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Photo-induced ligand exchange reactions of ferrocenylacetylacetone in the presence of pyridine or 4,4′-dipyridyl: Crystal and molecular structure of *trans*-bis(ferrocenylacetylacetonato)dipyridineiron(II), $[Fe(FAnato)_2(Py)_2]$

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Abstract

The photo-induced ligand exchange reactions of ferrocenylacetylacetone (FA) in the presence of pyridine (Py) or 4,4′-dipyridyl (Dipy) in deoxygenated acetonitrile under irradiation with visible light have been investigated. The mechanism of the reactions was proposed to involve three steps: the first is the photo-induced charge transfer, resulting in the deligation of FA to yield the free Fe(II) ion, cyclopentadienylacetylacetonate (CAnate) and η°-bonded cyclopentadienyl ring (η°-Cp). The second process is the proton-transfer from FA to CAnate and η°-Cp, forming cyclopentadienylacetylacetone (CA) and 1,3-cyclopentadiene, which were detected by GC–MS analyses. The third process is the complex formation, the photo-liberated Fe(II) ion was coordinated with deprotonated FA(FAnate), generating the mononuclear complex, $[Fe(FAnato)_2(Py)_2]$, or polynuclear complex, $[\{Fe(FAnato)_2(Dipy)_{2\times 1/2}\}_n]$, which were characterized by elemental analyses, IR and X-ray structure analysis. Crystallographic data for complex, $[Fe(FAnato)_2(Py)_2]$: monoclinic, space group $P2_1/c$, $a = 8.212(3)$, $b = 9.945(2)$, $c = 19.953(3)$ Å, $\beta = 98.18(3)°$, $R = 0.0705$, $WR = 0.0803$. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Photolysis; Photo-induced ligand exchange; β-Diketone; Proton transfer; Charge transfer

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1. Introduction

Ligand exchange reactions of metal-sandwich complexes have attracted considerable attention due to their synthetic utility [1–3] and mechanistic interest [4–10]. These ligand exchanges can be carried out through thermal or photochemical routes. For instance, one cyclopentadienyl ring (Cp) of ferrocene can be replaced by various arene ligands in the presence of $AlCl_3/Al$ under thermal conditions (Fischer–Haffner process). By this means, several hundred cationic $[CpFe(arene)]^+$ complexes have been synthesized [2].

However, under photo-induced conditions, these exchange reactions can not occur because of ferrocene's distinct lack of photochemical reactivity [11].

On the other hand, many cationic $[CpFe(arene)]^+$ or $[Fe(arene)_2]^{2+}$ complexes are extremely stable to heat, but they can readily take place photo-induced ligand exchanges with more basical arenes in visible or sun light [6,9,12,13].

$$[CpFe(arene1)]^+ + arene2 \xrightarrow{\text{Visible light}} [CpFe(arene2)]^+ + arene1$$

$$(\text{basicity: arene2} > \text{arene1})$$

It has been shown [14–16] that an electron-withdrawing acyl substituent on the Cp ring may provide a greater photolability for ferrocenes. Therefore, in a previous paper [17] we demonstrated the possibility of photo-ligand exchange reactions between diacylferrocenes and 1,10-phenanthroline(phen) under irradiation with visible light:

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$$[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_4COR})_2] + 3\mathrm{phen} \xrightarrow{\text{Visible light}} [\mathrm{Fe(phen)_3}]^{2+}(\eta^\circ\text{-}\mathrm{C_5H_4COR})_2^-$$

$$(\mathrm{R{=}CH_3,\ ph})$$

It seems of interest to examine further the photolysis of acylferrocene derivatives in which the substituent on the Cp ring not only contains photoactive acyl groups, but also exhibits chelating ability, such as ferrocenylacetylacetone (FA), $\mathrm{FcC(O)CH_2C(O)CH_3}$. This derivative may serve as a chelating ligand to take place photo-induced ligand exchange with itself. In this paper the photolysis of FA in the presence of pyridine (Py) or 4,4′-dipyridyl (Dipy) as co-ligand in MeCN solution were presented. In order to obtain more detailed information on its reaction mechanism, the photoproducts were characterized structurally by X-ray crystallography, GC–MS and IR.

2. Experimental

2.1. Materials and analytical equipment

All solvents were dried and distiled before use [18]. Other materials were of reagent grade. FA was prepared following the literature method [19]. IR spectra were recorded on a Shimadzu IR-435 instrument using KBr pellets in the 400–4000 $\mathrm{cm^{-1}}$ region. Elemental analyses were carried out on a MOD 1106 analyzer.

A Hewlett-Packard capillary column gas chromatography (Model 5890 Series II) interfaced by direct capillary inlet to a Hewlett-Packard MS (Model 5988A) was used for the analysis of photoproduct **2** (vide infra).

2.2. General procedures for irradiation

All manipulations were carried out by standard Schlenk techniques. The reaction solutions consisted of FA and Py or Dipy in deoxygenated acetonitrile, and irradiated for 1–2 h under visible light from a 200-W Xenon lamp with a Pyrex filter. The reaction temperature was kept at 0°C in an ice bath.

2.3. Photolysis of FA in the presence of Py

A solution of FA (45.0 mg, 0.167 mmol) and Py (0.5 ml, 6.2 mmol) in 15 ml of MeCN was prepared and sealed in a glass pipe under the condition of reduced pressure to remove the air in it, irradiated for 1.5 h, and upon standing at room temperature for 1–2 days, dark red crystals suitable for X-ray crystallography were obtained. Yield 18.75 mg (44.87%, based on Fe, 15%, based on photolytic Fe) of photoproduct **1**, $[\mathrm{Fe(FAnato)_2(Py)_2}]$. Anal. Calc. for $(\mathrm{C_{38}H_{36}O_4N_2Fe_3})$ (FAnato = ferroceneylacetylacetonato): C, 60.67; H, 4.82; N, 3.72%. Found: C, 60.52; H, 4.85; N, 4.36%.

2.4. Photolysis of FA in the presence of Dipy

A solution of FA (45.0 mg, 0.167 mmol) and Dipy (32.0 mg, 0.147 mmol) in 10 ml of MeCN was employed. After irradiation, the red–brown precipitate was separated by filtration, washed several times with MeCN to remove the unreacted materials and dried in vacuo. Yield 22.50 mg (53.99%, based on Fe, 18%, based on photolytic Fe) of the complex, $[\{\mathrm{Fe(FAnato)_2(Dipy)_{2\times 1/2}}\}_n]$. Anal. Calc. for $(\mathrm{C_{38}H_{34}O_4N_2Fe_3})_n$: C, 60.84; H, 4.54; N, 3.74%. Found: C, 60.71; H, 4.59; N, 3.68%.

2.5. X-ray crystallography

A dark red needle-plate crystal complex, $[\mathrm{Fe(FAnato)_2(Py)_2}]$, having dimensions 0.40 × 0.20 × 0.10 mm was mounted on Rigaku AF C6S Diffractometer with graphite monochromatized Mo–$\mathrm{K_\alpha}$ radiation ($\lambda = 0.71073$ Å). The intensity data were collected by using symbol ω-2θ scan mode in the range $4° \leq 2\theta \leq 50°$. A variable scan speed 4-16° $\mathrm{min^{-1}}$. Scan range (ω) 1.30°

Table 1
Crystallographic data and experimental parameters for $[\mathrm{Fe(FAnato)_2(Py)_2}]$

Empirical formula	$\mathrm{C_{38}H_{36}Fe_3N_2O_4}$
Formula weight	752.2
Crystal size (mm)	0.40 × 0.20 × 0.10
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	8.212(3)
b (Å)	9.945(2)
c (Å)	19.953(3)
β (°)	98.18(3)
V (Å^3)	1613.0(8)
Z	2
$D_{\text{calc.}}$ (g cm^{-3})	1.549
Absorption coefficient	1.376 mm^{-1}
2h range	4.0–50.0°
Scan type	ω-2θ
Scan speed	Variable; 4.00–16.00° min^{-1}
Scan range (ω)	1.30°
Standard reflections	3 measured every 150 reflections
Index range	$0 \leq h \leq 9$, $-11 \leq k \leq 11$, $-23 \leq l \leq 23$
Reflections collected	4868
Independent reflections	3894 ($R_{\text{int}} = 3.30\%$)
Observed reflections	1676($F > 4.01(F)$)
Absorption correction	Y/A
Number of parameters refined	214
Final R indices (obs. data)	$R = 7.05\%; WR = 8.03\%$
R indices (all data)	$R = 12.69\%; WR = 9.40\%$
Largest and mean Δ/σ	0.682,0.079
Data-to-parameter ratio	7.8:1
Largest difference peak	0.55 e Å^{-3}
Largest difference hole	−0.72 e Å^{-3}

$R = \Sigma|(F_\mathrm{o} - F_\mathrm{c})|/\Sigma|F_\mathrm{o}|$, $Rw = \Sigma\sqrt{W}|(F_\mathrm{o} - F_\mathrm{c})|/\Sigma N\varpi|F_\mathrm{o}|$.

Table 2
Selected atomic coordinates ($\times 10^4$) and U_{eq}^{a} (Å$^2 \times 10^3$) for [Fe(FAnato)$_2$(Py)$_2$]

Atom	x	y	z	U_{eq}
Fe(1)	0	0	0	28(1)
Fe(2)	−2359(2)	3065(2)	2205(1)	52(1)
Plane I				
C(1)	−514(11)	1857(8)	1943(4)	37(3)
C(2)	127(13)	2868(10)	2442(5)	52(4)
C(3)	−612(13)	2629(11)	3036(5)	55(4)
C(4)	−1725(14)	1590(11)	2912(4)	58(4)
C(5)	−1668(12)	1073(9)	2240(4)	48(4)
Plane II				
O(1)	949(7)	1879(5)	−103(3)	34(2)
O(2)	−518(7)	638(5)	940(3)	33(2)
C(16)	−102(10)	1720(8)	1235(4)	36(3)
C(17)	682(11)	2791(8)	961(4)	40(3)
C(18)	1137(10)	2825(8)	319(5)	38(3)
Plane III				
N(1)	−2499(9)	743(7)	−458(3)	35(3)
C(11)	−2874(11)	2051(10)	−485(5)	53(4)
C(12)	−4443(13)	2532(11)	−696(6)	63(4)
C(13)	−5696(13)	1659(12)	−879(5)	62(4)
C(14)	−5341(12)	314(12)	−864(5)	61(4)
C(15)	−3759(12)	−99(11)	−661(5)	57(4)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

was used. A total of 3894 independent reflections ($R_{int} = 0.033$) was measured, among which 1676 were accepted as observable ($F > 4\sigma(F)$). The intensities were fully corrected for Lp factors and empirical absorption.

The structure was solved by Patterson synthesis using SHELX-86 computer program. One independent Fe atom was located on an E-map. The other non-hydrogen atoms were found in the successive difference Fourier syntheses. The positions of the hydrogen atoms were computerized, and refined with an overall isotropic temperature factor. All non-hydrogen atoms were refined with anisotropy thermal parameter.

The structure determinations are summarized in Table 1. Selected atomic coordinates are given in Table 2. Selected bond lengths, bond angles, and dihedral angles are listed in Table 3, respectively.

3. Results and discussion

According to our previous paper [17], photolysis of FA will make the charge transfer from metal to acylclopentadienyl group, leading to yield the cyclopentadienylacetonate anion (CAnate), $C_5H_4C(O^-)CHC(O)CH_3$, and free iron(II) cation. We originally assumed that the former would act as a β-diketonate ligand to co-ordinate the latter, forming the complex [Fe(CAnato)$_2$(Py)$_2$] in the presence of Py, but beyond our expectation the photoproduct **1** was the complex [Fe(FAnato)$_2$(Py)$_2$], in which the deprotonated ferrocenylacetylacetonate anion (FAnate) as ligand replaced the photo-liberated CAnate, and the later protonized as photo-product **2**, cyclopentadienyl acetylacetone (CA), existed in MeCN reaction solution.

Similarly, the photolysis of FA with Dipy in MeCN solution has also been examined, the photoproduct was a red–brown polynuclear complex, [{Fe(FAnato)$_2$ (Dipy)$_{2\times 1/2}$}$_n$] precipitated from the solution upon irradiation.

3.1. Structural features of the photoproduct 1

An ORTEP drawing for the structure of photoproduct **1**, [Fe(FAnato)$_2$(Py)$_2$], was presented in Fig. 1 together with the atomic labeling scheme. It can be considered to be *trans*-dipyridine adduct of iron(II) β-diketonate compound. The Fe(II) ion liberated photochemically from the cleavage of ferroceny group in the FA molecule, is *trans* coordinated by two Py molecules, with the remaining sites occupied by two bidentate ferrocenylacetylacetonate anions (FAnate). The coordinated polyhedron of the Fe(II) center is a perfect octahedron coordinated by four oxygen atoms of two FAnates and two nitrogen atoms of both Pys in *trans* position. The three Cartesian axes (O(2)–Fe(1)–

Table 3
Selected bond lengths (Å), bond angles (°) and dihedral angles (°) for [Fe(FAnato)$_2$(Py)$_2$]

C(1)–C(2)	1.460(12)	Fe(1)–O(1)	2.046(5)
C(2)–C(3)	1.425(15)	Fe(1)–O(2)	2.080(5)
C(3)–C(4)	1.378(15)	O(1)–C(18)	1.257(10)
C(4)–C(5)	1.442(13)	C(17)–C(18)	1.385(14)
C(1)–C(5)	1.420(13)	C(16)–C(17)	1.396(12)
C(1)–C(16)	1.504(13)	O(2)–C(16)	1.251(9)
Fe(1)–N(1)	2.249(7)		
N(1)–C(11)	1.336(12)		
C(11)–C(12)	1.382(14)		
C(12)–C(13)	1.357(15)		
C(14)–C(15)	1.367(14)		
N(1)–C(15)	1.349(12)		
N(1)–Fe(1)–N(1A)	180.0(1)	Plane I/Plane II 16.9°[a]	
O(1)–Fe(1)–O(1A)	180.0(1)	Plane II/Plane III 84.8°	
O(1)–Fe(1)–O(2A)	180.0(1)		
N(1)–Fe(1)–O(1A)	90.1(2)		
O(1)–Fe(1)–N(1A)	90.1(2)		
O(1)–Fe(1)–N(1)	89.9(2)		
O(1A)–Fe(1)–N(1A)	89.9(2)		
O(2)–Fe(1)–N(1)	88.5(2)		
O(2A)–Fe(1)–N(1A)	88.5(2)		
N(1)–Fe(1)–O(2A)	91.5(2)		
O(2)–Fe(1)–N(1A)	91.5(2)		
O(1)–Fe(1)–O(2A)	93.4(2)		
O(2)–Fe(1)–O(1A)	93.4(2)		
O(1)–Fe(1)–O(2)	86.6(2)		
O(1A)–Fe(1)–O(2A)	86.6(2)		

[a] Plane I, defined by atoms C(1), C(2), C(3), C(4), C(5). Plane II, O(1), O(2), C(16), C(17), C(18), C(19). Plane III, N(1), C(11), C(12), C(13), C(14), C(15).

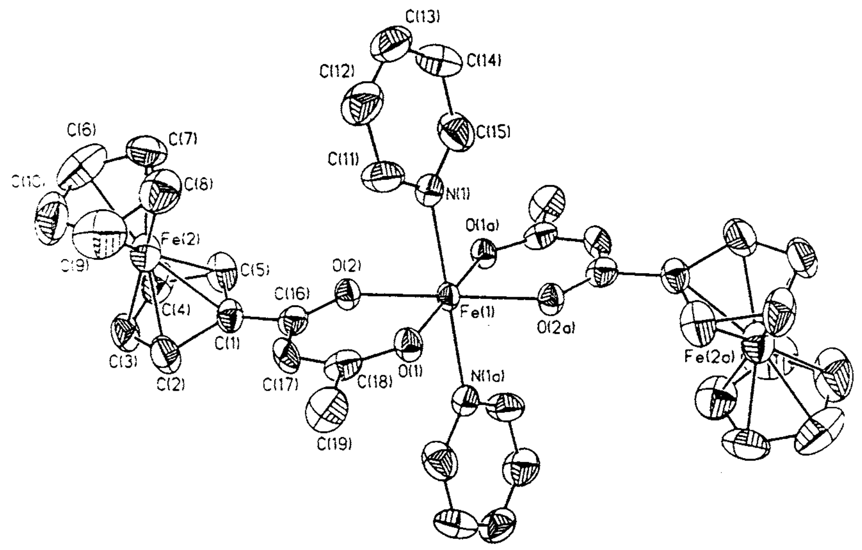


Fig. 1. ORTEP drawing and atom numbering scheme of the photoproduct **1**, $[Fe(FAnato)_2(Py)_2]$.

O(2A), O(1)–Fe(1)–O(1A), N(1)–Fe(1)–N(1A)) are linear, the bond angles being 180.0° (Table 3). The angles between O–Fe(1) and N–Fe(1) within the coordination octahedron are slightly distorted, all of them being close to 90° with deviation below 4°. The equatorial Fe–O distances (2.080 and 2.046 Å) are nearly equal; and both axial Fe–N distances (2.249Å) are elongated. The chelate rings of the β-diketonate are coplanar, which contains the metal as well. The deviations of each atom from this plane are: 0.0110 Å (O1), − 0.0093 Å (O2), 0.0092 Å (C16), 0.0033 Å (C17), − 0.0141 Å (C18), − 0.0120 Å (C19), 0.0000 Å (Fe1). The two Py rings lie in the mirror plane passing between the two acetylacetonate ligands in the eclipsed configuration as observed in the *trans*-bipyridine adduct of bis(pentane-2,4-dionato)nickel(II), $[Ni(AA)_2(Py)_2]$ [20].

The dihedral angle between the β-dionato chelate ring and Py ring is 84.8° (Table 3).

The structure of the symbol β-dionato chelate ring has been determined many times and these bond distances and angles are as expected [20,21].

3.2. IR spectroscopy

The IR spectra of $[Fe(FAnato)_2(Py)_2]$ shows characteristic bands at 3100 and 480 cm^{-1} due to $\nu_{(C-H)}$, and $\nu_{(Fe\text{-}ring)}$ vibrations of cyclopentadienyl group and metal-ring modes, respectively.

The IR bands in the region 1500–1600 cm^{-1} for the complex can be explained to be due to the coupling of the C=C (aromatic) vibration and the C=O and C=C vibrations of the 1,3-diketonato anion. This indicates O,O bonding of the β-diketon to Fe(II) in the complex [22].

The absorption due to coordinated Py appeared in the region 1000–1025 cm^{-1} [23]. The absorptions at 1630 cm^{-1} could be attributed to the $\nu_{(C=N)}$ vibration mode from the Py group. This band appears at 1612 cm^{-1} in the free ligand, the increase observed in the wave number may be related to the π-back-donation from the metal orbitals to the ligand ones.

It is to be pointed out that the IR spectra of the polynuclear complex, $[\{Fe(FAnato)_2(Dipy)_{2\times 1/2}\}_n]$, are completely consistent with the photoproduct **1** in the main characteristic absorptions. This implicates that both complexes have similar coordination mode, as shown in Fig. 2. Additional support for this suggestion is given by the elemental analysis which is in good agreement with the molecular formula.

3.3. GC–MS analysis of photoproduct 2

The cyclopentadienyacetylacetone (CA) as photoproduct **2** existed in the MeCN solution, which was characterized by GC–MS analysis. Its molecular ion peak with $m/z = 150$ and the peaks corresponding to the fragment ions were detected, MS (EI), m/z (M^+, relative intensity): 150 (M^+, 100), 135 (M^+–CH_3, 56),

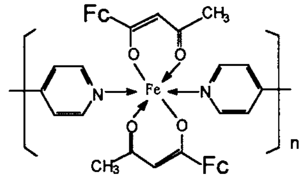
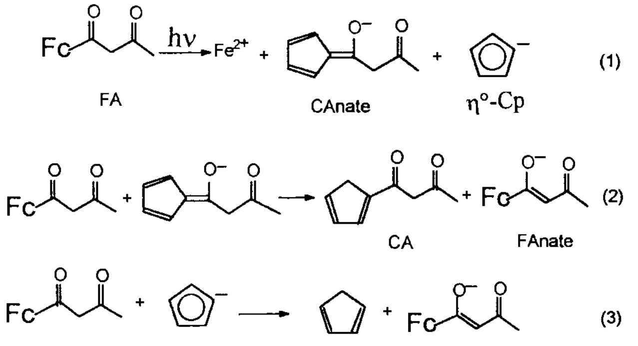


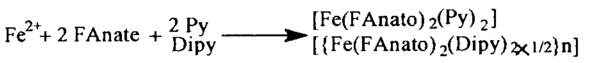
Fig. 2. Proposed structure for the polynuclear photoproduct, $[\{Fe(FAnato)_2(Dipy)_{2\times 1/2}\}_n]$, (Fc = ferrocenyl).

85 (M^+–C_5H_5, 50), 65 (M^+–$C(O)CH_2(O)CH_3$, 85), 43 (M^+–$C_5H_5C(O)CH_2$, 50).

3.4. Mechanism of the photochemical reactions

The photoproducts of FA in the presence of Py or Dipy are the complexes [Fe(FAnato)$_2$(Py)$_2$] or [{Fe(FAnato)$_2$(Dipy)$_{2\times 1/2}$}]$_n$ as well as cyclopentadieneacetylacetone (CA) and 1,3-cyclopentadiene (C_5H_6). Consequently, the photo-reactions probably involve three steps: the first is the photo-induced charge transfer from metal to ferrocenoylgroup resulting in the deligation of the ferrocenes (Eq. 1), and the second process is the proton-transfer from FA to CAnate and $\eta°$-bonded Cp ring ($\eta°$-Cp), yielding the CA and 1,3-cyclopentadiene (Eqs. 2 and 3). Apparently, the proton affinity of CAnate and Cp ring may be larger than FAnate, this would be favorable to the proton-transfer process and the third process is the complex formation (Eq. 4). Therefore, the decisive factor for the photo-ligand exchange of FA is the photo-induced charge transfer from metal to the ferrocenoyl group.





$$Fe^{2+} + 2\,FAnate + \begin{matrix} 2\,Py \\ Dipy \end{matrix} \longrightarrow \begin{matrix} [Fe(FAnato)_2(Py)_2] \\ [\{Fe(FAnato)_2(Dipy)_{2\times 1/2}\}n] \end{matrix} \qquad (4)$$

4. Supplementary material

A complete table of crystallographic data, bond distance, bond angles, dihedral angles, atomic positional and thermal parameters, GC–MS, as well as the IR spectra of photoproducts are available.

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