yield) and **6e** (10.2% yield), were obtained.

If the reaction was stopped after 3 h of reaction, 8.2% of **2b**, 5.6% of **3b**, 8.8% of **5e**, and 20.6% of **6e** were isolated.

3.2.6. Reaction of **1f** with  $Fe_2(CO)_9$  to give  $[\mu_3-((N-1-\eta)-1-phenylethyl-(3-methyl-2-thienyl)-formidoyl-N,C)]nonacarbonyl-<math>\mu$ -hydrido-triangulo-triiron (**4f**) and  $[\mu$ -N-(((1,2-\eta^1:\eta^2)-1-phenyl)ethyl)- $\eta^1:\eta^1-(N)$ -3-methyl-2-thienylmethylamino]-hexacarbonyldiiron (**6f**)

Complex 4f (16.4% yield): <sup>1</sup>H NMR:  $\delta$  7.49 (d, J = 4.8 Hz, 1H), 7.35 (m, 5H), 7.02 (d, J = 4.8 Hz, 1H), 5.33 (q, J = 6.6 Hz, 1H), 2.48 (s, 3H), 1.83 (d, J = 6.6Hz, 3H), -25.9 (s, 1H). <sup>13</sup>C NMR:  $\delta$  210.2, 150.1, 147.1, 144.5, 143.4, 133.2, 131.8, 129.3, 128.9, 125.6, 66.0, 17.2, 11.2. IR (CHCl<sub>3</sub>) v<sub>CO</sub>: 2081, 2045, 2010 cm<sup>-1</sup>. MS (FAB): m/z 649 ( $M^+$ ), 621 ( $M^+$  – CO), 593  $(M^+ - 2CO)$ , 565  $(M^+ - 3CO)$ , 537  $(M^+ - 4CO)$ , 509  $(M^+ - 5CO), 481 (M^+ - 6CO), 425 (M^+ - 8CO), 397$  $228(L^+ - 1).$  $(M^{+} - 9CO),$ Anal. Calc. For C<sub>23</sub>H<sub>15</sub>Fe<sub>3</sub>NO<sub>9</sub>S: C, 42.53; H, 2.31; N, 2.16. Found: C, 42.61; H, 2.33; N, 2.13%. Complex 6f (31.4% yield): <sup>1</sup>H NMR:  $\delta$  8.05 (d, J = 8.1 Hz, 1H), 7.70. (d, J = 8.1 Hz, 1H), 7.44 (d, J = 5.1 Hz, 1H), 7.36 (m, 1H), 7.15 (m, 1H), 6.89 (d, J = 5.1 Hz, 1H), 4.52 (q, J = 6.0 Hz, 2H), 4.40 (d, J = 15 Hz, 1H), 4.15 (d, J = 15 Hz, 1H), 2.32 (s, 3H), 0.88 (d, J = 6.0 Hz, 3H). <sup>13</sup>C NMR:  $\delta$  211.7, 150.1, 147.0, 136.7, 135.4, 131.0, 130.2, 130.1, 126.6, 126.5, 125.1, 74.5, 60.8, 24.3, 14.1. IR (CHCl<sub>3</sub>)  $v_{\rm CO}$ : 2062, 2022, 1979 cm<sup>-1</sup>. MS (FAB): m/z 509 ( $M^+$ ), 481 ( $M^+ -$  CO), 453 ( $M^+ -$  2CO), 425 ( $M^+ -$  3CO), 397 ( $M^+ -$  4CO), 369 ( $M^+ -$  5CO), 341 ( $M^+ -$  6CO), 229 (L<sup>+</sup>). Anal. Calc. For C<sub>20</sub>H<sub>15</sub>Fe<sub>2</sub>NO<sub>6</sub>S: C, 47.15; H, 2.95; N, 2.75. Found: C, 47.23; H, 2.91; N, 2.79%.

# 3.3. Reaction of complex 2a-2b with complex 6d-6e to give complex 3a-3b

Equimolar quantities (1.0 mmol) of complexes 2a-2band 6d-6e in a 30 ml anhydrous benzene solution were stirred under nitrogen at 45°C for 4 h. The reaction mixture was filtered through Celite 545 and the solvent was removed under reduced pressure. The residue was chromatographed on a silica gel column with ethyl acetate-chloroform-*n*-hexane (1:5:20) as eluent. The products thus isolated were identified to be **3a** (91% yield)-**3b** (94% yield); 2,3-dimethylthiophene (84–81% yield): <sup>1</sup>H NMR:  $\delta$  7.10 (d, J = 5.1 Hz, 1H), 6.55 (d, J = 5.1 Hz, 1H), 2.36 (s, 3H), 2.25 (s, 3H). MS (EI): m/z 112 ( $M^+$ ); 5-methyl-2-(aminomethyl)thiophene (73–70% yield) <sup>1</sup>H NMR:  $\delta$  6.57 (m, 2H), 3.86 (s, 2H), 2.40 (s, 3H), 1.50 (s, 2H). MS (EI): m/z 127 ( $M^+$ ).

# 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 146435 for complex **2a**, CCDC no. 146436 for complex **3a** and CCDC no. 146438 for complex **2c**. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http:// www.ccdc.cam.ac.uk).

#### Acknowledgements

Financial support from the National Science Council (Taiwan, ROC) is gratefully acknowledged.

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