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Endo and *exo* cyclometallated iron carbonyl complexes derived from *N*-(*N*′-methyl-2-pyrrolylmethylidene)-2-thienylmethylamine

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Abstract

The reaction of *N*-(*N*′-methyl-2-pyrrolylmethylidene)-2-thienylmethylamine (**1**) with $Fe_2(CO)_9$ in refluxing toluene gives *endo* cyclometallated iron carbonyl complexes **2** and **5**, *exo* cyclometallated iron carbonyl complex **3**, and unexpected iron carbonyl complex **4**. Complexes **2**, **3**, and **5** are geometric isomers. Complex **5** differs from complex **2** in the switch of the original substituent from α to β position of the pyrrolyl ring, and the pyrrolyl ring bridges to the diiron centers in μ-(3,2-η^1:η^2) coordination mode in stead of μ-(2,3-η^1:η^2). In complex **4**, the pyrrolyl moiety of the original ligand **1** has been displaced by a thienyl group, which comes from the same ligand. Single crystals of **2**, **3**, and **5** were subjected to the X-ray diffraction analysis. The major product **2** undergoes: (i) thermolysis to recover the original ligand **1**; (ii) reduction to form a hydrogenation product, **6**, of the original ligand; (iii) substitution to form a monophosphine-substituted complex **7**; (iv) chemical as well as electrochemical oxidation to produce a carbonylation product, γ-butyrolactam **8**.

Keywords: *Endo* cyclometallation; *Exo* cyclometallation; Iron carbonyl complex; Carbonylation; γ-butyrolactam

1. Introduction

One of the prominent challenges in organometallic chemistry in past decades has been the transition-metal mediated activation of C–H bond. Cyclometallation 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 metallacycle [2]. In systems, where there is a possibility of choice between several modes of metallation, five-membered metallacyclic complexes are always the major compounds obtained [3]. It is also known that, Schiff bases have a strong tendency to give *endo* cyclometallated 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 benzyl ring [1f,1i,1j,4b]. Usually, the tendency to proceed *endo* cyclometallation 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* cyclometallation was therefore observed.

We report here, the interesting results from the action of diiron nonacarbonyl on *N*-(*N*-methyl-2-pyrrolylmethylidene)-2-thienylmethylamine (**1**). During the course of reaction, we observe products resulting from *endo* cyclometallation followed by 1,3-hydrogen shift (**2**), *exo* cyclometallation followed by 1,5-hydrogen shift (**3**), substitution of the *N*-methyl-2-pyrrolylmethyl group

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of *exo* cyclometallated intermediate by a thienylmethyl group (**4**), and *endo* cyclometallation which involved a β to α azomethine group transformation (**5**).

2. Results and discussion

The pyrrolyl Schiff bases *N*-(*N*-methyl-2-pyrrolylmethylidene)-2-thienylmethylamine (**1**), were prepared in high yields by condensation of *N*-methyl-2-pyrrolecarboxaldehyde with 2-thiophenemethylamine in methanol and was fully characterized spectrally.

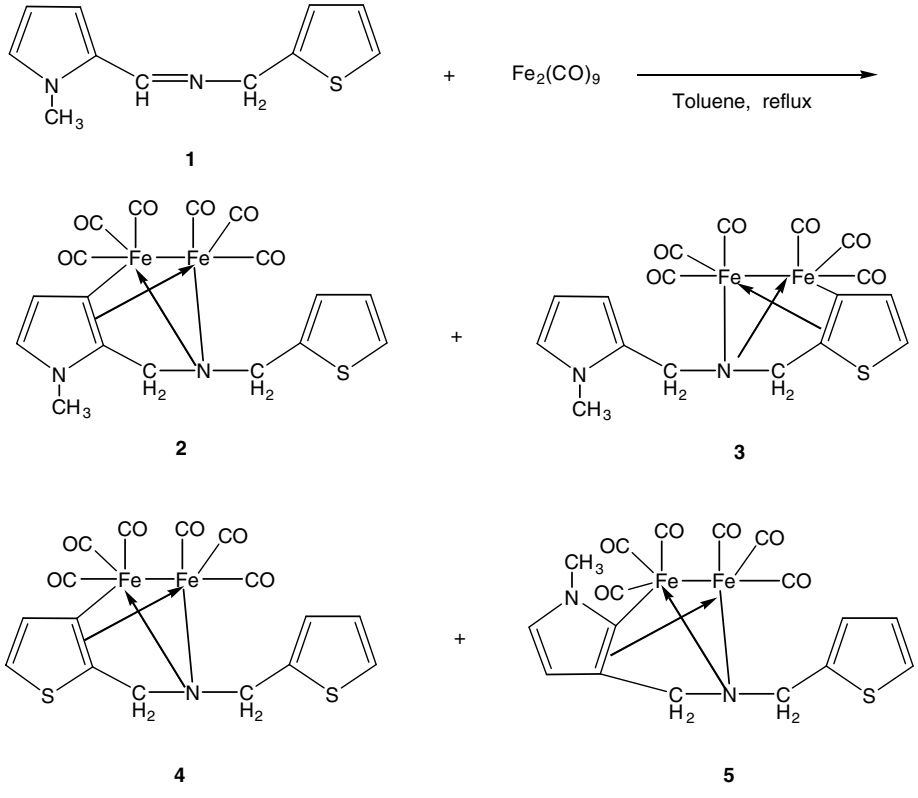
Each thienyl or pyrrolyl proton in the ligand can be easily assigned from the ^{1}H NMR spectrum according to its specific position and the characteristic coupling constant(s). The ligand is further identified by the presence of a singlet methine proton at δ 8.24 ppm and another singlet methylene resonance at 4.84 ppm. Ligand **1** also shows a characteristic C=N stretching absorption at 1640 cm^{-1} in its IR spectrum and shows a molecular ion peak in its mass spectrum.

2.1. Complexes formation and characterization

The pyrrolyl schiff base **1** reacted with $Fe_2(CO)_9$ in refluxing toluene for 12 h to give off a major product, **2** (46% yield), and three minor products, **3** (9%), **4** (8%), and **5** (5%), as formulated in Scheme 1. All four products from the reaction are cyclometallated diiron hexacarbonyl complexes, in which the complexes **2**, **3**, and **5** are geometric isomers.

If the reaction was conducted in benzene, either at room temperature or at reflux, only iron carbonyl complex **2** was obtained with a much lower product yield (12% and 27%, respectively). Obviously, higher temperature would increase the rate of complex **2** formation but solvent effect drives the formations of other three minor products.

The ^{1}H NMR spectral data of complexes **2**–**5** are shown in the Section 3. The thienyl as well as pyrrolyl protons in each complex can be easily assigned according to their specific chemical shift and characteristic coupling constants. The most significant feature of the ^{1}H NMR spectrum of each of complexes is the disappearance of methine proton resonance, which appears at δ 8.28 ppm in free ligand **1**, and the missing of either one β-thienyl (**3** and **4**) or one β-pyrrolyl proton (**2** and **5**) relative to the free ligand **1**. However, a new singlet resonance representing a methylene group appears at δ 4.3–3.7 ppm in addition to the up-field shifted vested methylene signal, indicating a hydrogen has been transferred through an intramolecular hydrogen shift from the β-carbon of the pyrrole (**2** and **5**) or thiophene (**3** and **4**) ring towards the methine carbon during the course of cyclometallation, thus producing a new methylene group. The lack of diastereotopicity of the methyl-



Scheme 1. ORTEP diagram of complex **5** at the 30% probability level.

ene protons in the azametallacycle of these complexes indicates that a fluxional process, the so-called "wind-shield-wiper type oscillation", of the ligand might occur in these four complexes [6].

In their IR spectra, while the C═N stretching is absent, there are sharp and intense CO stretches appearing at 2066–1963 cm^{-1}, indicating the presence of terminal carbonyl ligands on metal center. The mass spectra of four products all show their own specific molecular ion peak (M^+), six fragments corresponding to the sequential loss of six COs, and the ligand ion peak, in accordance with the formulated structures.

The molecular structures of complexes **2**, **3**, and **5**, as determined by means of single-crystal X-ray diffraction analysis, are shown in Figs. 1–3, respectively. Their crystal and data collection parameters are tabulated in Table 1 and selected bond lengths and bond angles are summarized in Table 2.

Regarding the *endo* cyclometallated complex **2**, it is readily seen from Fig. 1 that C(3) of the pyrrolyl ring is σ bonded to Fe(2) with a bond distance of 1.977(6) Å. C(2) and C(3) are π bonded to Fe(1) with bond distances of 2.447(6) and 2.151(6) Å, respectively, and the bond distance between C(2) and C(3) is lengthened to 1.401(10) Å. The pyrrolyl ring serves as a three-electron donor and bridges the two iron centers. The bond distance from N(1) to C(1), 1.487(8) Å, is in the single bond range and is comparable to that of N(1)–C(7) distance, 1.486(9) Å. The nitrogen atom, N(1), acts as another three-electron donor bridge and the bond distances to Fe(1) and Fe(2) are 1.958(5) and 1.997(6) Å, respectively. An iron–iron distance of 2.4262(13) Å is shorter than usual for bridged diiron complexes [7]. The Fe(1)–N(1)–Fe(2) angle is 75.68(20)° and Fe(1)–C(3)–Fe(2) angle is 71.86(20)°. The compression of these two angles from the tetrahedral value is a result of the ligand con-

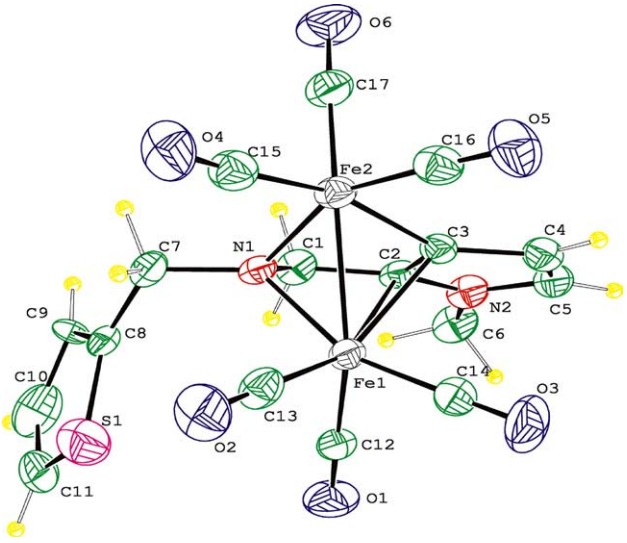


Fig. 1. ORTEP diagram of complex **2** at the 30% probability level.

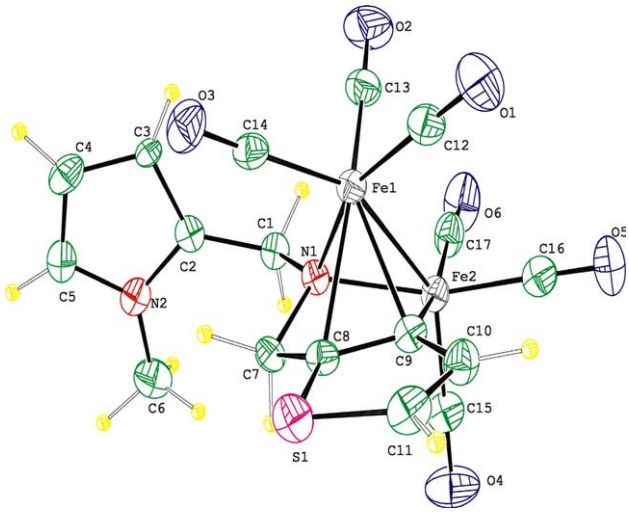


Fig. 2. ORTEP diagram of complex **3** at the 30% probability level.

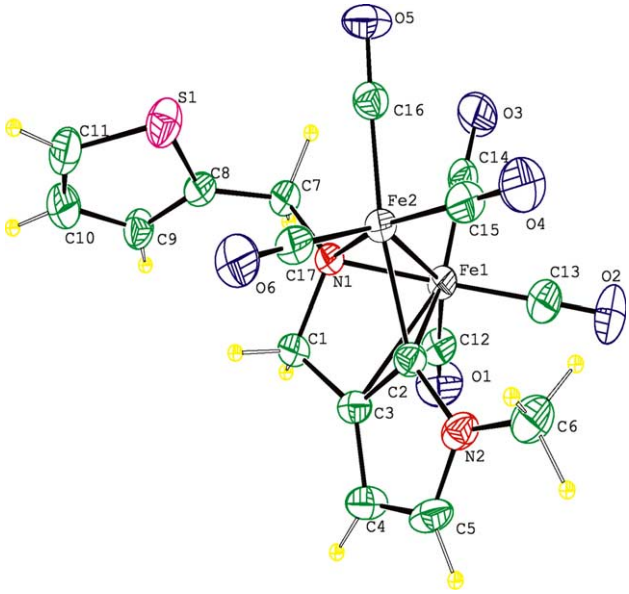


Fig. 3. ORTEP diagram of complex **5** at the 30% probability level.

strains of double bridging, which also brings about the shorter iron–iron distance.

The molecular structure of complex **3**, as shown in Fig. 2, clearly shows that the compound is an *exo* cyclometallated product in which C(9) of the thienyl ring is σ bonded to Fe(2) with a bond distance of 1.970(5) Å. C(9) and C(8) are π bonded to Fe(1) with bond distances of 2.169(5) and 2.341(5) Å, respectively, and the bond distance between C(8) and C(9) is lengthened to 1.383(8) Å. The thienyl ring acts as a three-electron donor and bridges the two iron centers. The bond distances from N(1) to C(1) and C(7) are 1.486(7) and 1.484(6) Å, respectively, and both are in the single bond range. The N(1) atom also serves as another three-electron bridge and the bond distances from N(1) to Fe(1) and Fe(2)

Table 1
Crystal and data collection parameters for compounds **2**, **3**, and **5**

Compound	**2**	**3**	**5**
Formula	$C_{17}H_{12}Fe_2N_2O_6S$	$C_{17}H_{12}Fe_2N_2O_6S$	$C_{17}H_{12}Fe_2N_2O_6S$
Formula weight	484.04	484.06	484.04
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$
Unit cell dimensions			
a (Å)	7.7944(11)	7.9844(25)	7.983(3)
b (Å)	11.8488(13)	10.2069(19)	11.614(4)
c (Å)	20.5274(18)	11.869(3)	20.735(10)
α (°)		98.529(19)	
β (°)	91.319(9)	95.226(25)	93.61(4)
γ (°)		94.989(21)	
Volume (Å^3)	1939.1(4)	974.6(4)	1918.6(13)
Z	4	2	4
D_{calc} (g/cm^3)	1.658	1.696	1.676
Crystal size (mm)	$0.30 \times 0.12 \times 0.10$	$0.45 \times 0.25 \times 0.20$	$0.60 \times 0.50 \times 0.36$
Temperature (K)	293	293	293
$2\theta_{max}$(°)	49.8	49.8	49.8
Scan type	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$
No. of reflections measured			
Total unique	3507, 3406	3499, 3324	3477, 3376
No. of observed reflections	2709 ($I > 2.00\sigma(I)$)	2876 ($I > 2.00\sigma(I)$)	2952 ($I > 2.00\sigma(I)$)
No. of variables	254	253	254
F_{000}	976	488	976
μ (Mo Kα) (cm^{-1})	16.4	16.8	16.6
R_1	0.046	0.046	0.038
R_w	0.049	0.053	0.040

are 1.971(4) and 1.982(4) Å, respectively. The iron–iron distance, 2.4370(2) Å, is longer than that in complex **2**. The Fe(1)–N(1)–Fe(2) bond angle, 76.13(15)°, and Fe(1)–C(9)–F(2) angle, 71.95(17)°, are very closely resemble that of complex **2** described above. It seems that, after the coordination of the azomethine nitrogen to one of the iron centers, a C–H activation occurs at the β-carbon of the thienyl ring instead of pyrrolyl ring to form a five-membered *exo* metallacycle and then the methine carbon adopts the hydrogen originated from the β-carbon of the thienyl ring to form the complex **5.** This is a consecutive process of coordination, *exo* cyclometallation, and 1,5-hydrogen shift.

The molecular structure of complex **5**, as shown in Fig. 3, is similar to that of complex **2**. However, the pyrrolyl ring in **5** is arranged up-side-down relative to that in **2** and the α-substituted group is found to migrate to the β-position of the pyrrolyl ring. The α-carbon, C(2), of the pyrrolyl ring, instead of β-carbon, C(3), in that of complex **2**, is σ bonded to Fe(2) with a bond distance of 1.977(6) Å, which is about same value as that of Fe(2)–C(3) bond distance in **2**. Other corresponding structure parameters in complex **5**, as shown in Table 2, closely resemble that in complex **2**. Since the free Shiff base itself was stable to the blank experiment, the iron center must be responsible for the migration of the substituent from the β- to the α-position of the pyrrolyl ring and led to the formation of complex **5**. At this stage, we do not have any idea concerning with the transformation.

2.2. Formation of complex *4*

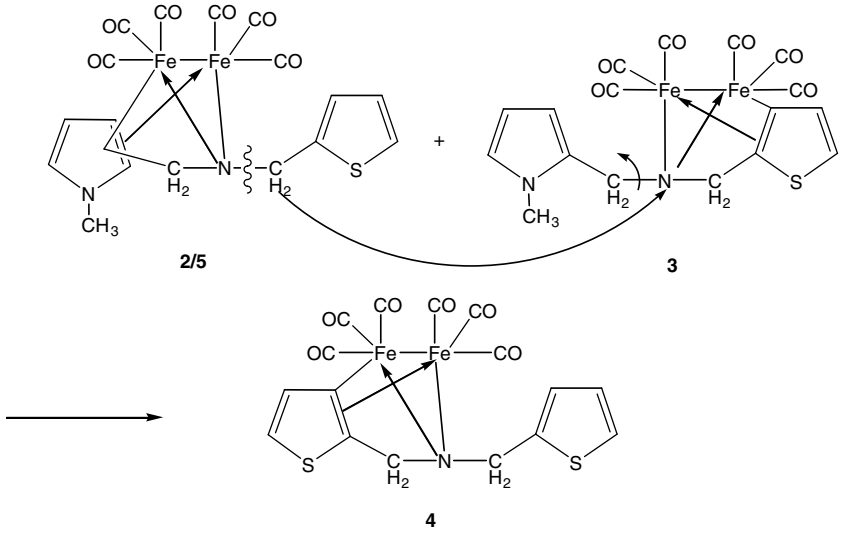
Complex **4** had been obtained from the reaction of *N*-(2-thienylmethylidene)-2-thienylmethylamine with $Fe_2(CO)_9$ and its molecular structure had been confirmed by single crystal X-ray diffraction analysis [6]. It is an unexpected product from this reaction. Although the original Schiff base contains a *N*-methylpyrroly unit, it is interesting to find that the *N*-methylpyrrolyl group of the original Schiff base has been displaced with a thienyl ring in **4**. The Schiff base in the complex has therefore undergone a chemical transformation. Since the Schiff base itself is very thermally stable, obviously, a C–N bond cleavage or a C–C bond cleavage must be involved during 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 C–N bond cleavage occurs on **2** and **3**. The thienyl group that was cleaved from *endo* cyclometallated product **2** might substitute the *N*-methyl-2-pyrrolylmethyl moiety of the *exo* cyclometallated product **3**, thus directed to the formation of complex **4**.

It is interesting to find that, if the reaction time for the reaction of Schiff base **1** with $Fe_2(CO)_9$ was prolonged

Table 2
Selected bond lengths (Å) and bond angles (°) for complexes **2**, **3**, and **5**

Complex **2**			
Fe(1)–Fe(2)	2.4262(13)	Fe(1)–N(1)	1.958(5)
Fe(1)–C(2)	2.447(6)	Fe(2)–N(1)	1.997(6)
Fe(1)–C(3)	2.151(6)	Fe(2)–C(3)	1.977(6)
N(1)–C(1)	1.487(8)	C(2)–C(3)	1.401(10)
N(1)–C(7)	1.486(9)	C(4)–C(5)	1.345(11)
Fe(2)–Fe(1)–N(1)	52.88(16)	Fe(2)–Fe(1)–C(2)	70.57(15)
Fe(2)–Fe(1)–C(3)	50.73(17)	N(1)–Fe(1)–C(2)	60.59(22)
N(1)–Fe(1)–C(3)	74.31(24)	C(2)–Fe(1)–C(3)	34.7(3)
Fe(1)–Fe(2)–N(1)	51.43(14)	Fe(1)–Fe(2)–C(3)	57.42(18)
N(1)–Fe(2)–C(3)	77.5(3)	Fe(1)–N(1)–Fe(2)	75.68(20)
Fe(1)–N(1)–C(1)	103.2(4)	Fe(1)–N(1)–C(7)	127.8(4)
Fe(2)–N(1)–C(1)	113.1(4)	Fe(2)–N(1)–C(7)	120.5(4)
C(1)–N(1)–C(7)	111.6(5)	N(1)–C(1)–C(2)	99.3(5)
Fe(1)–C(2)–C(1)	83.6(4)	Fe(1)–C(2)–C(3)	61.0(3)
C(1)–C(2)–C(3)	119.5(6)	Fe(1)–C(3)–Fe(2)	71.86(20)
Fe(1)–C(3)–C(2)	84.3(4)	Fe(2)–C(3)–C(2)	111.8(5)
Complex **3**			
Fe(1)–Fe(2)	2.4370(13)	Fe(1)–N(1)	1.971(4)
Fe(1)–C(8)	2.341(5)	Fe(2)–N(1)	1.982(4)
Fe(1)–C(9)	2.169(5)	Fe(2)–C(9)	1.970(5)
N(1)–C(1)	1.486(7)	C(8)–C(9)	1.383(8)
N(1)–C(7)	1.484(6)	C(10)–C(11)	1.331(8)
Fe(2)–Fe(1)–N(1)	52.14(12)	Fe(2)–Fe(1)–C(8)	71.69(13)
Fe(2)–Fe(1)–C(9)	50.22(14)	N(1)–Fe(1)–C(8)	62.48(17)
N(1)–Fe(1)–C(9)	74.35(19)	C(8)–Fe(1)–C(9)	34.45(19)
Fe(1)–Fe(2)–N(1)	51.73(12)	Fe(1)–Fe(2)–C(9)	57.82(15)
N(1)–Fe(2)–C(9)	78.75(19)	Fe(1)–N(1)–Fe(2)	76.13(15)
Fe(1)–N(1)–C(1)	127.1(3)	Fe(1)–N(1)–C(7)	100.4(3)
Fe(2)–N(1)–C(1)	121.8(3)	Fe(2)–N(1)–C(7)	112.5(3)
C(1)–N(1)–C(7)	113.1(4)	N(1)–C(7)–C(8)	99.0(4)
Fe(1)–C(8)–C(7)	85.5(3)	Fe(1)–C(8)–C(9)	65.5(3)
C(7)–C(8)–C(9)	119.1(4)	Fe(1)–C(9)–Fe(2)	71.95(17)
Fe(1)–C(9)–C(8)	79.1(3)	Fe(2)–C(9)–C(8)	112.0(4)
Complex **5**			
Fe(1)–Fe(2)	2.4227(12)	Fe(1)–N(1)	1.971(3)
Fe(1)–C(2)	2.122(4)	Fe(2)–N(1)	1.996(3)
Fe(1)–C(3)	2.534(4)	Fe(2)–C(2)	1.976(4)
N(1)–C(1)	1.476(5)	C(2)–C(3)	1.382(6)
N(1)–C(7)	1.474(5)	C(4)–C(5)	1.364(8)
Fe(2)–Fe(1)–N(1)	52.84(9)	Fe(2)–Fe(1)–C(2)	51.03(11)
Fe(2)–Fe(1)–C(3)	70.13(14)	N(1)–Fe(1)–C(2)	73.05(14)
N(1)–Fe(1)–C(3)	60.00(14)	C(2)–Fe(1)–C(3)	33.05(15)
Fe(1)–Fe(2)–N(1)	51.89(9)	Fe(1)–Fe(2)–C(2)	56.58(12)
N(1)–Fe(2)–C(2)	75.74(15)	Fe(1)–N(1)–Fe(2)	75.27(12)
Fe(1)–N(1)–C(1)	103.76(23)	Fe(1)–N(1)–C(7)	123.98(23)
Fe(2)–N(1)–C(1)	113.03(23)	Fe(2)–N(1)–C(7)	124.86(24)
C(1)–N(1)–C(7)	110.6(3)	N(1)–C(1)–C(3)	101.9(3)
Fe(1)–C(2)–C(3)	90.1(3)	Fe(1)–C(3)–C(1)	80.9(3)
C(1)–C(3)–C(2)	115.5(3)	Fe(1)–C(2)–Fe(2)	72.38(13)
Fe(1)–C(3)–C(2)	56.9(34)	Fe(2)–C(2)–C(3)	114.9(3)

from 12 to 24 h in refluxing toluene, only **2** and **4** two complex products were isolated. While the yield of product **4** increases to 17%, the yield of **2** was found decreases to 41%. The increment of 9% for product **4** is exactly the amount of disappeared **3** and is about the sum of the decrement of product **2** and the amount of disappeared **5**. On the other hand, if the reaction was stopped after six hours of reaction under the same reaction condition, 32% of complex **2,** 4% of complex **3,** and 3% of complex **5** were obtained accompanying with 10% of complex **4**. Therefore, the formation of product **3** might be tentatively proposed to follow the underlying process.



There are two potential sites, the β-position of pyrrolyl ring and the β-position of thienyl ring, in the Schiff base **1** that might involve in the cyclometallation and leads to the formation of *endo* and *exo* five-membered metallacycle. The products and yields distribution clearly show that the C–H activation that occurs at the β-position of pyrrolyl ring, which directs to the *endo* cyclometallation, is relatively more favorable than that of thienyl ring (with ~77/23 ratio). The minor *exo* cyclometallated intermediate **3** thus formed might react further with excess amount of *endo* cyclometallated product **2** (product **5** might also be involved) and led to the formation of net product **4**. A reaction of equimolar quantities of complex **2** and complex **3** was conducted under exactly the same reaction condition. More than 90% of complex **4**, 78% of *N*-methyl-2-methylpyrrole, and 73% of *N*-methyl-2-(aminomethyl)-pyrrole were obtained and no thienyl-contained complex was found, confirming the substitution process suggested.

2.3. Electrochemical properties of complexes 2–5

Cyclic voltammetry experiments on complexes **2**–**5** showed a well-defined cathodic wave with a peak potential of 0.75, 0.94, 0.94, and 0.74 V vs. Ag–AgCl electrode, respectively, at 100 mV/s sweep rate. The maximum currents are directly proportional to the square root of the sweep rate in the investigated range of 50-800 mV/s. No reduction wave in the reverse cathodic sweep was observed, demonstrating a totally irreversible overall process [8]. The voltammetry curve is consistent with an E_rC_i mechanism [8a,d], i.e., heterogeneous electron transfer followed by an irreversible chemical reaction.

2.4. Reactions of complex 2

Thermolysis of complex **2** in a refluxing *n*-heptane, acetonitrile, or toluene solution led to the decomposition of the complex and the recovery of the original Schiff base **1** in more than 80% after 48 h. If the reaction was proceeded in a deuterated solvent such as d_8-toluene or d_3-acetonitrile, similar result was obtained and there was no deuterium atom attached Schiff base **1** observed. This is a reverse process of the consecutive reactions of coordination, cyclometallation and 1,3-hydrogen shift. Hydrogen from the inner methylene group transferred back to the β-carbon of the pyrrolyl ring and led to the de-cyclometallation of the pyrrole group from the iron center. If the thermal reaction was proceeded under carbon monoxide atmosphere, only a few percent of complex **2** decomposed after four days under the same reaction condition. Since the methylene hydrogen might act as a β-hydrogen, the thermal reaction of complex **2** might proceed through the following consecutive processes: dissociation of a carbonyl ligand, β-hydrogen elimination, reductive elimination, and the Schiff base **1** released from the metal centers.

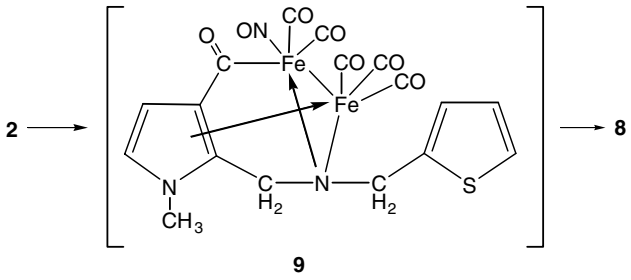
Reduction of complex **2** by lithium aluminum hydride led to the formation of high yield of the corresponding secondary amine, *N*-(*N*′-methyl-2-pyrrolylmethyl)(2-thienylmethyl)amine (**6**), which is a hydrogenation product of the original Schiff base **1**. Product **6** was identified by its NMR, IR, and Mass spectra.

Schiff bases derived from aromatic aldehyde are known to yield lactam products such as *N*-phenylphthalimidine on carbonylation at high temperature and high carbon monoxide pressure in the presence of metal carbonyl [9]. Carbonylation of an organic ligand from its metalcarbonyl complex could be achieved by treating the complex with a variety of Lewis bases such as

phosphines [10,11], by oxidation, or by photochemical reaction [11]. However, treatment of cyclometallated complex **2** with excess amount of triphenylphosphine (1:5 molar ratio) results only in substitution of one carbonyl ligand from complex **2** to give a pentacarbonylphosphinodiiron complex **7** in 82% yield. In its ^{1}H NMR spectrum, there are two multiplet signals appearing at δ 7.38 and 7.00 ppm and showing a total of fifteen phenyl protons, in additional to the three thienyl and two pyrrolyl protons in the aromatic region. There also exists one set of methylene resonance consisting of two well-separated doublets, a typical AB spin pattern, with a coupling constant of J_{H-H} = 14.4 Hz at δ 4.18 and 3.46 ppm, representing the inner methylene group. Another singlet signal representing the outer methylene moiety appears at 3.80 ppm. The IR spectrum of complex **7** shows four sharp and intense C═O stretches at 2024, 1968, 1946, and 1922 cm^{-1}, which are lower energy shifted relative to that of complex **2** (2055, 2011, 1963 cm^{-1}) due to the substitution of a more σ donor triphenylphosphine ligand. The mass spectrum shows a molecular ion peak at *m/z* 718 and the entirely loss of five COs and a PPh_3 group in a sequential manner, in accordance with the formulated structure.

On the other hand, from the reaction of complex **2** with nitrosonium salt, we obtained a novel bi-heterocyclic lactam, *N*-2-thienylmethyl-*N*′-methyl-2-methylpyrrolo[2,3b]-γ-butyrolactam (**8**), in 66% yield, instead of the expected nitrosyl substituted diiron complex. Compound **8** shows a characteristic IR stretching absorption at 1687 cm^{-1}. In its ^{1}H NMR spectrum, while the two pyrrolyl protons up-field shift to δ 6.95 and 6.18 ppm and the two methylene groups down-field shift to δ 4.93 and 4.32 ppm, the thienyl protons do not show a significant shift relative to that of complexes **2**. The mass spectrum and elemental analysis clearly indicate the structure formulated.

During the course of working up, we also isolated trace among of unstable intermediate (**9**), which decomposed rapidly to form compound **8**. The IR spectrum of the intermediate shows two extra absorption bands at 1788 and 1660 cm^{-1} in addition to the terminal carbonyl stretching frequencies that appear in the range of 2100–2000 cm^{-1}, indicating that the intermediate complex might contain a linear nitrosyl ligand and an inserted carbonyl group. Therefore, the formation of compound **8** might be suggested by assuming that on addition of a nitrosonium cation to one of the iron centers in complex **2**, a carbonyl ligand inserted into the Fe–C bond concomitantly to form the unstable intermediate **9**, and followed by a ring closure process via a reductive elimination of the chelating organic ligand to form a lactam. The intermediate **9** bears some resemblance to the carbonyl inserted complex from diphenylthioketon reported by Alper [10], which led to the formation of a thiolacton. In this reaction, the nitrosonium cation might serve as an oxidant that not only promotes the carbonyl insertion but also accelerates the reductive elimination as a result of iron oxidation.



In order to obtain some evidences for the pathway of the oxidation induced carbonylation, we have conducted the direct chemical and electrochemical oxidation of complex **2**. Chemical oxidation of complex **2** by anhydrous ferric chloride in ethyl alcohol afforded 53% yield of carbonylation product **8** while by ceric ammonium nitrate in acetone resulted in only 37% yield of the same product **8**.

Control potential bulk electrolysis of complexes **2** was conducted in acetonitrile solution containing 0.10 M of tetraethylammonium perchlorate (TEAP) with platinum gauze electrode at 0.95 (vs. Ag–AgCl reference electrode), respectively. The process is a one-electron oxidation from the iron metal. Isolation and characterization of the product from the electrochemical oxidation of complex **2** showed an identical lactam **8** (89% yield) to that obtained by chemical oxidation. The electrochemical experiment is strongly indicative that the carbonylation process involves cationic intermediate. Since both the cyclometallation and subsequent oxidation induced carbonylation proceed in good yields, this two-step sequence is a very convenient and useful entry into the bicyclic γ-lactam ring system.

3. Experimental

Diiron nonacarbonyl was prepared through the photolysis of iron pentacarbonyl (Aldrich) in glacial acetic acid [12]. Solvents were dried (sodium/benzophenone, P_4O_{10}) and distilled under nitrogen prior to use. *N*-Methyl-2-pyrrolecarboxaldehyde (Acros) and 2-thiophenemethylamine (Aldrich) were distilled by a Kugelrohr distillation apparatus under reduced pressure (0.1 mmHg) prior to use. All other chemicals were reagent grade and used without further purification. The NMR spectra were recorded on a Bruker DX-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

secondary reference. Mass spectra were obtained from a Micromass Platform II spectrometer. IR spectra were recorded employing a Mattson Genesis FTIR spectrophotometer. Elemental analyses were performed using a Perkin–Elmer 2400, 2400II elemental analyzer. Crystals for X-ray diffraction were obtained from ethyl acetate/dichloromethane (1/3). A single crystal was mounted on a glass fiber and the X-ray diffraction intensity data were measured on a Kappa CCD XRD.

3.1. Syntheses of pyrrolyl Schiff bases N-(N′-methyl-2-pyrrolylmethylidene)-2-thienylmethylamine (1)

The synthesis of Schiff base employed the usual approach of condensation in alcohol [13]. Equimolar quantities of *N*-methyl-2-pyrrolecarboxaldehyde (1.09 g, 10.0 mmol) and 2-thiophenemethylamine (1.13 g, 10.0 mmol) were stirred in 50 ml methanol for 8 h at room temperature. The reaction mixture was then filtered and the solvent as well as unreacted starting materials were removed in vacuo over night to yield pure orange–yellow product **1** (1.86 g, 9.12 mmol, 91.2% yield); m.p. 121–122 °C. ^{1}H NMR (CD_3COCD_3): δ 8.28 (s, 1 H), 7.31 (d, J_{H-H} = 5.1 Hz, 1H), 7.01 (d, J_{H-H} = 3.6, 1H), 6.96 (dd, J_{H-H} = 3.6, 5.1 Hz), 6.86 (d, J_{H-H} = 2.4 Hz, 1H), 6.51 (dd, J_{H-H} = 3.6 Hz, 1H), 6.09 (J_{H-H} = 2.7, 3.9 Hz, 1H), 4.84 (s, 2H), 3.96 (s, 3H). ppm. ^{13}C NMR (CD_3COCD_3): δ 153.6, 144.1, 129.5, 128.3, 126.6, 124.1, 123.7, 116.9, 107.8, 59.5, 36.0 ppm. IR (KBr film) ν_{max} (CN) 1640 cm^{-1}. MS (FAB): *m/z* 204 (M^+). Anal. Calc. for $C_{11}H_{12}N_2S$: C, 64.70; H, 5.88; N, 13.72; S, 15.68. Found: C, 64.95; H, 5.88; N, 13.77; S, 15.59%.

3.2. Reaction of 1 with $Fe_2(CO)_9$ in refluxing anhydrous toluene to yield [μ-N-(((2,3-η^1:η^2)-N′-methyl-2-pyrrolyl)methyl)-η^1:η^1(N) -2-thienylmethylamino]hexacarbonyldiiron (2), [μ-N-(((2,3-η^1:η^2)-2-thienyl)methyl)-η^1:η^1(N)–N′-methyl-2pyrrolymethylamino]hexacarbonyldiiron (3), [μ-N-(((2,3-η^1:η^2)-2-thienyl)methyl)-η^1:η^1(N)-2-thienylmethylamino]hexacarbonyldiiron (4), and [μ-N-(((2,3-η^1:η^2)-N′-methyl-3-pyrrolyl)methyl)-η^1:η^1(N)-2-thienylmethylamino]hexacarbonyldiiron (5)

0.820 g (4.02 mmol) of ligand **1** and 12.0 mmol of $Fe_2(CO)_9$ were heated at reflux in 80 ml of anhydrous toluene solution in the dark under nitrogen for 12 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/*n*-hexane (1/3) as eluent to separate the resulting red product **2** from the rest of other products. The column was further treated with *n*-hexane as eluent to obtain other three red products **3**, **4**, and **5**.

Compound ***2***: 0.895 g (1.85 mmol), 46.0% yield; m.p. 142–143 °C. ^{1}H NMR (CD_3COCD_3): δ 7.48 (d, J_{H-H} = 5.1 Hz, 1H), 7.17 (d, J_{H-H} = 2.7 Hz, 1H), 7.12 (d, J_{H-H} = 3.3 Hz, 1H), 7.03 (dd, J_{H-H} = 5.1, 3.6 Hz, 1H), 6.49 (d, J_{H-H} = 2.7 Hz, 1H), 4.26 (s, 2H), 3.88 (s, 2H), 3.74 (s, 3H). ppm. ^{13}C NMR (CD_3COCD_3): δ 211.9, 147.3, 140.4, 131.9, 128.3, 126.6, 126.3, 126.1, 110.8, 66.0, 62.7, 34.7 ppm. IR (KBr film) ν_{max} (CO) 2055, 2011, 1963 cm^{-1}. MS (FAB): *m/z* 484 (M^+), 456 (M^+ – CO), 428 (M^+ – 2CO), 400 (M^+ – 3CO), 372 (M^+ – 4CO), 344(M^+ – 5CO), 316 (M^+ – 6CO), 260 (M^+ – 6CO – Fe), 204 (L^+). Anal. Calc. for $C_{17}H_{12}Fe_2N_2O_6S$: C, 42.14; H, 2.47; N, 5.78; S, 6.61. Found: C, 42.30; H, 2.68; N, 5.68; S, 6.70%.

Compound ***3***: 0.175 g (0.362 mmol), 9.0% yield; m.p. 142–143 °C. ^{1}H NMR (CD_3COCD_3): δ 7.70 (d, J_{H-H} = 5.1 Hz, 1H), 7.39 (d, J_{H-H} = 5.1 Hz, 1H), 6.88 (s, 1H), 6.23 (d, J_{H-H} = 3.6 Hz, 1H), 6.05 (dd, J_{H-H} = 2.7, 3.6 Hz, 1H), 3.96 (s, 2H), 3.95 (s, 2H), 3.68 (s, 3H) ppm. ^{13}C NMR (CD_3COCD_3): δ 207.4, 154.9, 139.3, 131.7, 129.9, 122.9, 117.8, 110.4, 106.9, 67.2, 60.7, 33.4 ppm. IR (KBr film) ν_{max} (CO) 2063, 2026, 1981 cm^{-1}. MS (FAB): *m/z* 484 (M^+), 456 (M^+ – CO), 428 (M^+ – 2CO), 400 (M^+ – 3CO), 372 (M^+ – 4CO), 344 (M^+ – 5CO), 316 (M^+ – 6CO), 260 (M^+ – 6CO – Fe), 204 (L^+). Anal. Calc. for $C_{17}H_{12}Fe_2N_2O_6S$: C, 42.14; H, 2.47; N, 5.78; S, 6.61. Found: C, 42.26; H, 2.71; N, 5.71; S, 6.67%.

Compound ***4***: 0.158 g (0.324 mmol), 8.1% yield; m.p. 96–97 °C. ^{1}H NMR (CD_3COCD_3): δ 7.69 (d, J_{H-H} = 5.1 Hz, 1 H), 7.48 (d, J_{H-H} = 5.1 Hz, 1H), 7.40 (d, J_{H-H} = 5.1 Hz, 1H), 7.14 (d, J_{H-H} = 3.3 Hz, 1H), 7.04 (dd, J_{H-H} = 5.1, 3.6 Hz, 1H), 4.20 (s, 2H), 3.96 (s, 2H) ppm. ^{13}C NMR (CD_3COCD_3): δ 210.4, 154.7, 139.3, 131.8, 128.6, 126.5, 126.2, 117.3, 115.2, 67.9, 65.2 ppm. IR (CH_2Cl_2) ν_{max} (CO) 2066, 2024, 1975 cm^{-1}. MS (FAB): *m/z* 487 (M^+), 459 (M^+ – CO), 431 (M^+ – 2CO), 403 (M^+ – 3CO), 375 (M^+ – 4CO), 347(M^+ – 5CO), 319 (M^+ – 6CO), 263 (M^+ – 6CO – Fe), 207 (L^+). Anal. Calc. for $C_{16}H_9Fe_2NO_6S_2$: C, 39.42; H, 1.85; N, 2.88; S, 13.14. Found: C, 39.52; H, 1.95; N, 2.93; S, 13.06%.

Compound ***5***: 0.100 g (0.207 mmol), 5.2% yield; m.p. 142–143 °C. ^{1}H NMR (CD_3COCD_3): δ 7.77 (d, J_{H-H} = 2.4 Hz, 1H), 7.48 (d, J_{H-H} = 5.1 Hz, 1H), 7.13 (d, J_{H-H} = 3.6 Hz, 1H), 7.03 (dd, J_{H-H} = 5.1, 3.6 Hz, 1H), 6.27 (d, J_{H-H} = 2.4 Hz, 1H), 4.30 (s, 2H), 3.77 (s, 3H), 3.69 (s, 2H). ppm. ^{13}C NMR (CD_3COCD_3): δ 211.8, 144.5, 140.3, 138.2, 136.7, 128.4, 126.3, 126.1, 103.7, 65.7, 64.8, 37.7 ppm. IR (CH_2Cl_2) ν_{max} (CO) 2056, 2018, 1974 cm^{-1}. MS (FAB): *m/z* 484 (M^+), 456 (M^+ – CO), 428 (M^+ – 2CO), 400 (M^+ – 3CO), 372 (M^+ – 4CO), 344(M^+ – 5CO), 316 (M^+ – 6CO), 260 (M^+ – 6CO – Fe), 204 (L^+). Anal. Calc. for $C_{17}H_{12}Fe_2N_2O_6S$: C, 42.14; H, 2.47; N, 5.78; S, 6.61. Found: C, 42.26; H, 2.61; N, 5.72; S, 6.56%.

If the reaction time was prolonged from 12 to 24 h under the same reaction conditions, only 41% of

complex **2** and 17% of complex **4** were isolated. On the other hand, if the reaction was stopped after six hours of reaction under the same reaction conditions, 32% of complex **2,** 4% of complex **3,** 10% of complex **4,** and 3% of complex **5**.

If the reaction was carried out at r.t. in benzene for 12 h, only complex **2**, in 12% yield, was produced. Even if the reaction temperature was raised up to the reflux temperature in benzene, we still obtained complex **2**, in 30% yield, as the sole organometallic product.

3.3. Thermolysis of complex 2

0.87 g (1.8 mmol) of complex **2** was dissolved in 50 ml of solvent (*n*-heptane, acetonitrile, or toluene) and the solution was refluxed under N_2 atmosphere for 48 h. The solution was cooled and filtered, and the filtrate was flash evaporated in vacuo. The residue was chromatographed on a silica gel column with ethyl acetate/*n*-hexane (1:20) as eluent. Compound **1** (0.31 g, 1.5 mmol, 83% yield if the solvent is *n*-heptane and 0.35 g, 1.7 mmol, 94% yield if the solvent is acetonitrile or toluene) and compound **6** (0.14 mmol, 7.8% yield if the solvent is *n*-heptane) were isolated. Compound **6**: ^{1}H NMR (CD_3COCD_3): δ 7.21 (d, J_{H-H} = 5.1 Hz, 1H), 6.75 (d, J_{H-H} = 3.3 Hz, 1H), 6.71 (dd, J_{H-H} = 3.6, 5.1 Hz, 1H), 6.47 (dd, J_{H-H} = 2.7 Hz, 1H), 5.80 (d, J_{H-H} = 3.6 Hz, 1H), 5.55 (J_{H-H} = 2.7, 3.9 Hz, 1H), 4.86 (b, 1H), 4.34 (s, 2H), 4.01 (s, 2H), 3.61 (s, 3H). ppm. IR (KBr film) ν_{max} (NH) 3421 cm^{-1}. MS (FAB): *m/z* 206 (M^+). Anal. Calc. for $C_{11}H_{14}N_2S$: C, 64.07; H, 6.80; N, 13.59; S, 15.53. Found: C, 64.31; H, 6.98; N, 13.71; S, 15.67%.

Similar results were obtained if the thermolysis was proceeded in d_3-acetonitrile or d_8-toluene solvent.

Repetition of the thermolysis under carbon monoxide atmosphere afforded only trace amount of compound **1** after 4 days of reaction and more than 95% of unchanged complex **2** was recovered.

3.4. Lithium aluminum hydride reduction of complex 2

0.97 g (2.0 mmol) of complex **2** in 20 ml of THF was added drop wise with stirring to a 50 ml of ice-cold THF solution containing 0.16 g of suspension $LiAlH_4$. After the reaction mixture was stirred for 2 h, excess of $LiAlH_4$ was decomposed by the addition of 20 ml ethyl acetate. The reaction mixture was filtered and the solvent was removed in vacuo. The residue was chromatographed on a silica gel column with ethyl acetate/*n*-hexane (1:20) as eluent to give *N*-(*N*′-methyl-2-pyrrolylmethyl)(2-thienylmethyl)amine (**6**) (0.29 g, 1.4 mmol, 70% yield) and unchanged complex **2** (0.46 mmol, 23%).

A sample obtained similarly, but with lithium aluminum deuteride, was shown by NMR and Mass spectra to contain one derterium atom attached to the β-carbon of the pyrrolyl ring.

3.5. Reaction of complex 2 with triphenylphosphine to give [μ-N-(((2,3-η^1:η^2)-N′-methyl-2-pyrrolyl)methyl)-η^1:η^1-(N)-2-thienylmethylamino]pentacarbonyltiphenylphospinodiiron (7)

A mixture of complex **2** (0.42 g, 0.87 mmol), triphenylphosphine (1.23 g, 4.30 mmol), and trimethylamine *N*-oxide · $2H_2O$ (0.80 g) in 80 ml of acetonitrile was stirred at room temperature under nitrogen atmosphere for 48 h. The reaction mixture was filtered and the solvent was removed in vacuo. The residue was washed with several portions of *n*-hexane and was then dissolved in ethyl acetate. After the filtration, the filtrate was concentrated under reduced pressure to give deep red product **7** (0.61 g, 85% yield). ^{1}H NMR δ 7.48 (d, J_{H-H} = 5.1 Hz, 1H), 7.29 (m, 5H), 7.17 (d, J_{H-H} = 2.4 Hz, 1H), 7.12 (d, J_{H-H} = 3.6 Hz, 1H), 7.03 (m, 1H), 6.96 (m, 10H), 6.49 (d, J_{H-H} = 2.4 Hz, 1H), 4.26 (d, J_{H-H} = 14.4 Hz, 1H), 4.08 (d, J_{H-H} = 14.4 Hz, 1H), 3.88 (s, 2H), 3.74 (s, 3H). IR ($CHCl_3$) ν_{max} (CO) 2030, 1961, 1934, 1906 cm^{-1}. MS (EI): *m/z* 718 (M^+), 690 ($M^+ - CO$), 662 ($M^+ - 2CO$), 634 ($M^+ - 3CO$), 606 ($M^+ - 4CO$), 578 ($M^+ - 5CO$), 262 (PPh_3^+), 204 (L^+). Anal. Calc. for $C_{34}H_{27}Fe_2N_2O_5PS$: C, 56.82; H, 3.76; N, 3.90; S, 4.46. Found: C, 57.01; H, 3.80; N, 3.87; S, 4.38%.

3.6. Reaction of complex 2 with nitrosonium tetrafluoroborate to give N-2-thienylmethyl-N′-methyl-2-methylpyrrolo[2,3b]-γ-butyrolactam (8)

A mixture of complex **2** (0.42 g, 0.78 mmol) and nitrosonium tetrafluoroborate (0.10 g, 0.86 mmol) in 80 ml of acetonitrile was stirred at room temperature under nitrogen atmosphere for 72 h. The reaction mixture was filtered and the solvent was removed under reduced pressure. The residue was washed with several portions of *n*-hexane and was then dissolved in diethyl ether. After the filtration, the filtrate was concentrated under reduced pressure to give **8** (0.12 g, 0.52 mmol, 66% yield). ^{1}H NMR δ 7.58 (d, *J* = 5.1 Hz, 1H), 7.18 (d, *J* = 3.6 Hz, 1H), 7.06 (dd, *J* = 3.6, 5.1 Hz, 1H), 6.95 (d, J_{H-H} = 2.4 Hz, 1H), 6.18 (d, J_{H-H} = 2.4 Hz, 1H), 4.93 (s, 2H), 4.23 (s, 2H), 4.01 (s, 3H). IR ($CHCl_3$) ν_{max} (CO) 1687 cm^{-1}. MS (EI): *m/z* 232 (M^+), 204 ($M^+ - CO$). Anal. Calc. for $C_{12}H_{12}N_2SO$: C, 62.07; H, 5.17; N, 12.07; S, 13.79. Found: C, 61.92; H, 5.26; N, 12.22; S, 13.64%.

3.7. Oxidation of complex 2 with ferric chloride/ceric ammonium nitrate

The complex **2** (0.35 g, 0.72 mmol) in 30 ml of ethyl alcohol was added drop wise with stirring to a 30 ml ethyl alcohol solution of anhydrous ferric chloride (0.25 g, 1.5 mmol). The reaction mixture was stirred at room temperature for 3 h and then at 60 °C for 4 h. It

was filtered and evaporated under reduced pressure. The residue was washed with several portions of *n*-hexane and was then dissolved in diethyl ether. After the filtration, the filtrate was concentrated in vacuo to give **8** (0.088 g, 0.38 mmol, 53% yield). Similar procedure was performed for the oxidation of complex **2** with ceric ammonium nitrate in acetone solution to afford the same product **8** (0.064 g, 0.28 mmol, 37% yield).

3.8. Electrochemical experiment

Cyclic voltammetry was performed at room temperature in acetonitrile solution containing 0.1 M tetraethylammonium perchlorate (TEAP) as supporting electrolyte. The single sweep cyclic voltammogram (CV) of the complex of $\sim 10^{-3}$ M in a three-compartment cell was recorded with stationary platinum microelectrode. The peak potential E_p of the compound was independent of the concentration in the range between 10^{-2} and 10^{-4} M in acetonitrile solution and was always reproducible to within ±50 mV. Repeated CV scans did not affect the appearance of the voltammogrames.

3.8.1. Control potential bulk coulometry of complex 2

0.20 mmol of complex **2** in an acetonitrile solution containing 0.1 M of TEAP was exhaustively oxidized with platinum gauze electrode at 0.95 V vs. Ag–AgCl reference electrode. The electrolysis showed that the process is a 1.03 electron oxidation. After the electrolysis, the solution was filtered and the solvent was removed in vacuo. The residue was dissolved in diethyl ether. After the filtration, the filtrate was concentrated under reduced pressure to give pure **8** product in 92% yield.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 239379–239381 (**2**, **3**, and **5**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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