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# An effective method for the synthesis of monoferrocenylbenzene derivatives

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## An effective method for the synthesis of monoferrocenylbenzene derivatives

# RUI-JUN XIE<sup>†</sup>, LI-MIN HAN<sup>\*</sup><sup>†</sup>, YUAN-YUAN GAO<sup>‡</sup>, NING ZHU<sup>†</sup>, HAI-LONG HONG<sup>†</sup> and QUAN-LING SUO<sup>†</sup>

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Three new ferrocenylbenzene derivatives, 1-ferrocenyl-2,3,4,5-tetramethylbenzene (1), 1-ferrocenyl-2,4-diphenylbenzene (2), and 1-ferrocenyl-2,4-ditrimethylsilylbenzene (3), were synthesized by cycloaddition of ferrocenylacetylene cobalt cluster with different alkynes and characterized by elemental analysis, FT-IR, NMR, and MS. The molecular structures of 2 and 3 were identified by single-crystal X-ray diffraction. The oxidation potentials of ferrocenyl unit in these compounds were investigated by cyclic voltammetry and theoretical calculations. The results indicated that the electron-donating or electron-withdrawing effect of substituents on the central phenyl was the key factor that influenced the oxidation potential of the ferrocenyl unit.

Keywords: Ferrocenylbenzene derivatives; Ferrocenylacetylene cobalt cluster; Oxidation potential

#### 1. Introduction

Since aryl-ferrocene derivatives can be used in nonlinear optical materials [1], magnetic materials [2], biology, pharmacy [3], and asymmetric catalysis [4], attention has grown for synthesis of aryl-ferrocene derivatives. Several methods have been reported for synthesis of aryl-ferrocenes. The typical method is cross-coupling, such as arylation of ferrocene with aryldiazonium salts [5–8], the Negishi reaction of halobenzenes and ferrocenylzinc chloride with Pd(PPh<sub>3</sub>)<sub>4</sub> as catalyst [9], the Suzuki reaction of ferrocenylboronic acid and halobenzenes with PdCl<sub>2</sub> derivatives as catalyst [10], the Stille reaction of ferrocenyl mercury with halobenzenes [11], and the Pd-catalyzed cross-coupling of diferrocenyl mercury with halobenzenes [12]. The classical method is cycloaddition, such as the transition metal catalyzed [2+2+2] cycloaddition with ferrocenylacetylene [13–15], the [2+4] cycloaddition Diels–Alder reaction between tetraphenylcyclopentadienone and ferrocenylacetylene derivatives [16, 17] and the

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[3+3] cyclization reaction by using  $1-\eta^5$ -ferrocenyl-3,3-bis(methylthio)prop-2-en-1ones as the 1,3-electrophile [18]. Another method is reaction of tetraalkylcyclobutadiene–AlCl<sub>3</sub> complexes with 3-ferrocenylpropynoates [19].

Cobalt complex-catalyzed cycloaddition of acetylenes were reported by Krüerke, and a rational catalytic reaction mechanism was proposed (scheme 1) simultaneously [20]. Although  $Co_2(CO)_8$  and acetylene react in one pot, the four-step reactions were carried out. However, several cycloaddition products were produced when two alkynes were used in Krüerke's reaction. Based on this mechanism and our previous work on the synthesis of cobalt clusters [21–23], we decomposed Krüerke's reaction processes. In this article, the intermediate product with monoferrocenyl group,  $Co_2(CO)_6(\mu^2$ ferrocenylacetylene), was synthesized in advance. Then, it was used as a precursor to react with 2-butyne, phenylacetylene, and trimethylsilylacetylene, respectively. Three new monoferrocenylbenzene derivatives were synthesized (scheme 2). The redox potentials of the ferrocenyl unit were investigated by cyclic voltammetry and theoretical calculations, showing the effect of substituents on the central phenyl ring.

#### 2. Experimental

#### 2.1. General procedures

All operations were carried out under an atmosphere of purified argon using standard Schlenk techniques. Octacarbonyl dicobalt, 2-butyne, phenylacetylene,



Scheme 1. Mechanism of Co2(CO)8-catalyzed cycloaddition of alkynes.



1: R<sub>1</sub>=R<sub>2</sub>=CH<sub>3</sub>; 2: R<sub>1</sub>=Ph, R<sub>2</sub>=H; 3: R<sub>1</sub>=Si(CH<sub>3</sub>)<sub>3</sub>, R<sub>2</sub>=H

Scheme 2. Syntheses of 1-3.

and trimethylsilylacetylene were obtained from Alfa-Asia Chem. Ferrocenylacetylene and  $\text{Co}_2(\text{CO})_6(\mu^2$ -ferrocenylacetylene) were prepared according to the previously reported method [24]. Dioxane was distilled under nitrogen over sodium. Reactions were monitored by thin layer chromatography.

IR spectra were measured on a Nicolet FT-IR spectrometer using KBr pellets. Elemental analysis was carried out on an Elementar var III-type analyzer. <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded on a Jeol-Jnm-Al 500FT-MHz spectrometer in CDCl<sub>3</sub>. Mass spectra were determined using a Micromass LCT instrument. The crystal structures of 2 and 3 were measured on a Bruker SMART APEX CCD diffractometer with graphite monochromated Mo-K $\alpha$  ( $\lambda = 0.71073$  Å) radiation. Data were collected using the  $\phi$  and  $\omega$  scan techniques. The structures were solved using direct methods and expanded using Fourier techniques. An absorption correction based on SADABS was applied. Structure solution and refinement were performed using SHELXSL 97 [25]. Cyclic voltammetry experiments were performed on a CHI 760C electrochemical analyzer using a platinum disc of radius 0.8 mm as a working electrode. The electrode surface was polished with  $0.05 \,\mu m$  alumina before each run. The reference electrode was Ag/AgCl and the auxiliary electrode was a coiled platinum wire. The supporting electrolyte used in all electrochemical experiments was tetra-n-butylammonium hexafluorophosphate (TBAHFP) with concentration 0.1 in acetonitrile and dichloromethane (1:1, v:v). Oxygen was purged from the one-compartment cell before the electrochemical run. Calculations were carried out on a personal computer with Gaussian 03 program package.

#### 2.2. Synthesis of 1-ferrocenyl-2,3,4,5-tetramethylbenzene (1)

Co<sub>2</sub>(CO)<sub>6</sub>( $\mu^2$ -ferrocenylacetylene) (112.6 mg, 0.227 mmol) and 2-butyne (0.036 mL, 0.46 mmol) were dissolved in dioxane (10 mL) at 0°C. The reaction solution was stirred for 1 h at 0°C and 3 h at 70°C, then cooled to room temperature. The solvent was removed in vacuum. The residues were dissolved in a minimum of dichloromethane and subjected to chromatographic separation on a neutral alumina column ( $\Phi = 2.0 \times 30.0$  cm. Elution with a mixture of hexane and dichloromethane (3 : 1, v/v) afforded a yellow band (1). Crystals of **1** were obtained by recrystallizing from a mixture of hexane and dichloromethane. Yield: 73.0%; m.p. 90–91°C. Anal. Calcd for C<sub>20</sub>H<sub>22</sub>Fe: C, 75.48; H, 6.97. Found: C, 75.19; H, 6.38. IR (KBr, disc): 3093.19 [Cp,  $\nu_{C-H}$ ]; 3007.57 [Ph,  $\nu_{C-H}$ ]; 2918.05, 2859.68 [CH<sub>3</sub>,  $\nu_{C-H}$ ]; 1603.29, 1497.51 [Ph,  $\nu_{C=C}$ ]; 1104.43, 1053.84, 995.35 [Cp,  $\delta_{C-H}$ ]; 820.32 [Cp,  $\gamma_{C-H}$ ]. <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ ): 2.21 [s, 3H, CH<sub>3</sub>–H], 2.22 [s, 3H, CH<sub>3</sub>–H], 2.27 [s, 3H, CH<sub>3</sub>–H], 2.33 [s, 3H, CH<sub>3</sub>–H]; 4.16 [s, 5H, Cp–H], 4.26 [s, 2H, Cp–H], 4.38 [s, 2H, Cp–H]; 7.43 [s, 1H, Ph–H]. <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>,  $\delta$ ): 16.20, 16.69, 17.77, 21.00 [CH<sub>3</sub>]; 67.56, 69.64, 70.61 [Cp]; 130.57, 132.48, 133.04, 133.50, 134.52, 135.45 [Ph]. MS (ESI, relative abundance): 318.3 (M<sup>+</sup>, 100%).

#### 2.3. Synthesis of 1-ferrocenyl-2,4-diphenylbenzene (2)

 $Co_2(CO)_6(\mu^2$ -ferrocenylacetylene) (101.2 mg, 0.204 mmol) and phenylacetylene (0.045 mL, 0.41 mmol) were dissolved in dioxane (10 mL) at room temperature. The solution was stirred for 1 h at room temperature and 3 h at 70°C. The solvent was removed in vacuum. The residues were dissolved in a minimum of dichloromethane and

subjected to chromatographic separation on а neutral alumina column  $(\Phi = 2.0 \times 30.0 \text{ cm})$ . Elution with a mixture of hexane and dichloromethane (5:1, v/v) afforded a yellow band (2). Crystals of 2 were obtained by recrystallizing from a mixture of hexane and dichloromethane. Yield: 72.6%; m.p. 185-186°C. Anal. Calcd for  $C_{28}H_{22}Fe: C, 81.17; H, 5.35.$  Found: C, 81.30; H, 5.48. IR (KBr, disc): 3085 [Cp,  $\nu_{C-H}$ ]; 3050 [Ph,  $\nu_{C-H}$ ]; 1602, 1485 [Ph,  $\nu_{C=C}$ ]; 1108, 999 [Cp,  $\delta_{C-H}$ ]; 820 [Cp,  $\gamma_{C-H}$ ]; 761, 695 [Ph,  $\gamma_{C-H}$ ]. <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ ): 4.06 [s, 5H, Cp–H], 4.08 [s, 2H, Cp–H], 4.11 [s, 2H, Cp-H]; 7.20-7.35 [m, 6H, Ph-H], 7.42-7.46 [m, 3H, Ph-H], 7.58 [d, 1H, J=8.0 Hz, central Ph–H], 7.58 [d, 2H, J = 7.5 Hz, Ph–H], 7.91 [d, 1H, J = 8.0 Hz, central Ph–H]. <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>, δ): 68, 69, 70, 86 [Cp], 125, 126, 127, 127, 128, 128, 129, 129, 131, 136, 138, 140, 141, 142 [Ph]. MS (ESI, relative abundance): 414.2 (M<sup>+</sup>, 100%).

#### 2.4. Synthesis of 1-ferrocenyl-2,4-ditrimethylsilylbenzene (3)

 $Co_2(CO)_6(\mu^2$ -ferrocenylacetylene) (96.3 mg, 0.194 mmol) and trimethylsilylacetylene (0.056 mL, 0.4 mmol) were dissolved in dioxane (10 mL) at room temperature. The solution was stirred for 1 h at room temperature and 3 h at 70°C and then cooled to room temperature. The solvent was removed in vacuum. The residues were dissolved in a minimum of dichloromethane and subjected to chromatographic separation on a neutral alumina column ( $\Phi = 2.0 \times 30.0$  cm. Elution with a mixture of hexane and dichloromethane (5:1, v/v) afforded a yellow band (3). Crystals of 3 were obtained by recrystallizing from a mixture of hexane and dichloromethane. Yield: 68.4%; m.p. 105-106°C. Anal. Calcd for C<sub>22</sub>H<sub>30</sub>FeSi<sub>2</sub>: C, 65.00; H, 7.44. Found: C, 65.25; H, 7.18. IR (KBr, disc): 3093 [Cp,  $\nu_{C-H}$ ]; 3046 [Ph,  $\nu_{C-H}$ ]; 2953, 2890 [CH<sub>3</sub>,  $\nu_{C-H}$ ]; 1579, 1497 [Ph, ν<sub>C=C</sub>]; 1248 [Si(CH<sub>3</sub>)<sub>3</sub>, δ<sub>C-H</sub>]; 1123, 1061, 1003 [Cp, δ<sub>C-H</sub>]; 855 [Si(CH<sub>3</sub>)<sub>3</sub>, ν<sub>Si-C</sub>]; 828 [Cp, γ<sub>C-H</sub>]. <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>, δ): 0.07 [s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>-H], 0.30 [s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>–H]; 4.20 [s, 5H, Cp–H], 4.26 [s, 2H, Cp–H], 4.41 [s, 2H, Cp–H]; 7.94 [d, 1H, J = 7.5 Hz, Ph–H], 7.64 [s, 1H, Ph–H], 7. 55 [dd, 1H,  $J_1 = 7.5$  Hz,  $J_2 = 1.0$  Hz, Ph–H]. <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>,  $\delta$ ): -1 [Si(CH<sub>3</sub>)<sub>3</sub>], 0.96 [Si(CH<sub>3</sub>)<sub>3</sub>]; 67, 69, 71, 93 [Cp]; 131, 133, 137, 138, 139, 145 [Ph]. MS (ESI, relative abundance): 406.3 (M<sup>+</sup>, 100%).

#### 3. Results and discussion

#### 3.1. Syntheses of 1-3

If  $Co_2(CO)_8$ -catalyzed cycloaddition reactions of ferrocenylacetylene and other alkynes (2-butyne, phenylacetylene or trimethylsilylacetylene) were carried out in one pot, self-cycloaddition or co-cycloaddition occurs; the molar ratio of alkynes may be different (1:2 or 2:1) in co-cycloaddition reactions. These reactions are seldom specific; products are varied and difficult to separate (scheme 3).

In this article, to obtain monoferrocenyl-substituted benzene, the monoferrocenyl cobalt carbonyl cluster  $\text{Co}_2(\text{CO})_6(\mu^2$ -ferrocenylacetylene) was synthesized first, then used as a reaction precursor to perform cycloaddition with other alkynes, and the molar ratio of  $\text{Co}_2(\text{CO})_6(\mu^2$ -ferrocenylacetylene) and alkynes was controlled strictly in 1:2. Only the 1,2,4-substituted benzenes were obtained and 1,3,5-substituted benzenes were



R<sub>1</sub> = CH<sub>3</sub>, Ph, Si(CH<sub>3</sub>)<sub>3</sub>; R<sub>2</sub> = CH<sub>3</sub>, H, H.

Scheme 3. The Co<sub>2</sub>(CO)<sub>8</sub>-catalyzed cycloaddition of different alkynes in one pot.

not found in reactions of 2 and 3. This may be ascribed to steric hindrance. The reactions carried out in this work are illustrated in scheme 2.

#### 3.2. Characterizations of 1–3

The three compounds were confirmed by FT-IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, elemental analysis, and MS (data listed in section 2). The molecular structures of **2** and **3** were determined by single-crystal X-ray diffraction (figures 1 and 2). Crystal data and relevant structural parameters are enumerated in table 1. Selected bond lengths and torsion angles are listed in table 2.

Both 2 and 3 crystallize in the monoclinic space group C2/c. The average C–C bond lengths in Fc units are 1.41 Å, while the average Fe–C bond lengths are 2.04 Å. The length from Fe to Cp ring plane is 1.643 to 1.650 Å. There is no significant difference from other ferrocenyl groups. The dihedral angle of two Cp ring planes in each ferrocene of 2 and 3 is 0.82° and 2.46°, indicating the Cp rings are nearly parallel. The dihedral angles of Cp ring plane to central phenyl ring plane in 2 are 41.54° and 51.90°. The maximum torsion angle of central benzene rings in 2 and 3 is 2.69° (table 2), showing that six carbons of phenyl are approximately co-planar. Ferrocenes are attached to the central phenyl ring with bonds lengths of C<sub>9</sub>–C<sub>11</sub> 1.484 Å (2) and C<sub>3</sub>–C<sub>4</sub> 1.481 Å (3).

As expected, chemical shifts of protons on the central phenyl are sensitive to the electron-withdrawing or electron-donating effect of substituent groups. For example, **1** with four electron-donating substituents (methyl) on the central phenyl has proton NMR of central benzene ring at 7.43 ppm, upfield from ferrocenylbenezene. The central phenyls of **2** and **3** are substituted by strong electron-withdrawing groups (phenyl and trimethylsilyl), so the proton NMR of central benzene shows downfield shift at 7.58–7.91 ppm and 7.55–7.94 ppm, respectively.

#### 3.3. Electrochemistry

Oxidation potential and reversibility of 1-3 and ferrocenylbenzene (FcB) were determined by cyclic voltammetry (synthesis and characterization of FcB are seen in



Figure 1. Molecular structure of 2.



Figure 2. Molecular structure of 3.

Compounds	2	3
Empirical formula	$C_{28}H_{22}Fe$	C <sub>22</sub> H <sub>30</sub> FeSi <sub>2</sub>
Formula weight	414.31	406.49
Temperature (K)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	C2/c
Unit cell dimensions (Å, °)		
a	34.0052(12)	37.105(5)
b	6.0997(2)	6.1225(8)
С	20.8358(6)	22.062(3)
α	90.00	90.00
β	112.690(2)	119.234(2)
γ	90.00	90.00
Volume (Å <sup>3</sup> ), Z	3987.3(2), 8	4373.6(10), 8
Calculated density $(Mg m^{-3})$	1.380	1.235
Absorption coefficient (mm <sup>-1</sup> )	0.768	0.801
F(000)	1728	1728
Crystal size (mm <sup>3</sup> )	$0.15 \times 0.03 \times 0.03$	$0.15 \times 0.05 \times 0.05$
$\theta$ range for data collection (°)	1.30-28.31	1.86-28.24
Limiting indices	$-41 \le h \le 45;$	$-48 \le h \le 40;$
	$-7 \le k \le 8;$	$-7 \le k \le 8;$
	$-26 \le l \le 27$	$-18 \le l \le 28$
Reflections collected	18,964	13,450
Independent reflections	4920	5266
Completeness to $\theta$ (%)	99.4	97.5
Max. and min. transmission	0.8936/0.9773	0.8936/0.9773
Data/restraints/parameters	4920/0/262	5266/0/232
Goodness-of-fit on $F^2$	0.963	1.022
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0513, wR_2 = 0.0859$	$R_1 = 0.0418, wR_2 = 0.1057$
R indices (all data)	$R_1 = 0.1525, wR_2 = 0.1129$	$R_1 = 0.0723, wR_2 = 0.1190$
Largest difference peak and hole $(e \AA^{-3})$	0.327 and -0.511	0.313 and -0.232

Table 1. Crystal data and structural parameters of 2 and 3.

Table 2. Selected bond lengths (Å) and torsion angles (°) of  ${\bf 2}$  and  ${\bf 3}.$ 

1.391(4)	C12-C13	1.374(4)	C13-C14	1.387(4)
1.391(4)	C15-C16	1.395(4)	C16-C11	1.406(4)
1.484(4)	C14-C23	1.480(4)	C11-C16	1.406(4)
0.28	C12-C13-C14-C15	-0.87	C13-C14-C15-C16	0.43
0.61	C15-C16-C11-C12	-1.19	C16-C11-C12-C13	0.78
1.387(3)	C2–C5	1.389(3)	C5–C8	1.378(3)
1.388(3)	C3–C6	1.405(3)	C6-C1	1.401(3)
1.481(3)	C6–Si2	1.882(2)	C2-Si3	1.870(2)
-1.41	C2-C5-C8-C3	0.89	C5-C8-C3-C6	1.27
-2.69	C3-C6-C1-C2	2.24	C6-C1-C2-C5	-0.19
	$\begin{array}{c} 1.391(4)\\ 1.391(4)\\ 1.484(4)\\ 0.28\\ 0.61\\ \end{array}$ $\begin{array}{c} 1.387(3)\\ 1.388(3)\\ 1.481(3)\\ -1.41\\ -2.69\\ \end{array}$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$

"Supplementary material"). The cyclic voltammograms (CVs) of 1-3 and FcB, depicted in figure 3, display one electrochemically reversible redox wave, assigned to the Fe(II)/Fe(III) redox couples. The oxidation potentials of 1, 2, 3, and FcB are 499 mV, 536 mV, 541 mV, and 526 mV, respectively (table 3). The oxidation potential of 1 shifts negatively and the oxidation potentials of 2 and 3 shift positively compared to FcB, indicating the substituent of central phenyl influences oxidation potential of ferrocenyl.



Figure 3. The CVs of 1, 2, 3, and ferrocenylbenzene.

Compounds	Oxidation potential (mV)	Mulliken charge density of "Fe" atom
1	499	0.624
2	536	0.575
3	541	0.561
FcB	526	0.600

Table 3. CV data and Mulliken charge density of 1-3 and FcB.

The difference in oxidation potential can be ascribed to the electron-donating and electron-withdrawing effects of groups on the central phenyl. The electron-donating effect of methyl has been identified by <sup>1</sup>H-NMR of **1** and the protons of the central phenyl shift upfield, so the oxidation potential of **1** is negative to that of **FcB**. The electron-withdrawing effect of phenyl and trimethylsilyl in **2** and **3** can also be identified by <sup>1</sup>H-NMR, and the oxidation potentials of **2** and **3** are positive to that of **FcB**. Configuration of central phenyls were not obviously changed, maintaining planar character. Thus the electron-donating and electron-withdrawing effects of substituents partially transfer to ferrocenyl unit through central phenyl. This result is consistent with that obtained in our previous work [26].

Based upon a starting geometry from the X-ray structure analysis of **2**, **3**, and **FcB**, Mulliken population analyses were carried out using the B3LYP density function and the 6–31G basis set [27]. We also obtained optimized geometry and Mulliken atomic charge of **1** using the B3LYP density function and the 6–31G basis set. The Mulliken atomic charge density of "Fe" in **1**, **2**, **3**, and **FcB** are 0.624, 0.575, 0.561, and 0.600, respectively (table 3), indicating the charge density of iron increased by the electron-donating of methyl in **1**. The charge density of iron was decreased by the electron-withdrawing of phenyl and trimethylsilyl in 2 and 3, consistent with oxidation potentials positive to that of **FcB**.

#### 4. Conclusion

Three monoferrocenylbenzene derivatives, 1-ferrocenyl-2,3,4,5-tetramethylbenzene (1), 1-ferrocenyl-2,4-diphenylbenzene (2), and 1-ferrocenyl-2,4-ditrimethylsilylbenzene (3), were obtained by cycloaddition with  $\text{Co}_2(\text{CO})_6(\mu^2$ -ferrocenylacetylene) as precursor. The oxidation potentials of 1–3 and FcB were investigated by cyclic voltammetry and theoretical calculations; the electron-donating or electron-withdrawing of substituent on the central phenyl affected oxidation potential of the ferrocenyl unit.

#### Supplementary material

Crystallographic data for structures reported in this article in the form of CIF files have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC Nos 816932 and 816930 for **2** and **3**, respectively. Copy of the data can 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).

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