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Synthesis and Electrochemistry of 1,2,4-Triferrocenylbenzene

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1,2,4-Triferrocenylbenzene (TFB) was synthesized by the [$Co_2(CO)_6(\mu_2,\eta_2$-ferrocenyl acetylene)]-catalyzed cyclization reaction of ferrocenyl acetylene. The molecular structure of 1,2,4-triferrocenylbenzene was determined by X-ray single crystal diffraction. The position selectivity of ferrocenyl was interpreted by K-Hübel's mechanism. The electrode reaction behaviours were demonstrated by cyclic voltammetry and microelectrode chronoamperometry.

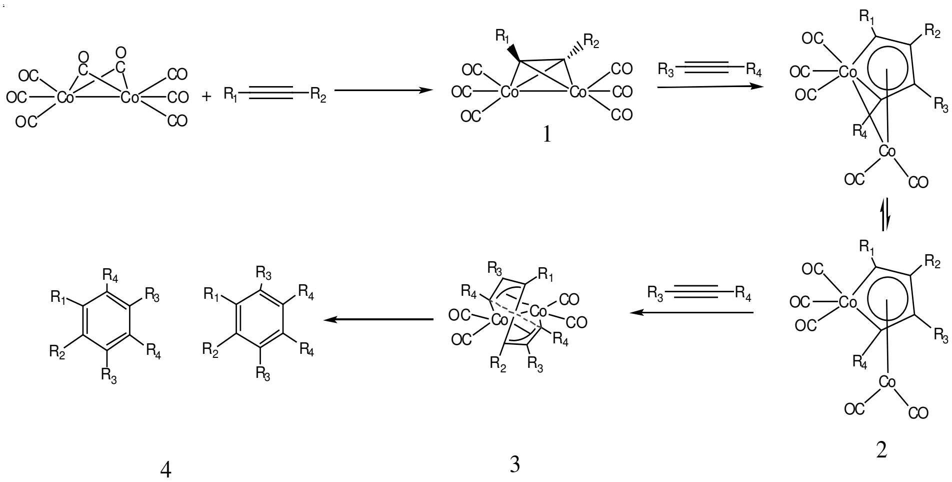
Key Words: 1,2,4-Triferrocenylbenzene, Ferrocenyl acetylene, Trimerization, Selectivity of position, Single crystal structure.

INTRODUCTION

Multi-ferrocenyl compounds, especially, those linear conjugated multiferrocenyl derivatives, have received considerable attentions due to their ideal redox reactions, detectable intravalence charge transfer (IVCT), electron transfer processes[1-4] and their potential applications in the molecular electronic devices[5-7]. Nevertheless, more and more attentions are required for the synthesis and electrochemistry of cross-conjugated multiferrocenyl derivatives. For example, Patoux reported the synthesis and intermolecular electron transfer of various diferrocenylbenzene[8], Yu reported the synthesis and electrochemical properties of 1,3,5-triferrocenylbenzene[9], Vollhardt elucidated the synthesis and intramolecular electronic communication of hexaferrocenylbenzene[10].

Generally, the *n*-ferrocenylbenzene derivatives is synthesized by the cross-coupling reactions of multi-halobenzene and ferrocenylzinc chloride at the Negishi's reaction conditions[10,11], but it is failed for synthesize of *para* and *meta* diferrocnylbenzene[8]. We attempted to prepare 1,2,4-triferrocenylbenzene by this method, but it is also failed. Fortunately, a catalytic reaction mechanism (**Scheme-I**) was proposed by Krüerke and Hübel[12]. While alkyne reacted with octacarbonyldicobalt, a well-known dicobaltatetrahedranes compound **1** was formed (**Scheme-I**). As original catalytic compound, it further reacted with a molecule of alkyne ($R_3C_2R_4$) to form intermediate **2**, then the intermediate **2** reacted with another alkyne ($R_3C_2R_4$) to form a "flyover" structure **3**. The rationality of the mechanism was determined by the successful isolation and X-ray crystallography characterization of intermediate **2**, "flyover" structure **3**[13,14] and trimer of alkyne **4**[15].

Previously, [Co$_2$(CO)$_6$(μ_2,η_2-ferrocenylacetylene)] have been synthesized by our research group[16], which is an analogous species of compound **1** in Krüerke and Hübel's mechanism[12]. In this paper, the preparations of 1,2,4-triferrocenylbenzene by using of [Co$_2$(CO)$_6$(μ_2,η_2-ferrocenylacetylene)] as a catalyst are introduced and the electron transfer processes of 1,2,4-triferrocenylbenzene are also investigated by cyclovoltametry and microelectrode chronoamperometry.



Scheme-I

EXPERIMENTAL

All reactions and manipulations were carried out under an atmosphere of pure argon using standard Schlenk techniques. Reactions were monitored by TLC. Ferrocenyl acetylene and [Co$_2$(CO)$_6$(μ_2,η_2-ferrocenylacetylene)] were prepared according to reported method[16]. Co$_2$(CO)$_8$ was obtained from Alfa-Asia Chem. Benzene, cyclohexane, were distilled under nitrogen over metal sodium. IR spectra were measured on a Nicolet FT-IR spectrometer using KBr pellets. Elemental analyses were carried out on an Elementar var III-type analyzer. ^{1}H, ^{13}C NMR spectra in CDCl$_3$ were recorded on a Jeol-Jnm-Al 500FT-MHz spectrometer. The mass spectra were determined using a Micromass LCT instrument. The electrochemical experiments were performed in dry acetonitrile with a CHI 760C electrochemical analyzer. The crystal structure of compound A was measured on the Bruker SMART APEX CCD diffractometers with graphite monochromated Mo-K$_\alpha$ (λ = 0.71073 Å) radiation. Data were collected at 20 °C using the ϕ and ω scan techniques. The structure was solved by direct methods and expanded using Fourier technique. An absorption correction based on the SADABS was applied. The structure solution and refinement were performed by SHELXSL 97.

Synthesis of 1,2,4-triferrocenylbenzene: The $[Co_2(CO)_6(\mu_2,\eta_2\text{-ferrocenylacetylene})]$ (100 mg 0.156 mmol), ferrocenyl acetylene (66 mg, 0.312 mmol) were added into a stirred cyclohexane under argon, the reaction mixture were subjected to reflux for 6 h, then cooled down to room temperature. The solvent was removed under reduced pressure, the residue was subjected to chromatographic separation on the neutral alumina column (2.0 × 30.0 cm). Elution with a mixture of hexane-CH_2Cl_2 (3:1, v/v) afforded a yellow band. The yellow crystal of (B) was obtained by recrystallizing from hexane-CH_2Cl_2. Yield 85 %; anal. calcd. (%) for $C_{36}H_{30}Fe_3$: C, 68.61; H, 4.79. Found. (%): C, 68.57; H, 4.83. ^1H NMR (500 MHz $CDCl_3$, δH): 4.03-4.75 (27H, (η5-C_5H_5)), 7.34-7.87 (3H, benzene C-H); ^{13}C NMR (500 MHz $CDCl_3$, δc) 66.42-71.19 (Cp carbons), 128.86-136.89 (aromatic carbons); MS (ESI, m/z): 630.05 (M^+).

RESULTS AND DISCUSSION

Crystal molecular stucture of 1,2,4-triferrocenylbenzene: The molecular structure of 1,2,4-triferrocenylbenzene has been established by single-crystal X-ray diffraction analysis. The crystallographic data and parameters for structure refinements are given in Table-1. The selected bond lengths and torsion angles were listed in Table-2. The molecular structure of 1,2,4-triferrocenylbenzene is shown in Fig. 1.

TABLE-1
CRYSTAL DATA (cm^{-1}) OF 1,2,4-TRIFERROCENYL BENZENE

m.f.	$C_{36}H_{30}Fe_3$	Absorption coefficient (nm^{-1})	1.626
m.w.	630.15	θ (°)	1.98-26.00
Crystal system	Monoclinic	B (°)	95.244(3)
Space group	P2(1)/c	$D_{(c)}$	1.560 mg/m^3
a (nm)	181.51(4)	F(000)	1296
b (nm)	124.73(3)	Goodness-of-fit on F^2	0.744
c (nm)	119.03(3)	Final R indices [$I > \sigma(I)$]^a	R1 = 0.0359, wR_2 = 0.06633
V/A	2682.9(11) $Å^3$	Largest diff. peak and hole/(e nm^{-3})	445, 474

TABLE-2
SELECTED BONDS (Å) LENGTH AND ANGLE (°)

C(1)-C(7)	1.480(4)	C(2)-C(3)	1.398(3)	C(4)-C(3)-C(2)	123.0(3)
C(2)-C(12)	1.487(4)	C(3)-C(4)	1.383(3)	C(6)-C(1)-C(7)- C(11)	30.94 (0.14)
C(4)-C(17)	1.474(4)	C(4)-C(5)	1.386(4)	C(21)-C(17)-C(4)- C(3)	2.71 (0.17)
C(6)-C(1)	1.407(3)	C(5)-C(6)	1.368(4)	C(13)-C(12)-C(2)- C(3)	48.35 (0.11)

Unlike the reported c_3-symmetric structure of 1,3,5-triferrocenylbenzene, the molecular structure of 1,2,4-triferrocenylbenzene is a trisubstituted benzene with ferrocenyl groups at the 1, 2 and 4 positions. The C-C bond distances in the centra benzene ring are 1.368(4)-1.407(5) Å lie within the range typical of an aromatic ring system. The bond angles, C(2)-C(1)-C(6) 117.3(3)°, C(1)-C(2)-C(3) 119.4(2)°,

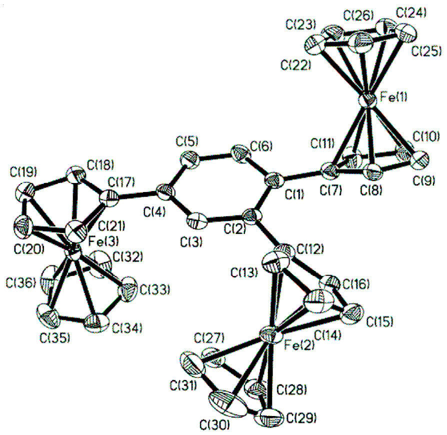


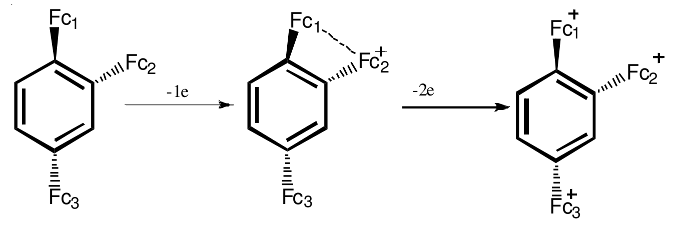
Fig. 1. Molecular structure of 1,2,4-triferrocenylbenzene

C(4)-C(3)-C(2) 123.0(3)°, also indicate that the acetylenic bond in ferrocenyl acetylene is formally reduced as a result of the cyclotrimerization.

The cyclopentadienyl rings of Fc(3) are nearly parallel to the centra benzene mean plane with angle of 2.71(0.17)°, the angle of cyclopentadienyl rings plane of Fc(1) to centra benzene plane is 31.84 (0.14)° and the angle of cyclopentadienyl rings plane of Fc(2) to the benzene plane is 49.26 (0.11)°. The interannular distances C(17)-C(4), C(12)-C(2), C(11)-C(1) were 1.474, 1.487 and 1.480 Å, which indicated the conjugation between the ferrocenyl and benzene ring were a little different. Because we did not observed any other isomers in reaction mixtures, therefore, their orientation selectivity is minimized to steric hindrance. Such structural character can also be understood by the mechanism proposed by Krüerke and Hübel[12] (**Schemes I** and **II**). In order to reduce the steric repulsion of ferrocenyl to carbonyl cobalt, in the formation processes of intermedia **2**, ferrocnyl select their position at R_2 and R_3 and spontaneously adopt an E-configuration, the position of R_1 and R_4 was hydrogen atoms. While the ferrocenyl acetylene further reacted with intermediate **2**, they formed a "flyover" structure **3** (**Scheme-I**). At the temperature condition of cyclohexane-reflux, two carbonyl cobalt depart from "flyover" structure and a new covalence bond was formed between two carbon atoms connected to R_4 (the dash line in **Scheme-I**), thus, the ultimated 1,2,4-triferrocenylbenzene was obtained. We attempt to isolate intermidiate **2**, **3**, but no detected them, they may be too short-lived to be detected or isolated in the synthesis processes.

Electrochemistry of 1,2,4-triferrocenylbenzene: The platinum disk in radius 25 μm and 1.6 mm were used as working electrode for the experiments of voltammetry and potential step. The auxiliary electrode was a coiled platinum wire. The reference electrode was a SCE electrode. Oxygen was purged from the one-compartment cell before each electrochemical run.

The synthesis and electrochemistry of C_3-symmetric 1,3,5-triferrocenylbenzene has been reported by Yu and Iyoda[9,17], only one pair of redox peaks appeared in the



Scheme-II

conventional cyclic voltammograms (CV), it carried out one step three electron redox process. But for the 1,2,4-triferrocenylbenzene, the asymmetric isomer of 1,3,5-triferrocenylbenzene, the structural character of ferrocenyl is different to the 1,3,5-triferrocenylbenzene. Thus, the redox properties of it should be dissimilar. They would be expected to show three pairs of redox waves for its CV responses. However, as shown in Fig. 2, only two pair of redox peaks appeared in conventional CV and the same phenomena also appeared in the microelectrode CV of 1,2,4-triferrocenylbenzene (Fig. 3). In the microelectrode CV, the second peak current is two times than the first one. Therefore, three ferroceyls take part in two steps redox reaction, the first one should take one electron transfer process, second one should be two electron transfer processes. Because the angle of cyclopentadienyl rings plane of Fc(2) to the benzene plane is 49.26 (0.11)° (**Scheme-II**), the electron withdrawing action of phenyl is the minimal to Fc(2), hence, the Fc(2) should be oxidized at first step. After the Fc(2) was oxidized, the electron communication between the Fc(1) and Fc(2) make the oxidation potential of Fc(1) to more positive potential (P1) *via* the conjugated alkene bridge. The cyclopentadienyl rings of Fc(3) are nearly parallel to the centra benzene mean plane with angle of 2.71(0.17)°, the stronger conjugated action exist between the benzene mean plane and cyclopentadienyl rings of Fc(3), the electron withdrawing function of benzene make the oxidation potential of Fc(3) to another more positive potential (P3). From the conventional CV (Fig. 2) and microelectrode CV (Fig. 3), the second step looks proceeding one step redox reaction with two electron transfer, so the P3 is approximate to P1. The electrode reaction processes of 1,2,4-triferrocenylbenzene is described in **Scheme-II**.

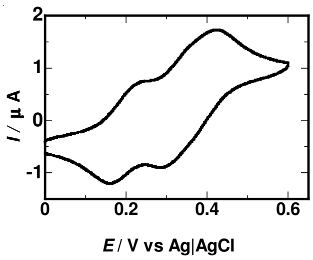


Fig. 2. Conventional cyclic voltammogram of TFB

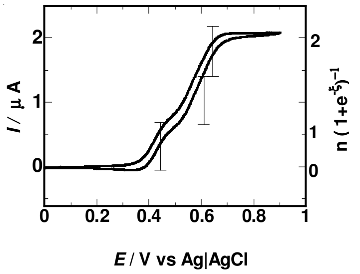


Fig. 3. Microelectrode cyclic voltammogram of TFB

In order to identify the electron transfer numbers of second step, the microelectrode chronoamperometry of 1,2,4-triferrocenylbenzene was performed. When the potential was stepped from 0.45-0.85 V, curve of current *versus* time (Fig. 4) and Cottrell plots (Fig. 5) were obtained. According to the documental methods[18-20], within diffusion controlled potential domain, the Cottrell plot (I *versus* $t^{-1/2}$) at a microelectrode can gives the slope, s and intercept, p, respectively.

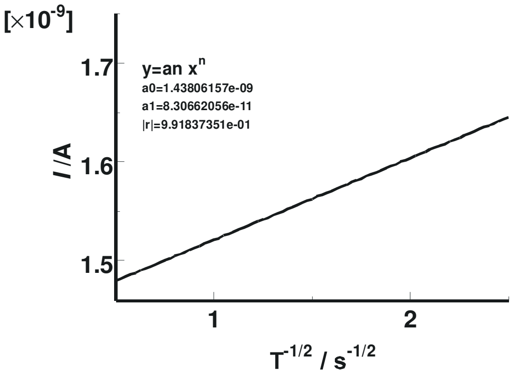


Fig. 4. Chronoamperometry curve of TFB at micro electrode with radius of 0.25 μm

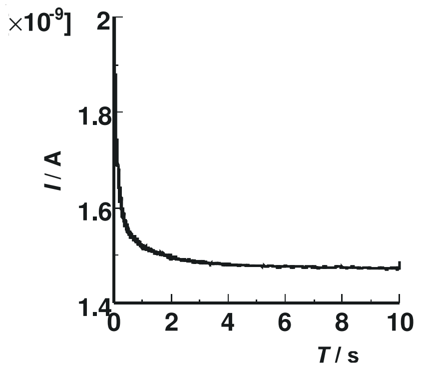


Fig. 5. Cottrell plot of the background-sunstracted currents for 2 mM TFB in CH_2Cl_2 when potential was stepped from 0.3-0.7 V

$$s = \pi^{1/2} n D^{1/2} F a^2 c^*(1 + e^{\zeta})^{-1}, \ \rho = \pi n F D a c\,^*(1 + e^{-\zeta})^{-1} \quad (1)$$

where $\zeta = (F/RT)(E - E^0)$, n = electron transfer number, D = diffusion coefficent, F = Faraday constant, C* = concentration of solution. And from the ratio of s^2 to π, the electron transfer number can be expressed as eqn. 2.

$$n = s^2/pFa^3c^*(1 + e^{-\zeta})^{-1} \quad (2)$$

by the eqn. 2 and the value of S, P in the Fig. 4, the calculated value of electron transfer numbers of second step is appropriated to 2, that consisted with the predicted of electron transfer numbers of CV.

Conclusion

[$Co_2(CO)_6$(μ_2,η2-ferrocenylacetylene)] was an effective catalyst for the preparation of 1,2,4-triferrocenylbenzene from cycloaddtion reaction of ferrocenyl acetylene, besided asymmetric1,2,4-triferrocenylbenzene. The cyclic voltammetry and microelectrode chronoamperometry demonstrated that the electrode reaction of 1,2,4-triferrocenylbenzene was dissamilar to that of 1,3,5-triferrocenylbenzene, it took place two steps redox reactions, the first was one step one electron, the second was one step two electron transfer processes.

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