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Reaction of *N*-(3-methyl-2-thienylmethylidene)aniline with diiron nonacarbonyl: cyclometalation induced methyl migration, imidoyl complex formation, and hydrogenation

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Abstract

The reaction of *N*-(3-methyl-2-thienylmethylidene)aniline with $Fe_2(CO)_9$ under mild conditions in anhydrous benzene gives ironcarbonyl organometallic products **2b**, **2c**, **5**, and an organic product **4c**. Complexes **2b** and **2c** are cyclometalated diironhexacarbonyl isomers, in which the methyl group has migrated from β- to β′- and α′-carbon of the thienyl ring, respectively. Complex **5** is a triironnonacarbonyl cluster with an imidoyl ligand capped on the top of the three-iron plane and a hydrogen atom bridged to two irons. The organic product **4c** is a hydrogenated product of the original Schiff base. Single crystals of **2c** and **5** were subjected to the X-ray diffraction analysis and their structures thus confirmed. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: *N*-(3-methyl-2-thienylmethylidene)aniline; Cyclometalation; Methyl migration; Imidoyl complex; Hydrogenation

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1. Introduction

Although impressive advances have been made in activating the carbon–hydrogen bonds of hydrocarbons, transition-metal-promoted activation of unreactive carbon–carbon bonds remains one of the most prominent challenges in organometallic chemistry. Most of the reported cases of carbon–carbon bond activation by transition-metal complexes involve strained systems such as cyclopropane or cubane [1], intramolecular ligand activation, or activated system such as aromatic nitriles and alkyl-substituted cyclopentadienes [2]. Those cases in which unstrained carbon–carbon bonds are cleaved typically rely upon formation of an η^5-cyclopentadienyl or η^6-arene ring, or an intramolecular addition in which the carbon–carbon bond is forced to react with the metal center by proximity [3]. β-Alkyl migration [4] and metal insertion into carbon–carbon single bond of cyclopentadiene [5] have also been observed.

We have reported recently on the reaction of *N*-(2-thienylmethylidene)aniline (**1**) with $Fe_2(CO)_9$ [6]. Two cyclometalated (μ–η^1: η^2-thienyl; η^1: $\eta^1(N)$)hexacarbonyldiiron complexes, **2** and **3**, and an organic product **4** were obtained (Scheme 1). The reaction involves a C–H activation on the thienyl ring, a C–C coupling via the methine carbon, and a hydrogenation of the imine group. In order to study the other possible types of coordination between the thienyl ring and iron centers, we became interested in studying the reaction of β-methyl blocked thienyl Schiff base. We report here the interesting result of the reaction of a β-methyl blocked thienyl Schiff base with diiron nonacarbonyl. Cyclometalation induced methyl migration, formation of imidoyl triironnonacarbonyl cluster, and hydrogenation of imine group are observed.

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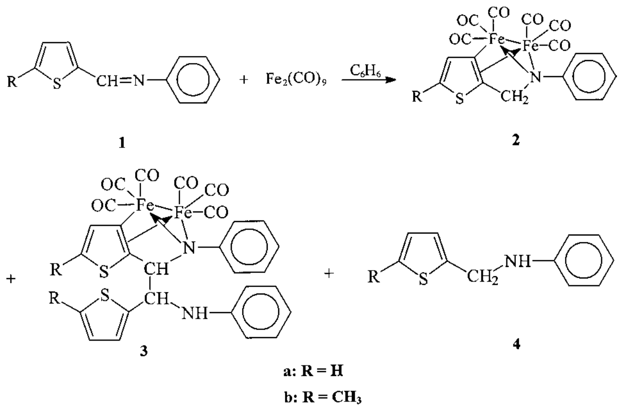
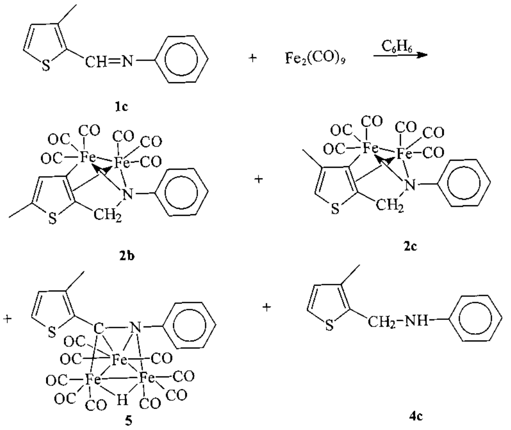
2. Results and discussion

The thienyl Schiff base *N*-(3-methyl-2-thienylmethylidene)aniline (**1c**) reacts with diiron nonacarbonyl in anhydrous benzene to give two isomeric cyclometalated diiron complexes, **2b** and **2c,** a triiron cluster, **5**, and an organic product, **4c,** as the major products (Scheme 2). Isomeric products **2b** and **2c** are unseparable by usual chromatography. Different reaction temperature led to the variation of product ratio between isomers **2b** and **2c** as described in Section 3**.** The product ratio **2b/2c** decreases from 1/1 at temperature above 30°C to 0.36/1 at 25°C, to 0.25/1 at 20°C, and to 0.18/1 at 15°C. When the reaction temperature was lowered down to 5°C, pure complex **2c** was obtained. No thermal interconversion of the two isomers was found after refluxing in benzene for 24 h.

The ^{1}H-NMR spectrum of complex **2c** shows the absence of the methine proton (resonance at δ 8.76 ppm in **1c**), and a singlet methylene resonance appears at δ 4.39 ppm. In the aromatic region, two multiplet appear at δ 7.32 and 7.15 ppm, the integrated intensities clearly show that only six protons are left. Subtracting all signals that characterize the complex **2c** from the spectrum of a mixture of **2b** and **2c** leave the spectrum of complex **2b** [6]. The IR spectrum of complex **2c** shows the absence of C=N stretching and the presence of three sharp and intense C=O stretches appearing at 2068, 2028, and 1988 cm^{-1}. The mass spectrum of **2c** shows the same spectral pattern as that of a mixture of **2b** and **2c**. Both cases show the same molecular weight and the complete loss of six COs ligands sequentially, in accordance with the formulated structures **2b** and **2c**.



Scheme 1.



Scheme 2.

A red prism crystal of **2c** was subjected to a single-crystal X-ray analysis. Crystal and data collection parameters are shown in Table 1. An ORTEP diagram of **2c** is shown in Fig. 1. Selected bond distances and bond angles are tabulated in Table 2. It is readily seen that C(2) of the thienyl ring is σ bonded to Fe(1) with a bond distance of 1.981(5) Å. C(1) and C(2) are bonded to Fe(2) with bond distances of 2.276(5) and 2.149(5) Å, respectively. Hence, Fe(2) is bonded to thiophene by the π bond between C(1) and C(2), and the bond distance between C(1) and C(2) is lengthened to 1.422(7) Å. The thienyl ring in the organic ligand serves as a three-electron donor and bridges the two iron centers. The bond distance from N(1) to C(6), 1.484(6) Å, is in the single bond range, while the bond distances to Fe(1) and Fe(2) are 1.981(4) and 2.003(4) Å, respectively. Therefore, the nitrogen atom acts as another

Table 1
Crystal and data collection parameters for compounds **2c** and **5**

Compound	**2c**	**5**
Formula	$C_{18}H_{11}NO_6Fe_2S$	$C_{21}H_{11}NO_9Fe_3S$
f_w	481	620
Cryst syst	Triclinic	Triclinic
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a (Å)	7.629(2)	9.281(2)
b (Å)	8.711(2)	9.318(1)
c (Å)	15.459(4)	14.457(3)
α (°)	100.37(2)	85.68(1)
β (°)	103.32(2)	87.24(2)
γ (°)	100.74(2)	77.08(1)
V (Å^3)	955.1(5)	1214.4(4)
Z	2	2
D_{calc} (g cm^{-3})	1.673	1.695
Cryst size (mm)	$0.33\times0.50\times0.58$	$0.33\times0.35\times0.38$
$2\theta_{max}$ (°)	50.1	50.1
Scan type	ω-2θ	ω-2θ
No. of reflns measd: total, unique	3622, 3382	4544, 4261
No. of obsd reflns ($I>3.00\sigma(I)$)	2513	2585
No. of variables	253	316
F_{000}	484.00	618.00
μ, (Mo–K$_\alpha$) (cm^{-1})	16.61	19.02
R	0.045	0.037
R_w	0.047	0.027

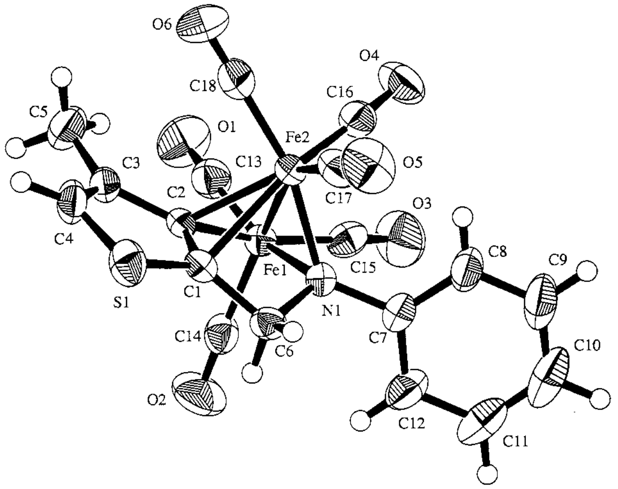


Fig. 1. ORTEP diagram of compound **2c** at the 50% probability level.

three-electron donor bridge in **2c** complex. An iron–iron distance of 2.471(1) Å is shorter than in normal diiron complexes [7] but is in accordance with other nitrogen-bridged diiron complexes [6,8]. The Fe(1)–N–Fe(2) angle is 76.6(2)° and Fe(1)–C(2)–Fe(2) is 73.4(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. Except for the position of the methyl group, the structure feature of complex **2c** closely resembles that of complex **2b**, as explicated in our previous report [6]. Both complexes **2b** and **2c** are analogous to that of nitrogen-containing organometallic complexes reported by Baikie and Mills [8a] and also bears some resemblance to $Fe_2(CO)_6$ complexes with bridging η^1:η^2-vinyl, furyl, and thienyl ligands reported by Seyferth [9].

Since the free Schiff base itself was stable to the reaction condition, the iron center must be responsible for the methyl migration leading to the formation of products **2b** and **2c**. A plausible explanation can be suggested as follows: upon coordination of the methine nitrogen of the 3-methylthienyl Schiff base to one of the iron centers, a cyclometalation-induced carbon–carbon bond cleavage occurs between the methyl group and the β-carbon of the thienyl ring to form a methyl–iron intermediate with a stable five-membered metalacycle. We tried to trap the presumed methyl-iron intermediate but without success. However the cleaved methyl group migrates back and attacks the β′- or α′-carbon of the thienyl ring, leading to the activation of the β′- or α′-hydrogen. Finally, the methine carbon becomes a methylene group by accepting the hydrogen that was removed from the β′- or α′-carbon and the nitrogen coordinates to another iron center concomitantly to give the product **2c** or **2b**. The methyl migration process might be similar to the iridium catalyzed ethyl migration reaction of 1,1-diethylcyclopentadiene reported by Crabtree et al. [2k]. In their case, the driving force is the formation of an ethylcyclopentadienyl–iridium–ethyl intermediate.

Table 2
Selected bond lengths (Å) and bond angles (°) of compound **2c**

Fe(1)–Fe(2)	2.471(1)	Fe(2)–C(1)	2.276(5)
Fe(2)–C(2)	2.149(5)	Fe(2)–N(1)	1.981(4)
Fe(1)–C(2)	1.981(5)	Fe(1)–N(1)	2.003(4)
C(1)–C(2)	1.422(7)	C(6)–N(1)	1.484(6)
Fe(1)–N(1)–Fe(2)	76.6(2)	Fe(1)–C(2)–Fe(2)	73.4(2)

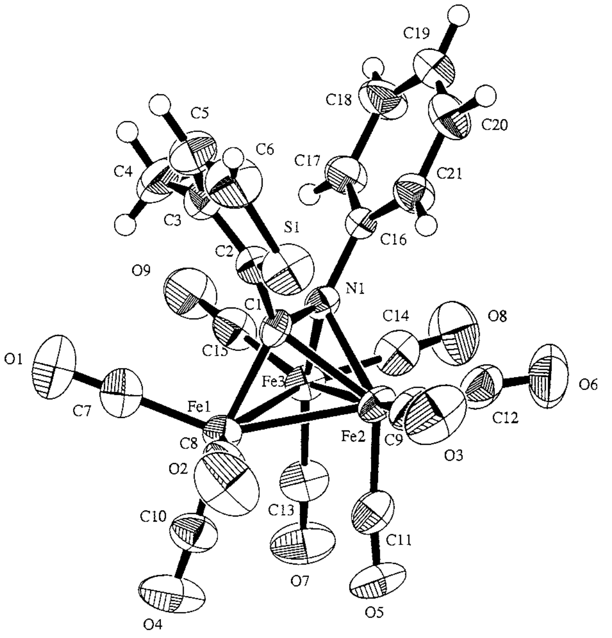


Fig. 2. ORTEP diagram of compound **5** at the 50% probability level.

The variation of the isomer ratio **2b**/**2c** with different reaction temperature might be attributed to the stability of the initial cyclometalated intermediate. At higher reaction temperature (above 30°C), the methyl group migrates back and attacks randomly on β′- and α′-carbon of the thienyl ring resulted to obtain **2b** and **2c** in equal quantity. At lower temperature (5°C), the methyl group selectively attacks the nearby β′-carbon and end up **2c** isomer as the sole product.

The molecular structure of compound **5**, determined by a single-crystal X-ray diffraction analysis, is shown in Fig. 2. Crystal and data collection parameters are tabulated in Table 1. Selected bond distances and bond angles are reported in Table 3. The crystal consists of discrete molecular units of HFe_3(3-methyl-2-thienyl–C=N–Ph)$(CO)_9$. All three iron interactions are within bonding distances (2.553(1), 2.532(1), and 2.739(1) Å) and define a nearly isosceles triangle. Each iron atom is also bonded to three terminal carbonyl ligands. Of these nine carbonyl ligands, three of the carbonyls extend axially below the triiron plane, four of the

Table 3
Selected bond lengths (Å) and bond angles (°) of compound **5**

Fe(1)–Fe(2)	2.553(1)	Fe(1)–Fe(3)	2.739(1)
Fe(2)–Fe(3)	2.532(1)	Fe(3)–N(1)	1.960(4)
Fe(2)–C(1)	2.070(5)	Fe(2)–N(1)	2.021(4)
Fe(1)–C(1) 1.931(5) C(1)–N(1) 1.394(6)	1.931(5)	C(1)–N(1)	1.394(6)
Fe(2)–Fe(1)–Fe(3)	57.03(3)	Fe(1)–Fe(3)–Fe(2)	57.80(3)
Fe(1)–Fe(2)–Fe(3)	65.17(3)	Fe(1)–C(1)–Fe(2)	79.2(2)
Fe(1)–C(1)–N(1)	112.5(3)	N(1)–C(1)–C(2)	117.4(5)
Fe(1)–C(1)–C(2)	127.4(4)	Fe(2)–C(1)–C(2)	134.1(4)
Fe(2)–C(1)–N(1)	68.2(3)	Fe(2)–N(1)–Fe(3)	79.0(1)
Fe(2)–N(1)–C(1)	72.0(3)	Fe(3)–N(1)–C(1)	107.9(3)
C(1)–N(1)–C(16)	124.3(4)	Fe(2)–N(1)–C(16)	124.6(3)
Fe(3)–N(1)–(16)	126.6(3)	Fe(1)–Fe(3)–N(1)	70.3(1)
Fe(2)–Fe(3)–N(1)	51.6(1)	Fe(1)–Fe(2)–C(1)	48.0(1)
Fe(1)–Fe(2)–N(1)	73.8(1)	Fe(2)–Fe(1)–C(1)	52.8(1)
Fe(3)–Fe(1)–C(1)	69.1(1)	Fe(3)–Fe(2)–N(1)	49.4(1)
Fe(3)–Fe(2)–C(1)	72.0(1)		

carbonyls are equatorially disposed, while the remaining two carbonyls intersect the triiron plane at an angle of ca. 30° (–C(7) 34.5°; –C(15) 27.2°). The open face of the $Fe_3(CO)_9$ cluster is capped by the triply bridging imidoyl (–C=N–) group. The hydride ligand, which is not shown in Fig. 2, bridges Fe(1) and Fe(3) centers with the longest Fe–Fe separation. The bonding of the triply bridging imidoyl group to the metal triangle could be described as two σ bonds, Fe(1)–C(1) = 1.931(5) and Fe(3)–N(1) = 1.960(4) Å, and a π bond, Fe(2)–C(1) = 2.070(5) and Fe(2)–N(1) = 2.021(4) Å. There is a slight twist about the C–N bond which is correlated with an asymmetry in the bonding of the bridging imidoyl group. The C–N bond length of 1.394(6) Å in the –C=N– group is between that of a C–N single bond (1.47 Å) and of a C=N double bond (1.28 Å) [10]. The lengthening of the C=N double bond upon π coordination is attributed to the σ donation and back π bonding of the highly conjugated imidoyl ligand. This C–N distance is longer than the corresponding distance of 1.344(2) Å observed in $HFe_3(MeC{=}NH)(CO)_9$ [11] but is shorter than that of 1.415(11) Å found in $HOs_3(HC{=}NPh)(CO)_9$ [12]. The metal–metal distance of the hydrogen-bridged metal–metal bond which is also bridged by the hetero-π group could in part be responsible for this difference. The fact that the disappearance of the methine proton resonance and the appearance of a singlet resonance at -26.29 ppm in the ^{1}H-NMR spectrum of complex **5** indicates that the hydrogen of methine is removed and a bridging metal hydride is formed. In its IR spectrum, the C–N stretching frequency of 1342 cm^{-1} (relative to the corresponding band at 1616 cm^{-1} in the free Schiff base) is in agreement with the C–N bond length as described above. There are four sharp and intense C=O stretches appearing at 2088, 2052, 2016 and 1972 cm^{-1}. The mass spectrum also shows the complete loss of nine COs successively, and the molecular ion peak at m/z 622 consists with the formulated structure. The structure of complex **5** is analogous to that of triironnonacarbonyl complex with a triply bridging acetimidoyl ligand and an η^2-hydride reported by Kaesz et al. [11].

Complex **5** is stable in its solid state at room temperature. However, prolonged stirring of the complex **5** in n-hexane or in benzene at room temperature for several days leads to the decomposition of the complex. Two organic products, the original Schiff base **1c** and compound **4c**, were recovered with a ratio of 2.5:1. Decomposition reaction that proceeded in a deuterated benzene gives a similar result and no any deuterated organic product was found. At this stage, we have no answer regarding to the source of hydrogen that leads to the product **4c**.

The absence of a methine proton but the presence of a broad amine resonance and a doublet methylene resonance at δ 5.25 and δ 4.40 ppm, respectively, in the ^{1}H-NMR spectrum indicate that compound **4c** is a hydrogenated product of the original Schiff base **1c**. The elemental analysis and other spectral data including the presence of an NH stretching at 3421 cm^{-1} and the absence of a C=N stretching in its IR spectrum confirm the structure of **4c**. The hydrogenation of a CN double bond normally requires more extreme conditions, and there is no doubt that compound **4c** arises as a result of coordination of **1c** to an iron carbonyl.

3. Experimental

Diiron nonacarbonyl was prepared by photolysis of iron pentacarbonyl (Aldrich) in glacial acetic acid [13]. Solvents were dried (sodium/benzophenone, P_4O_{10}) and distilled under nitrogen prior to use. All other chemicals were reagent grade and used without purification. The NMR spectra were recorded on a Varian VXR-300

NMR spectrometer (^{1}H, 299.95 MHz; ^{13}C, 75.43 MHz). Chemical shifts were referenced to TMS, and deuterated acetone (Janssen) was used as a solvent and as a second 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 from *n*-hexane solution. 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-(3-methyl-2-thienylmethylidene)-aniline (**1c**)*

The synthesis of Schiff base employed the normal procedure of condensation in alcohol solution [14]. Equimolar quantities of 3-methyl-2-thiophenecarboxaldehyde (Aldrich, 5.0 g, 40 mmol) and aniline (E. Merck, 4.5 g, 40 mmol) were heated at reflux in ethanol (E. Merck, 100 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 **1c** was obtained (7.22 g; 90% yield) at 185°C. ^{1}H-NMR δ 8.75 (s,1H), 7.58 (d, $J = 5.1$ Hz, 1H), 7.39 (t, $J = 8.1$ Hz, 2H), 7.21(m, 3H), 7.00 (d, $J = 4.8$ Hz, 1H), 2.50 (s 3H). ^{13}C-NMR δ 152.9, 143.56, 132.1, 130.6, 130.0, 126.6, 122.0, 14.0. IR (CHCl$_3$) $\nu_{\mathrm{C=N}}$: 1616 cm^{-1}. MS (EI): *m*/*z* 201(M$^+$), 200 (M$^+$ H). Anal. Calc. for $C_{12}H_{11}NS$: C, 71.60; H, 5.51; N, 6.96. Found: C, 71.53; H, 5.53; N, 6.98.

*3.2. Reaction of **1c** with Fe$_2$(CO)$_9$ in benzene to give [μ-N-(((2,3-η^1;η^2)-5-methyl-2-thienyl)methyl)-η^1:η^1-(N)-anilino]hexacarbonyldiiron (**2b**), [μ-N-(((2,3-η^1;η^2)-4-methyl-2-thienyl)methyl)-η^1:η^1-(N)-anilino]hexacarbonyldiiron (**2c**), [μ$_3$- ((N-1-η)-phenyl-(3-methyl-2-thienyl)-formidoyl-N,C)]nonacarbonyl-μ-hydrido-triangulo-triiron (**5**), and N-((3-methyl-2-thienyl)-methyl)aniline (**4c**)*

A total of 6.0 mmol of compound **1c** in 30 ml of anhydrous benzene was added gradually to a 70 ml of anhydrous benzene solution containing 7.2 mmol of Fe$_2$(CO)$_9$ in the dark under nitrogen, and the reaction mixture was stirred for 20 h at 25°C. The residue was filtered and the solvent was removed under reduced pressure. The residue was separated by a 3.5 cm × 40 cm height column (230–400 mesh ASTM silica gel (E. Merck)) with ethyl acetate/*n*-hexane (1:20) as an eluent. The red band produced 418 mg of a mixture of compounds **2b** and **2c** (15% yield with **2b**/**2c** = 0.36/1). The deep-red band produced 1347 mg of compound **5** (36% yield). The orange band collected was further purified by a 20 cm × 20 cm × 0.25 mm TLC plate (silica gel 60(MN)) with ethyl acetate/*n*-hexane (1/10) as an eluent to give 181 mg of compound **4c** (15% yield). Substantial amounts of Fe$_3$(CO)$_{12}$ and trace amount of *N*-((4-methyl-2-thienyl)methyl)aniline and *N*-((5-methyl-2-thienyl)methyl)aniline also were collected.

Product ratio **2b**/**2c** was found to be reaction temperature dependent. If the reaction was proceeded at 30–50°C, product ratio **2b**/**2c** rises to 1/1 (products yield: at 30°C, compound **2a** + **2b**, 16%; compound **5**, 35%; compound **4c**, 15%; at 50°C, compound **2a** + **2b**, 22%; compound **5**, 36%; compound **4c**, 15%). Product ratio **2b**/**2c** decreases to 0.25 at 20°C and to 0.18 at 15°C. At 5°C, compound **2c** is the sole isomeric product (products yield: compound **2c**, 12%; compound **5**, 32%; compound **4c**, 13%). Reaction temperature higher than 50°C will cause the decrease of the yield of products **2a** and **2b.**

Compound **2c**: m.p. 105 ~ 106°C. ^{1}H-NMR: δ 7.29 (m, 3H), 7.15 (m, 3H), 4.39 (s, 2H), 2.43(s,3H). ^{13}C-NMR: δ 211.3, 161.8, 159.5, 150.2, 129.9, 127.9, 126.8, 124.2, 115.2, 73.9, 19.2. IR(CHCl$_3$) ν_{CO}: 2068, 2028, 1988 cm^{-1}. MS(EI): *m*/*e* 481 (M$^+$), 453 (M$^+$ − CO), 425 (M$^+$ − 2CO), 397 (M$^+$ − 3CO), 369 (M$^+$ − 4CO), 341 (M$^+$ − 5CO), 313 (M$^+$ − 6CO), 201 (L$^+$). Anal. Calc. for $Fe_2C_{18}H_{11}NSO_6$: C, 44.91; H, 2.28; N, 2.91. Found: C, 44.78; H, 2.30; N, 2.91. Compound **5**: m.p. 134 ~ 135°C. ^{1}H-NMR: δ 7.30 (d, $J = 4.8$ Hz, 1H), 7.23 (m, 2H), 7.16 (m, 3H), 6.59 (d, $J = 4.8$ Hz, 1H), 1.77 (s, 3H), −26.29 (s, 1H). ^{13}C-NMR: δ 210.0, 156.1, 147.4, 138.2, 133.6, 131.1, 129.0, 128.6, 127.3, 125.5, 16.4. IR (CHCl$_3$) ν_{CN}: 1342 cm^{-1}, ν_{CO}: 2088, 2052, 2016 and 1972 cm^{-1}. MS(EI): *m*/*e* 622 (M$^+$ + 1), 621 (M$^+$), 593 (M$^+$ − CO), 565 (M$^+$ − 2CO), 537 (M$^+$ − 3CO), 509 (M$^+$ − 4CO), 481 (M$^+$ − 5CO), 453 (M$^+$ − 6CO), 425 (M$^+$ − 7CO), 397 (M$^-$8CO),369 (M$^+$ − 9CO), 201 (L$^+$), 200 (L$^+$ − 1). Anal. Calc. for $Fe_3C_{21}H_{11}NSO_9$: C, 40.58; H, 1.77; N, 2.25. Found: C, 40.48; H, 1.79; N, 2.27. Compound **4c**: ^{1}H-NMR: δ 7.17 (d, $J = 4.8$ Hz, 1H), 7.10 (t, $J = 8.1$ Hz, 2H), 6.83 (d, $J = 5.1$ Hz, 1H), 6.78 (d, $J = 7.8$ Hz, 2H), 6.50 (t, $J = 7.2$ Hz, 1H), 5.42 (broad, 1H), 4.40 (d, $J = 4.2$ Hz, 2H), 2.24 (s, 3H). ^{13}C-NMR: δ 149.5, 137.7, 134.2, 130.9, 129.7, 123.4, 117.7, 113.6, 41.9, 13.7. MS(EI): *m*/*z* 203 (M$^+$). Anal. Calc. for $C_{12}H_{13}NS$: C, 70.89; H, 6.44; N, 6.89. Found: C, 70.78; H, 6.44; N, 6.86.

*3.3. Decomposition of [μ$_3$-((N-1-η)-phenyl-(3-methyl-2-thienyl)formidoyl-N,C)] nonacarbonyl-μ-hydrido-triangulo-triiron (**5**)*

The title complex was stirred in a *n*-hexane or benzene solution at room temperature for several days. The reaction mixture was filtered to remove the insoluble precipitate and the filtrate was dried and separated to give compounds **1c** and **4c** with a ratio of 2.5: 1. A similar result was obtained if the decomposition reaction was carried out in a deuterated benzene solution.

4. Supplementary material

Text of the X-ray crystal structure experimental details, tables of atomic coordinates, anisotropic displacement parameters, and bond distances as well as angles of **2c** and **5** (34 pages) are available. Ordering information is given on any current masthead page.

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