

Reactions of cyclometalated carbonyliron complex derived from thienyl Schiff base

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Abstract

Cyclometalated hexacarbonyldiiron complex **2**, which derived from *N*-(2-thienylmethylidene)aniline, undergoes (1) thermolysis to recover the original Schiff base **1**, (2) reduction to form a hydrogenation product of the original thienyl Schiff base **3**, (3) substitution to form a phosphine-substituted complex **4**, and (4) chemical as well as electrochemical oxidation to produce a γ -lactam **5**. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: *N*-(2-thienylmethylidene)aniline; Cyclometalated hexacarbonyldiiron complex; Carbonylation; γ -Lactam

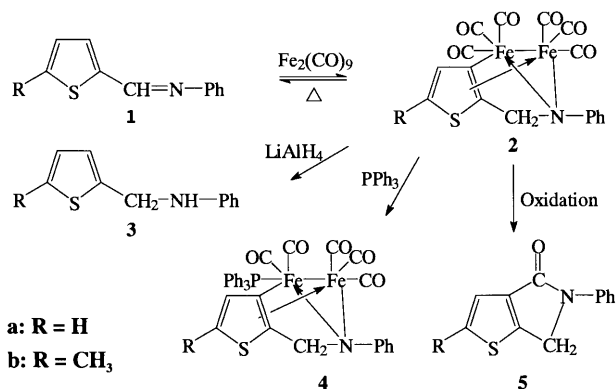
1. Introduction

Cyclometalated hexacarbonyldiiron complex **2** was obtained as a major product from the reaction of thienyl Schiff base **1** with diiron nonacarbonyl under mild conditions [1,2]. Complex **2** is a stable compound especially in its solid state. A study of the chemistry of the complex indicates that it might play as a potential intermediate for organic synthesis. In this paper we report some interest and synthetically useful results from reactions of the cyclometalated complexes **2**.

2. Results and discussion

The formation and reactions of the cyclometalated hexacarbonyldiiron complex **2** are outlined in the following scheme.

Thermolysis of complex **2** in a refluxed *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 90% after 48 h. If the reaction was proceeded in a deuterated solvent such as *d*₈-toluene or *d*₃-acetonitrile, a similar result was ob-



tained and there was no deuterium atom attached to the Schiff base **1** observed. This is a reverse process of the consecutive reactions of coordination, cyclometalation and 1,3-hydrogen shift. One of the methylene hydrogen transferred back to the β -carbon of the thienyl ring and led to the de-cyclometalation of the thienyl group from the iron center. If the thermal reaction proceeded under a carbon monoxide atmosphere, only a few percent of complex **2** decomposed after 4 days under the same reaction conditions. 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

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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 corre-

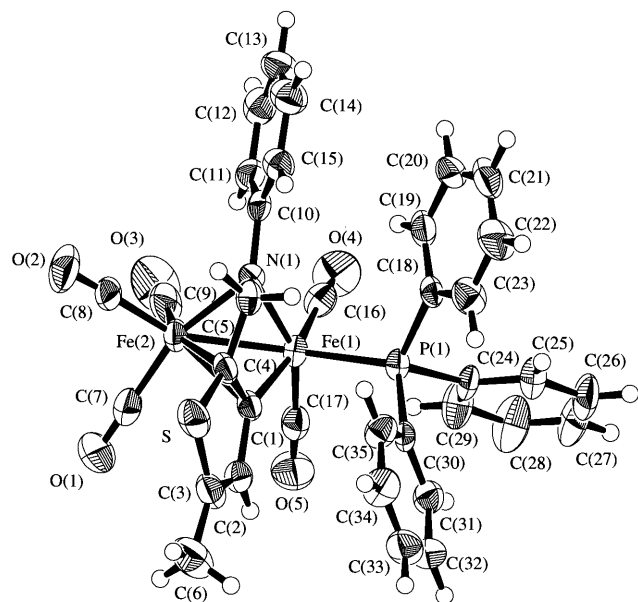


Fig. 1. ORTEP diagram of complex **4b** at the 50% probability level. Selected bond lengths (Å): Fe(1)–Fe(2) 2.473(1), Fe(1)–N(1) 2.060(4), Fe(2)–N(1) 2.015, Fe(1)–C(1) 1.968(5), Fe(2)–C(1) 2.174(5), Fe(2)–C(4) 2.223(5), Fe(1)–P(1) 2.233(2) N(1)–C(5) 1.500(6), C(1)–C(4) 1.399(7). Selected bond angles (°): Fe(1)–N(1)–Fe(2) 74.7(1), Fe(1)–C(1)–Fe(2) 73.1(2), N(1)–C(5)–C(4) 100.1(4), Fe(1)–P(1)–C(18) 116.0(2), Fe(1)–P(1)–C(24) 118.4(2), Fe(1)–P(1)–C(30) 113.7(2).

Table 1
Crystal and data collection parameters for compound **4b**

Formula	C ₃₅ H ₂₆ Fe ₂ NO ₅ PS
f_w	715.32
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
Unit cell dimensions	
a (Å)	11.784(3)
b (Å)	13.915(2)
c (Å)	10.891(3)
α (°)	100.42(2)
β (°)	111.42(3)
γ (°)	76.62(2)
V (Å ³)	1608.1(7)
Z	2
D_{calc} (g cm ⁻³)	1.477
Cryst size (mm)	0.33 × 0.43 × 0.45
Temp (K)	296
$2\theta_{\text{max}}$ (°)	50.2
Scan type	ω -2 θ
No. of reflections measured: total, unique	6006, 5699
No. of observed reflections ($I > 3.00\sigma(I)$)	3477
No. of variables	406
F_{000}	732.00
μ (Mo–K α) (cm ⁻¹)	10.59
R	0.043
R_w	0.033

sponding secondary amine, *N*-(2-thienylmethyl)aniline (**3**), which is a hydrogenation product of the original Schiff base **1**. Product **3** was identified by comparison of its NMR, IR, and mass spectra with that of an authentic sample [1]. Repetition of this reaction with deuteride in place of hydride gave the same product with one deuterium atom attached to the β -carbon of the thienyl ring, as expected if the hydrogen had been lost from the β -carbon in the complex.

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 [3]. 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 [4,5], by oxidation, or by photochemical reaction [5]. However, treatment of cyclometalated complex **2b** with excess amount of triphenylphosphine (1:10 molar ratio) results only in substitution of one carbonyl ligand from complex **2b** to give a pentacarbonylphosphinodiron complex **4b** in 86% yield with no gross structure change occurring. In its ¹H-NMR spectrum, there are four multiplet signals appearing in the region between δ 7.43 and 6.78 ppm and showing a total of 20 aromatic protons. The thienyl proton appears at δ 6.58 ppm and the two methylene protons show two sets of doublet signal at δ 4.14 and 3.42 ppm, respectively, with $J_{\text{H-H}} = 9.9$ Hz. The IR spectrum of complex **4b** shows four sharp and intense C=O stretches at 2028, 1978, 1962, and 1934 cm⁻¹, which are lower energy shifted relative to that of complex **2b** (2068, 2030, 1993 cm⁻¹) [1] due to the substitution of a more σ -donor triphenylphosphine ligand. The mass spectrum shows a molecular ion peak at m/z 715 and the entirely loss of five COs and a PPh₃ in a sequential manner, in accordance with the formulated structure. The molecular structure of complex **4b** was confirmed by a single-crystal X-ray diffraction analysis and is shown in Fig. 1. Crystal and data collection parameters are listed in Table 1.

On the other hand, from the reaction of complex **2b** with nitrosonium salt, instead of the expected nitrosyl substituted diiron complex, we obtained a novel bi-heterocyclic lactam, *N*-phenyl-5-methylthieno[2,3b]- γ -butyrolactam (**5b**), in 72% yield. Compound **5b** shows a characteristic IR stretching absorption at 1683 cm⁻¹. In its ¹H-NMR spectrum, the thienyl proton appears at δ 6.93 ppm and the two methylene protons down-field shift to δ 5.02 ppm. The mass spectrum and elemental analysis clearly indicate the structure formulated.

During the course of working up, we also isolated a trace of an unstable intermediate, which decomposed rapidly to form compound **5b**. The IR spectrum of the intermediate shows two extra absorption bands at 1792 and 1658 cm⁻¹ in addition to the terminal carbonyl stretching frequencies around 2100–2000 cm⁻¹, indi-

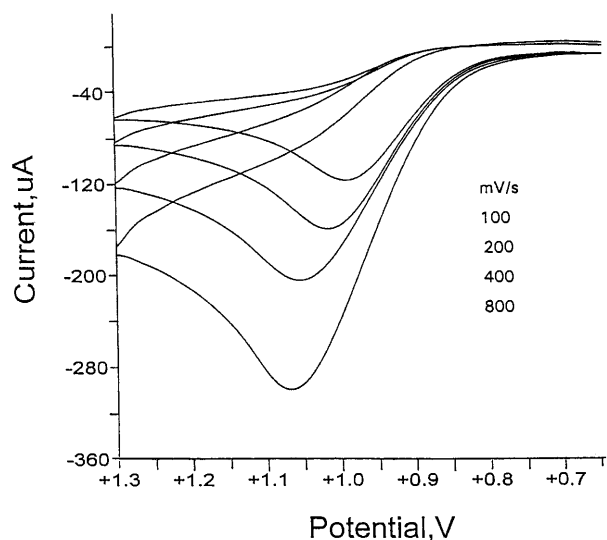
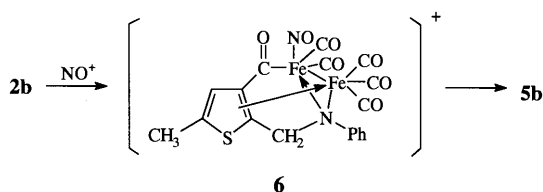


Fig. 2. Single sweep cyclic voltammograms of 2.45×10^{-3} M complex **2b** in acetonitrile containing 0.1 M TEAP at various scan rates. Electropotential in volts versus standard Ag/AgCl electrode.

cating that the intermediate complex might contain a linear nitrosyl ligand and an inserted carbonyl group. Therefore, the formation of compound **5** 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 **6**, and followed by a ring closure process via a reductive elimination of the chelating organic ligand to form a lactam. The intermediate **6** bears some resemblance to the carbonyl inserted complex from diphenylthioketone reported by Alper [4], 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 because of iron oxidation.



In order to obtain some evidence for the pathway of the oxidation-induced carbonylation, we have conducted the direct chemical and electrochemical oxidation of complex **2b**. Chemical oxidation of complex **2b** by anhydrous ferric chloride in ethyl alcohol afforded 55% yield of carbonylation product **5b** while by ceric ammonium nitrate in acetone resulted in only 40% yield of the same product **5b**.

Cyclic voltammetry experiments on both complexes **2b** and **4b** showed a well-defined oxidation wave with a peak potential of 0.99 and 0.64 V versus Ag/AgCl electrode, respectively, at 100 mV s⁻¹ 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⁻¹ (Fig. 2). No reduction wave in the reverse cathodic sweep was observed, demonstrating a totally irreversible overall process [6]. The voltammetry curve is consistent with an E_cC_i mechanism [6a,d], i.e. heterogeneous electron transfer followed by an irreversible chemical reaction. Control potential bulk electrolysis of complexes **2b** and **4b** was conducted in acetonitrile solution containing 0.10 M of tetraethylammonium perchlorate (TEAP) with platinum gauze electrode at 1.20 and 0.80 V (versus 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 complexes **2b** and **4b** showed an identical lactam **5b** (98% yield from **2b** and 93% yield from **4b**) to that obtained by chemical oxidation. The electrochemical experiment is strongly indicative that the carbonylation process involves a cationic intermediate. Since both the cyclometalation 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

Solvents were dried (sodium/benzophenone, P₄O₁₀) and distilled under nitrogen prior to use. Acetonitrile (E. Merck) for electrochemistry was refluxed over CaH₂ for several hours and then directly distilled. The distillate was redistilled twice from 3:2 mixture of KMnO₄ and anhydrous K₂CO₃. It was then refluxed over CaH₂ again and distilled from P₂O₅ under nitrogen atmosphere. All other chemicals were reagent grade and used without further purification. The NMR spectra were recorded on a Varian VXR-300 NMR spectrometer (¹H, 299.95 MHz; ¹³C, 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 (r.t.). Cyclic voltammetry and bulk coulometry were performed with a BAS-100W electrochemical analyzer.

3.1. Starting material **2**

[μ -N-(((2,3- η^1 ; η^2)-2-Thienyl)methyl)- η^1 : η^1 -(*N*-anilino)]hexacarbonyldiiron (**2a**) and [μ -N-(((2,3- η^1 ; η^2)-

5-methyl-2-thienyl)methyl)- $\eta^1:\eta^1$ -(*N*-anilino]hexacarbonyliron (**2b**) were prepared according to literature procedures [1,2].

3.2. Thermolysis of complex **2**

In a typical reaction, 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** (78% yield if the solvent is *n*-heptane, 96% yield if the solvent is acetonitrile or toluene) and compound **3** (12% yield if the solvent is *n*-heptane) were isolated and identified by comparison of spectral data with that of an authentic sample [1]. Similar results were obtained if the thermolysis proceeded in d_3 -acetonitrile or d_8 -toluene solvent.

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

3.3. Lithium aluminum hydride reduction of complex **2**

A total of 2.2 mmol of complex **2** in 20 ml of THF was added dropwise with stirring to 50 ml of ice-cold THF solution containing 0.16 g of suspension $LiAlH_4$. After the mixture had been stirred for 2 h, excess of $LiAlH_4$ was decomposed by the addition of 20 ml of ethyl acetate. The residue 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 orange product *N*-((2-thienyl)methyl)aniline (**3a**) (0.287 g, 69% yield)/*N*-((5-methyl-2-thienyl)methyl)aniline (**3b**) (0.344 g, 77% yield) and unchanged complex **2** (20%). Compounds **3a** and **3b** were identified spectrally by comparison with an authentic sample [1].

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

3.4. Reaction of complex **2b** with triphenylphosphine to give [μ -*N*-(((2,3- η^1 ; η^2)-5-methyl-2-thienyl)methyl)- $\eta^1:\eta^1$ -(*N*-anilino]pentacarbonyltiphenylphosphodiiron (**4b**)

A mixture of complex **2b** (0.35 g, 0.73 mmol), triphenylphosphine (1.02 g, 3.85 mmol), and trimethylamine *N*-oxide·2H₂O (0.80 g) in 80 ml of acetonitrile was stirred at r.t. 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 **4b** (0.45 g, 86% yield). M.p. 166–167°C. ¹H-NMR: δ 7.43 (m, 3H), 7.30 (m, 5H), 6.98 (m, 10H), 6.78 (m, 2H), 6.58 (s, 1H), 4.14 (d, $J = 9.9$ Hz, 1H), 3.42 (d, $J = 9.9$ Hz, 1H), 2.35 (s, 3H). ¹³C-NMR: δ 159.4, 157.9, 146.9, 144.9, 138.6, 129.9, 129.4, 129.0, 128.3, 126.4, 125.5, 117.9, 113.6, 86.8, 63.2. IR (CHCl₃): ν_{CO} : 2028, 1978, 1962, 1934 cm^{-1} . MS (EI): m/z 715, (M⁺), 687 (M⁺–CO), 659 (M⁺–2CO), 631 (M⁺–3CO), 603 (M⁺–4CO), 575 (M⁺–5CO), 263 (PPh₃ + 1), 200 (L⁺–1). Anal. Calc. for C₃₅H₂₆Fe₂NO₅PS: C, 58.79; H, 3.67; N, 1.96. Found: C, 58.99; H, 3.71; N, 1.97%.

3.5. Reaction of complex **2b** with nitrosonium tetrafluoroborate to give *N*-phenyl-5-methylthieno-[2,3*b*]- γ -butyrolactam (**5b**)

A mixture of complex **2b** (0.35 g, 0.73 mmol) and nitrosonium tetrafluoroborate (0.088 g, 0.75 mmol) in 80 ml of acetonitrile was stirred at r.t. 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 **5b** (0.12 g, 72% yield). ¹H-NMR: δ 7.84 (d, $J = 7.8$ Hz, 2H), 7.36 (t, $J = 6.9$ Hz, 2H), 7.09 (t, $J = 6.9$ Hz, 1H), 6.93 (s, 1H), 5.02 (s, 2H), 2.56 (s, 3H). ¹³C-NMR: δ 164.4, 149.1, 146.5, 141.6, 141.4, 129.8, 124.3, 119.6, 118.5, 74.6, 15.7. IR (CHCl₃): ν_{CO} : 1682 cm^{-1} . MS (EI): m/z 229 (M⁺), 201 (M⁺–CO). Anal. Calc. for C₁₃H₁₁NSO: C, 68.12; H, 4.80; N, 6.10. Found: C, 68.10; H, 4.71; N, 6.05%.

3.6. Oxidation of complex **2b** with ferric chloride/ceric ammonium nitrate

The complex **2b** (0.35 g, 0.73 mmol) in 30 ml of ethyl alcohol was added dropwise 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 r.t. 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 **5b** (0.092 g, 55% yield). A similar procedure was performed for the oxidation of complex **2b** with ceric ammonium nitrate in aceton solution to afford the same product **5b** (0.067 g, 40% yield).

3.7. Electrochemical experiment

Cyclic voltammetry was performed at r.t. 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 a 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 voltammograms.

3.8. Control potential bulk coulometry of complexes **2b** and **4b**

A total of 0.20 mmol of complexes **2b/4b** in an acetonitrile solution containing 0.1 M of TEAP was exhaustively oxidized with a platinum gauze electrode at 1.20/0.80 V versus Ag/AgCl reference electrode. The electrolysis showed that the process is a 0.98/1.02 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 **5b** product in 98%/92% yield.

4. Supplementary material

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 145120 for

4a. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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