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Synthesis, structure and electrochemistry of new diferrocenyl pyridine derivatives

Ya-Qi Wang, Li-Min Han, Quan-Ling Suo *, Ning Zhu, Jian-Min Hao, Rui-Jun Xie

Chemical Engineering College, Inner Mongolia University of Technology, Hohhot 010051, PR China

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ABSTRACT

Four diferrocenyl pyridine derivatives, 4,6-diferrocenyl-2-phenylpyridine (**1**), 3,6-diferrocenyl-2-phenylpyridine (**2**), 4,6-diferrocenyl-2-methylpyridine (**3**) and 3,6-diferrocenyl-2-methylpyridine (**4**) were synthesized via dicarbonylcyclo pentadienylcobalt or $Co_2(CO)_6(\mu_2\text{-}\eta^2\text{-ferrocenylacetylene})$ mediated [2+2+2] cycloaddition reaction and characterized by FT-IR, NMR, MS, CV, elemental analysis and X-ray single crystal diffraction analysis (**1**, **2**, **3**). Compounds **1**, **2**, **4** are new diferrocenyl pyridine derivatives and the molecular structures of **1**, **2**, **3** have been determined for the first time. It has been shown that cobalt-mediated [2+2+2] cycloaddition reaction is an efficient, simple new method to prepare diferrocenyl pyridine derivatives. The electrochemistry results reveal that the electronic communication between the two nonequivalent ferrocenyl units in **1**–**4** is electrostatic interactions.

1. Introduction

The ferrocenyl-substituted pyridines with perfect redox-active termini have attracted considerable attention due to their high thermal stability and excellent electrochemical reversibility of Fe^{II}/Fe^{III} redox couple in ferrocene [1–5]. They can be applied to the design of liquid crystal materials and molecular devices [6–8]. It is known from the literature that C–C cross-coupling reaction is a classic method in the synthesis of ferrocenyl-containing pyridines, such as Suzuki, Nigishi and Stille coupling reaction [9–16]. These coupling reactions could prepare the pyridine derivatives bearing ferrocenyl groups in certain positions by reacting appropriate pyridylhalides with ferrocenyl metal-salt intermediates which require laborious preparation. However, the vast majority of known ferrocenyl pyridines only contain a single ferrocenyl unit, and a few of them have two or more ferrocenyl units [17]. The studies on the chemical, physical, and electrochemical properties of diferrocenyl pyridines are relatively rare, especially for the diferrocenyl pyridines with other substituents. Therefore, an efficient method to synthesize diferrocenyl pyridines would be helpful in the deeper research of these compounds.

[2+2+2] Cycloaddition reaction is an atom-efficient, powerful and straightforward route to substituted pyridine derivatives [18–20]. Our research team has reported a new method to synthesize diferrocenyl benzene derivatives through the cycloaddition reactions of alkynes with cobalt cluster $Co_2(CO)_6(l\mu^2\text{-alkyne})$ [21], which the substituted positions of ferrocenyl groups in the benzene ring could be effectively controlled. It inspired us to try cycloaddition reactions of nitriles with Fc-C≡CH (Fc = ferrocenyl) to prepare diferrocenyl pyridine derivatives. Four diferrocenyl pyridine derivatives **1–4** were obtained when $Co_2(CO)_6(\mu_2\text{-}\eta^2\text{-FcC}{\equiv}\text{CH})$ was used as a catalyst in [2+2+2] cycloaddition reactions of ferrocenylacetylene with benzonitrile or acetonitrile.

In this paper, the synthesis, molecular structure and electrochemical property of **1–4** are reported.

2. Experimental

2.1. General procedures

All reactions and operations were carried out under an atmosphere of purified argon using standard Schlenk techniques. Solvents and reagents were purified, dried or distilled prior to use. Fc-C≡CH and $Co_2(CO)_6(\mu_2\text{-}\eta^2\text{-FcC}{\equiv}\text{CH})$ were prepared using the reported literature procedures [22,23]. $CpCo(CO)_2$ (Cp = cyclopentadienyl) was purchased from Alfa-Aesar Chem. and used as received. All reactions were monitored with thin-layer chromatography (TLC). Column chromatographic separations and purifications were performed on 200–300 mesh silica gel or neutral alumina.

^1H and ^{13}C NMR were recorded on a Bruker Avance-500 MHz spectrometer. FT-IR spectra were recorded on a Nicolet FT-IR spectrometer using KBr discs. Elemental analyses were carried out on an Elementar var III-type analyzer. Mass spectra were determined using a Shimadzu LCMS-2020 instrument.

Cyclic voltammetry was performed on a CHI-760C electrochemical analyzer using a platinum disk working electrode, an Ag|AgCl reference electrode and a platinum wire auxiliary electrode. The working electrode surface was polished with 0.05 μm alumina

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* Corresponding author. Tel./fax: +86 471 6575675.
E-mail addresses: szj010062@163.com, szj@imut.edu.cn (Q.-L. Suo).

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Table 1
Optimization results of cycloaddition reaction via cobalt catalysts.

Entry	Catalyst	Conversion (%)	Yield (%)[d]			Selectivity (%)		
		Fc-C$\equiv$CH	**1**	**2**	**5**	**1**	**2**	**5**
1[a]	CpCo(CO)$_2$	48.0	13.9	6.2	23.7	28.9	12.7	49.6
2[a]	Co$_2$(CO)$_6$(μ_2-η^2-FcC$\equiv$CH)	55.5	7.2	3.4	34.8	12.8	6.1	62.9
3[a]	Co$_2$(CO)$_8$	100	0	0	55.3	0	0	55.3
4[a]	CoCl$_2$	0	0	0	0	0	0	0
5[a]	Cobalt powder	0	0	0	0	0	0	0
6[b]	CpCo(CO)$_2$	100	51.3	21.6	10.3	51.3	21.6	10.3
7[b]	Co$_2$(CO)$_6$(μ_2-η^2-FcC$\equiv$CH)	85.1	8.4	4.1	38.2	9.9	4.9	44.9
8[c]	Co$_2$(CO)$_6$(μ_2-η^2-FcC$\equiv$CH)	100	0	0	94.9	0	0	94.9

[a] Fc-C$\equiv$CH:PhCN = 1:1.
[b] The reaction was carried out under the optimized conditions; Fc-C$\equiv$CH:PhCN = 1:6.
[c] Co$_2$(CO)$_6$(μ_2-η^2-FcC$\equiv$CH) as reactant reacted with PhCN; Co$_2$(CO)$_6$(μ_2-η^2-FcC$\equiv$CH):PhCN = 1:12.
[d] Isolated yield.

before each run. The samples of **1–4** were dissolved in a mixture of CH$_3$CN and CH$_2$Cl$_2$ with concentration 5.0×10^{-4} M. The supporting electrolyte was tetra-n-butylammonium hexafluorophosphate (TBAHFP, 0.01 M). The scan rate was 0.1 V/s. Oxygen was purged from the one-compartment cell before each electrochemical run.

Chromatographic analyses were realized by a Shimadzu SLC-10A High Performance Liquid Chromatography with a C18 column (methanol used as the mobile phase) and an UV–Vis detector.

2.2. Synthesis

*2.2.1. Synthesis of compounds **1**, **2***

2.2.1.1. Method I. Fc-C$\equiv$CH (100 mg, 0.48 mmol, 1 equiv.), benzonitrile (300 μL, 3.0 mmol, 6 equiv.), CpCo(CO)$_2$ [10 μL, 0.07 mmol, Co (15 mol.%)] and toluene (10 mL) were placed in a Schlenk flask, then the reaction mixture was refluxed for 5 h.

2.2.1.2. Method II. Fc-C$\equiv$CH (100 mg, 0.48 mmol, 1 equiv.), benzonitrile (300 μL, 3.0 mmol, 6 equiv.) and Co$_2$(CO)$_6$(μ_2-η^2-FcC$\equiv$CH) [18 mg, 0.035 mmol, Co (15 mol.%)] were dissolved in toluene (10 mL). The reaction solution was stirred for 5 h at 110 °C.

In a general procedure, the solvent was removed under vacuum and the residue was purified by silica gel column chromatography using a mixture of petroleum ether and ethyl acetate (20:1, V/V) as eluent. The 1:1 co-crystals (**I**) of compound **1** and compound **2**, the byproduct 1,2,4-triferrocenylbenzene (**5**), were obtained. The co-crystals **I** was further separated by PTLC (a mixture of petroleum ether and ethyl acetate, 200:1, V/V) to give the pure **1** and **2**. The orange crystals of co-crystals **I** and compounds **1, 2** were obtained by recrystallizing technique.

Compound **1**: 64 mg (yield, 51%, Method I) and 10 mg (yield, 8%, Method II). M.p. 171–172 °C; ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.16 (s, 1H, pyridyl), 8.15 (s, 1H, pyridyl), 7.59–7.40 (m, 5H, Ph = phenyl), 5.07–4.08 (m, 18H, Fc); ^{13}C NMR (500 MHz, CDCl$_3$): δ 158.70, 156.35, 148.72, 115.35, 114.35 (pyridyl), 139.88, 128.74, 128.59, 126.93 (Ph), 84.51, 82.03, 69.96, 69.74, 69.65, 67.58, 66.92 (Fc); FT-IR (KBr disk, cm^{-1}): 3131 (ν_{CH}, Cp), 1598, 1549 ($\nu_{C=C}$, Ph), 1401 ($\nu_{C=C}$, Cp), 1107, 1003 (δ_{CH}, Cp), 820 (γ_{CH}, Cp); ESI-MS (CH$_2$Cl$_2$, *m/z*): 524.10 [M+1]$^+$; *Anal.* Calc. for C$_{31}$H$_{25}$Fe$_2$N: C, 71.16; H, 4.82; N, 2.68. Found: C, 71.33; H, 4.78; N, 2.67%.

Compound **2**: 27 mg (yield, 22%, Method I) and 5 mg (yield, 4%, Method II). M.p. 180–182 °C; ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.02 (d, *J* = 8.0 Hz, 1H, pyridyl), 7.38 (d, *J* = 8.0 Hz, 1H, pyridyl), 7.43–7.40 (m, 2H, Ph), 7.31–7.29 (m, 3H, Ph), 4.98–4.05 (m, 18H, Fc); ^{13}C NMR (500 MHz, CDCl$_3$): δ 156.16, 156.03, 138.78, 129.37, 117.90 (pyridyl), 141.01, 129.95, 127.57, 127.53 (Ph), 85.47, 84.32, 70.02, 69.72, 69.60, 69.53, 68.12, 67.52 (Fc); FT-IR (KBr disk, cm^{-1}): 3123 (ν_{CH}, Cp), 1582, 1544 ($\nu_{C=C}$, Ph), 1402 ($\nu_{C=C}$, Cp), 1106, 1002 (δ_{CH}, Cp), 821 (γ_{CH}, Cp); ESI-MS (CH$_2$Cl$_2$): *m/z*: 524.10 [M+1]$^+$; *Anal.* Calc. for C$_{31}$H$_{25}$Fe$_2$N: C, 71.16; H, 4.82; N, 2.68. Found: C, 70.85; H, 5.05; N 2.57%.

*2.2.2. Synthesis of compounds **3**, **4***

2.2.2.1. Method III. Fc-C$\equiv$CH (150 mg, 0.71 mmol, 1 equiv.), CH$_3$CN (375 μL, 7.2 mmol, 10 equiv.), CpCo(CO)$_2$ [10 μL, 0.07 mmol, Co (10 mol.%)] and toluene (10 mL) were placed in a Schlenk flask, then the reaction mixture was refluxed for 5 h.

2.2.2.2. Method IV. Fc-C$\equiv$CH (100 mg, 0.48 mmol, 1 equiv.), CH$_3$CN (250 μL, 4.8 mmol, 10 equiv.) and Co$_2$(CO)$_6$(μ_2-η^2-FcC$\equiv$CH) [10 mg, 0.02 mmol, Co (8.2 mol.%)] were dissolved in toluene (10 mL). The reaction mixture was stirred for 5 h at a temperature of reflux.

In a general procedure, the solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography. Elution with a mixture of petroleum ether and ethyl acetate (20:1, V/V) afforded compounds **3**, **4** and **5**. The fuscous red crystals of **3** and **4** were obtained by recrystallizing technique.

Compound **3** has been prepared by a different synthetic route [24], however its molecular structure has not been reported to date.

Compound **3**: 26 mg (yield, 16%, Method III) and 10 mg (yield, 9%, Method IV). M.p. 191–192 °C; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.31 (s, 1H, pyridyl), 6.99 (s, 1H, pyridyl), 4.94–4.07 (m, 18H, Fc), 2.56 (s, 3H, CH$_3$); ^{13}C NMR (500 MHz, CDCl$_3$): δ 158.27, 157.59, 148.01, 117.18, 114.37 (pyridyl), 84.59, 81.88, 69.90, 69.84, 69.59, 67.47, 66.80 (Fc), 24.75 (CH$_3$); FT-IR (KBr disk, cm^{-1}): 3083 (ν_{CH}, Cp), 1599, 1549 ($\nu_{C=C}$, pyridyl), 1407 ($\nu_{C=C}$, Cp), 1105, 999 (δ_{CH}, Cp), 818 (γ_{CH}, Cp); ESI-MS (CH$_2$Cl$_2$, *m/z*): 462.05 [M+1]$^+$; *Anal.* Calc. for C$_{26}$H$_{23}$Fe$_2$N: C, 67.72; H, 5.03; N, 3.04. Found: C, 67.54, H, 5.14, N, 2.88%.

Compound **4**: 8 mg (yield, 5%, Method III) and 3 mg (yield, 3%, Method IV). M.p. 182–183 °C; ^{1}H NMR (500 MHz, CD$_3$OD): δ 8.04 (d, *J* = 6.5 Hz, 1H, pyridyl), 7.49 (d, *J* = 8.0 Hz, 1H, pyridyl), 4.99 (s, 2H, Fc), 4.60–4.09 (m, 16H, Fc), 2.61 (s, 3H, CH$_3$); ^{13}C NMR (500 MHz, CDCl$_3$): δ 155.79, 154.78, 137.32, 129.81, 117.47 (pyridyl), 85.57, 84.55, 69.56, 69.47, 68.36, 67.31 (Fc), 24.48 (CH$_3$); FT-IR (KBr disk, cm^{-1}): 3112 (ν_{CH}, Cp), 1583, 1560 ($\nu_{C=C}$, pyridyl), 1401 ($\nu_{C=C}$, Cp), 1104, 1000 (δ_{CH}, Cp), 820 (γ_{CH}, Cp); ESI-MS (CH$_2$Cl$_2$, *m/z*): 462.05 [M+1]$^+$; *Anal.* Calc. for C$_{26}$H$_{23}$Fe$_2$N: C, 67.72; H, 5.03; N, 3.04. Found: C, 67.45; H, 4.88; N, 2.97%.

Compound **5** (red-orange byproduct 1,2,4-triferrocenylbenzene): M.p. 255–257 °C; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.88–7.34 (m, 3H, Ph), 4.73–4.04 (m, 27H, Cp); ^{13}C NMR (500 MHz CDCl$_3$): δ 136.85, 136.10, 134.96, 131.18, 128.90, 123.64 (Ph), 88.05, 87.46, 85.40, 70.81, 70.48, 69.65, 69.60, 69.45, 69.43, 68.88, 67.29,