Synthesis, Crystal Structure and Electrochemistry of Carbon-Bridged Diferrocenyl Compounds

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Three carbon bridged diferrocenyl compounds: $\text{FcC}(\text{H}_2)\text{Fc}$ (**A**), $\text{FcC}(\text{O})\text{Fc}$ (**B**) and $\text{Fc}(\text{H})\text{C}(\text{OH})\text{Fc}$ (**C**) were synthesized and characterized by elemental analysis, FT-IR, NMR and MS. The molecular structures were determined by X-ray single crystal diffraction. The electrochemical interactions between two ferrocenyl units in these compounds were investigated by cyclic voltammetry and DFT calculation. By study of the relationship between the electron communication of the two ferrocenyl units and the property of the three carbon bridged diferrocenyl compounds, it is concluded that the polarity degree of the bridged C was a key factor for the electron communication of the two ferrocenyl units.

Key Words: Electron interaction, Cyclic voltammograms, Carbon-bridged diferrocene.

INTRODUCTION

In the past three decades, various atom-bridged diferrocenyl derivatives¹⁻⁵, such as the C, Si, P, Ga, Hg and chalcogen (S, Se and Te) bridged diferrocenes⁶, have been prepared due to their potential applications in magnetic, electronic and optical devices⁷⁻⁹. The current research interests were concentrated not only on how to construct these atom-bridged diferrocene systems, but also on the electrochemical interaction between the two ferrocenyl units. Generally, the redox potential difference value (ΔE) between the two ferrocenyl units provides an electrochemical method for direct measurement of electrochemical interaction and the potential difference values are affected by the bridged atom¹⁰, the type of bridge¹¹⁻¹⁵, the distance between the oxidation center and reduction center¹⁶, the charge density of the bridge¹⁷ and the molecular topology¹⁸.

Watts and co-workers¹ had proposed that there are two types of electrochemical interaction modes between the two ferrocenyl units of atom-bridged diferrocenyl compound. In the first mode, the electron of the two ferrocenyl units communicated through the bridge connected the two ferrocenyl units. In the second mode, the electron communicated directly between the two Fe atoms of the two ferrocenyl units. Yuan and his co-workers¹⁹ deduced that the Fe-Fe distance was the key factor for the electron interactions of the two ferrocenyl units in carbon-bridged diferrocenyl derivatives, but no single crystal data could support their conclusions.

In order to find the key factor for electron interactions between two ferrocenyl units of carbon-bridged diferrocenyl

derivatives, three diferrocenyl compounds were prepared in this paper. Electron interactions between two ferrocenyl units were investigated by a single-crystal structure analysis, cyclic voltammetry technique and theory calculation.

EXPERIMENTAL

All the manipulations were performed in a pure argon atmosphere. Solvents were purified, dried and distilled under argon prior to use. Reactions were monitored by TLC. Column chromatographic separations and purification were performed on 200-300 mesh neutral alumina. Dimethoxymethane²⁰ and ferrocenyl chloride²¹ were prepared according to reported method. All other chemicals were purchased from Alfa Aesar. IR spectra were recorded on a Nicolet FT-IR spectrometer in KBr discs. Elemental analyses were carried out on an Elementar var III-type analyzer. ¹H and ¹³C NMR spectra in CDCl₃ were recorded on a Bruker-500 MHz spectrometer. Mass spectra were determined using a Micromass LCT instrument and melting points were determined using an XT-4 melting point apparatus. The platinum disk of radius 0.8 mm was used as working electrode for cyclic voltammetry. The electrode surface was polished with 0.05 mm alumina before each run. The auxiliary electrode was a coiled platinum wire. The reference electrode was a Ag|AgCl electrode. The supporting electrolyte used in all electrochemical experiments was tetra-*n*-butylammonium hexafluorophosphate (TBAHFP) at 0.5 M. The potentiostat was CHI-760C. We employed argon as purge gas to eliminate oxygen from the one-compartment

cell before the electrochemical experiments. Single crystal structures were obtained by a Bruker SMART APEX CCD diffractometer with graphite monochromated $\text{MoK}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation. All data were collected at 296(2)K using the ϕ and ω scan techniques. The structure solution and refinement were performed by SHELXSL97. The theory calculations were carried out on the personal computer with Gaussian 03 program package.

Synthesis of diferrocenylmethane (A): Ferrocene (5.6 g, 0.03 mol) was dissolved in the mixture solution of toluene (30 mL), methanol (7 mL) and sulfuric acid (3.5 mL) in a three-neck flask under an atmosphere of pure argon. Then dimethoxymethane (4.0 mL, 0.045 mol) was added dropwise at 80 °C. After the solution was stirred for 6 h at 80 °C, the reaction solution was cooled to room temperature and then the reaction mixture was extracted with toluene. The organic phase was washed by saturated aqueous solution of Na_2CO_3 , distilled water and then desiccated with anhydrous MgSO_4 . The solvent was removed *in vacuo* and the residues were subjected to chromatographic separation on a neutral alumina column (2 cm $\times$ 35 cm). Elution with a mixture of hexane : dichloromethane (10 : 1, v/v) afforded a yellow band for **A**. Crystals of **A** were obtained by recrystallizing solid **A** from a mixture of hexane and dichloromethane at -20 °C. Compound **A**: Yield 43.2 %; m.p. 146-147 °C; Anal. calcd. (%) for $\text{C}_{21}\text{H}_{20}\text{Fe}_2$: C, 65.67; H, 5.25. Found. (%): C, 65.33; H, 5.61. IR (KBr disk): 3085.41 (Cp , $\nu_{\text{C-H}}$); 2925.84, 2886.92 (CH_2 , $\nu_{\text{C-H}}$); 1100.54, 999.36 (Cp , $\gamma_{\text{C-H}}$); 808.65, (Cp , $\delta_{\text{C-H}}$). ^1H NMR (500 MHz CDCl_3 , δ_{H}): 4.04 - 4.16 (18H, Fc); 1.50 (2H, CH_2). ^{13}C NMR (125 MHz CDCl_3 , δ_{C}): 67.33 - 68.70 (Cp carbons); 30.09 (CH_2); MS (ESI, m/z): 384.2 (M^+).

Synthesis of diferrocenylketone (B): Ferrocenoyl chloride (2.48 g, 10 mmol), anhydrous aluminum chloride (1.45 g, 11 mmol) and dichloromethane (30 mL) were added into a three-neck flask under an atmosphere of pure argon at 0 °C. After 0.5 h, ferrocene (2.23 g, 12 mmol) dissolved in dichloromethane (30 mL) was added dropwise and the reaction solution was stirred for 2 h at room temperature. Then the reaction mixture was poured into ice water to extract the target product with dichloromethane, the organic phase was washed by saturated aqueous solution of Na_2CO_3 , distilled water and then desiccated with anhydrous MgSO_4 . The solvent was removed *in vacuo* and the residues were subjected to chromatographic separation on a neutral alumina column (2 cm $\times$ 30 cm). Elution with anhydrous ether afforded a yellow band for **B**. Crystals of **B** were obtained by recrystallizing solid **B** from a mixture of hexane and dichloromethane at -20 °C. Compound **B**: Yield 56.0 %; m.p. 206-207 °C; Anal. calcd. (%) for $\text{C}_{21}\text{H}_{18}\text{OFe}_2$: C, 63.36; H, 4.56. Found. (%): C, 63.48; H, 4.62. IR (KBr disk): 3120.43, 3089.30 (Cp , $\nu_{\text{C-H}}$); 1602.49 (CO , $\nu_{\text{C=O}}$); 1104.43, 1003.21 (Cp , $\gamma_{\text{C-H}}$); 808.65, (Cp , $\delta_{\text{C-H}}$). ^1H NMR (500 MHz CDCl_3 , δ_{H}): 4.18-5.00 (18H, Fc). ^{13}C NMR (125 MHz CDCl_3 , δ_{C}): 70.12-71.57 (Cp carbons); 199.44 (CO); MS (ESI, m/z): 398.8 (M^+).

Synthesis of diferrocenylmethanol (C): Diferrocenylketone (2.0 g, 5 mmol) was dissolved into anhydrous ether (30 mL) in a three-neck flask under an atmosphere of argon at room temperature and then AlLiH_4 (0.21 g, 5.5 mmol) was

added slowly into the reaction solution. After 1 h, distilled water (20 mL) was added slowly at 0 °C. The reaction mixture was extracted with ether, the organic phase was washed by distilled water and desiccated with anhydrous MgSO_4 . The organic solvent was removed *in vacuo* and then the residues were recrystallized from a mixture of dichloromethane and hexane at -20 °C afforded yellow crystals for **C**. Compound **C**: Yield 60.0 %; m.p. 177-178 °C; Anal. calcd. (%) for $\text{C}_{21}\text{H}_{20}\text{OFe}_2$: C, 63.04; H, 5.04. Found. (%): C, 63.24; H, 4.96. IR (KBr disk): 3455.14 (OH , $\nu_{\text{O-H}}$); 3085.41 (Cp , $\nu_{\text{C-H}}$); 2956.97, 2921.95 (HC(OH) , $\nu_{\text{C-H}}$); 1104.43, 995.46 (Cp , $\gamma_{\text{C-H}}$); 816.43 (Cp , $\delta_{\text{C-H}}$). ^1H NMR (500 MHz CDCl_3 , δ_{H}): 5.20 (d, OH, 1H, $J = 3.5\text{Hz}$); 4.14-4.24 (18H, Fc); 2.37 (d, $(\text{HO})\text{CH}$, 1H, $J = 3.5\text{Hz}$). ^{13}C NMR (125 MHz CDCl_3 , δ_{C}): 66.26 - 68.63 (Cp carbons); 93.06 (HCOH); MS (ESI, m/z): 400.0 (M^+).

RESULTS AND DISCUSSION

Crystal structure of compounds A, B and C: The crystal structures of compounds **A**, **B** and **C** were determined by X-ray single crystal diffraction analysis. The crystal data and relevant structural parameters were given in Table-1. The selected bond lengths and bond angles were listed in Table-2. The crystal structures were shown in Figs. 1-3.

Fig. 1. Crystal structure of compound **A**

Fig. 2. Crystal structure of compound **B**

The compounds **A** and **C** crystallized in the monoclinic space group $P2_1/c$, but the compound **B** crystallizes in the monoclinic space group $P2_1/c$ and in the form of centrosymmetric structure. From the single crystal data of the three compounds **A**, **B** and **C**, it can be seen that the average bond

TABLE-1
 CRYSTALLOGRAPHIC DATA OF COMPOUNDS A, B AND C

Compounds	A	B	C
Empirical formula	C ₂₁ H ₂₀ Fe ₂	C ₂₁ H ₁₈ OFe ₂	C ₂₁ H ₂₀ OFe ₂
Formula weight	384.08	398.05	400.07
Temperature (K)	296(2)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P 21/c	P 2/c	P 21/c
a (Å)	10.5482(11)	10.4938(5)	9.0094(2)
b (Å)	7.7605(8)	6.1825(3)	9.5725(2)
c (Å)	20.585(2)	13.0393(5)	19.0128(3)
α (°)	90.00	90.00	90.00
β (°)	103.477(2)	110.909(2)	92.7450(10)
γ (°)	90.00	90.00	90.00
Volume (Å ³), Z	1638.7(3), 8	790.25(6), 2	1637.83(6), 4
Density (calculated) (Mg/m ³)	1.557	1.673	1.622
μ (mm ⁻¹)	1.766	1.839	1.775
F (000)	792	408	824
Crystal size (mm)	0.15 × 0.05 × 0.05	0.20 × 0.20 × 0.15	0.30 × 0.20 × 0.20
θ range (°)	1.99 to 28.34	2.08 to 27.87	2.14 to 27.50
Limiting indices	-14 ≤ h ≤ 12 -10 ≤ k ≤ 10 -22 ≤ l ≤ 27	-13 ≤ h ≤ 12 0 ≤ k ≤ 8 0 ≤ l ≤ 17	-11 ≤ h ≤ 11 -12 ≤ k ≤ 12 -22 ≤ l ≤ 24
Reflections collected	11644	11527	13574
Independent reflections	4073	1860	3751
Completeness to θ	99.5 %	99.0 %	99.5 %
Max. and min	0.9169/0.7776	0.7700/0.7100	0.7179/0.6181
Data/restraints/parameters	4073/0/208	1894/0/111	3751/0/217
Goodness-of-fit on F ²	1.034	1.029	1.068
Final r indices			
[I > 2σ(I)]	R ₁ = 0.0301, wR ₂ = 0.0739	R ₁ = 0.0307, wR ₂ = 0.0644	R ₁ = 0.0273, wR ₂ = 0.0716
R _{indices} (all data)	R ₁ = 0.0409, wR ₂ = 0.0793	R ₁ = 0.0463, wR ₂ = 0.0701	R ₁ = 0.0351, wR ₂ = 0.0745
Largest diff. peak and hole (e. Å ⁻³)	0.258/-0.570	0.270/-0.353	0.364/-0.319

 TABLE-2
 SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°) OF COMPOUNDS A, B AND C

Compound A					
C1-C11	1.504(2)	C11-C12	1.500(2)	C1-C11-C12	114.82(14)
Compound B					
C1-O1	1.226(4)	C1- C2	1.473(3)	C1- C2 ²	1.473(3)
C2-C1-O1	118.53(16)	C2-C1-C2 ²	122.9(3)	C2 ² -C1-O1	118.53(16)
Compound C					
C1-O1	1.432(2)	C1-C2	1.500(2)	C1- C12	1.501(2)
C2-C1-O1	107.50(13)	C2-C1-C12	113.14(13)	C12- C1-O1	111.55(14)

Fig. 3 Crystal structure of compound C

length of C-C bonds in ferrocenyl units is 1.41 Å, the average bond length of Fe-C bonds is 2.04 Å and the mean distance from Fe to Cp (cyclopentadiene) ring plane is 1.65 Å. The

bond distance between the bridged carbon atom and the ferrocenyl carbon atom (1.473(3)-1.504(2) Å) are in the range of C-C single bond length in A, B and C. The dihedral angle of two cyclopentadiene ring planes in each ferrocene is in the range of 1.62-2.79°, which indicate that the two cyclopentadiene rings are nearly parallel in the ferrocenyl of A, B and C. The bond angles around the bridged carbon atoms of A and C ranging from 104.6 to 114.8° are in accord with sp^3 hybridized bridging carbon atoms. However, the bond angles around the bridged carbon atom of B ranging from 118.5 to 122.9° are in accord with sp^2 hybridized bridging carbon atom.

Electrochemistry of compounds A, B and C: The cyclic voltammograms of A, B and C are shown in Fig. 4. There are two electrochemically reversible redox waves in the redox process of every compound. Each redox wave display one-electron transfer, which assigned to the two Fe(II)/Fe(III) redox couples. The oxidation potential differences (ΔE) between two

oxidation peak potentials of compounds **A**, **B** and **C** are $\Delta E_A = 187$ mV, $\Delta E_B = 210$ mV and $\Delta E_C = 158$ mV, respectively (Table-3). The differences value is greater than 100 mV, which indicates the stronger electronic communication between two ferrocenyl units²².

Fig. 4. Cyclic voltammograms of compounds **A** (a), **B** (b) and **C** (c)

TABLE-3
OXIDATION POTENTIAL DIFFERENCE (ΔE) AND MULLIKEN CHARGES OF BRIDGED 'C' OF COMPOUNDS **A**, **B** AND **C**

Compounds	$\Delta E/\text{mV}$	Mulliken atomic charges
A	187	-0.269329
B	210	0.288454
C	158	0.020845

The electronic distribution of the frontier orbitals of the compounds **A**, **B** and **C** were investigated by the B₃LYP density function theory method with 6-31G basis set, based upon a starting geometry obtained from the X-ray structure analysis of compounds **A**, **B** and **C** (Fig. 5). The computational results indicated that the electronic distribution of the HOMOs of compound **A** and **C** mainly localized on one ferrocenyl fragment and that of compound **B** localized evenly on two ferrocenyl fragments (Fig. 5), which induce that the first oxidation potential of compounds **A** and **C** were lower than that of **B**. The frontier orbital theory explain the corresponding electrochemical behaviour of cyclic voltammetry well²³.

Watts and Yuan^{1,19} had reported that the Fe-Fe distance should be the key factor for the separation of oxidation

potential (ΔE) and the ΔE will increase as the Fe-Fe distance decrease. The Fe-Fe distances of **A**, **B** and **C** are 5.765, 5.334 and 5.742 Å, respectively. However, the oxidation potential differences order should be $\Delta E_A < \Delta E_C < \Delta E_B$ according to the Fe-Fe distances and these results do not accord with the experimental results ($\Delta E_C < \Delta E_A < \Delta E_B$). Hence, the Fe-Fe distance is not the only factor for the electronic communication of the carbon-bridged diferrocenyl derivatives. Then we investigated other key factor for the electronic communication of the carbon-bridged diferrocenyl derivatives, such as the electronegativity of the substituent groups on the bridged carbon and Mulliken charges of the bridged carbon.

The electronegativity order of substituents on bridged carbon of these compounds were **A** < **C** < **B**, which was confirmed by the resonance peak of bridged carbon in ¹³C NMR spectra (**A**: 30.09 ppm, **C**: 93.06 ppm and **B**: 199.44 ppm). However, these results were also not consistent with the oxidation potential difference ($\Delta E_C < \Delta E_A < \Delta E_B$). Hence, the electronegativity of the substituents of bridged carbon is still not the key influence on the electronic communication of the carbon-bridged diferrocenyl derivatives.

The Mulliken charges of the bridged carbon of compounds **A**, **B** and **C** were also obtained by the theory calculations (Table-3). The Mulliken charge density of the bridged carbon in compound **A**, **B** and **C** are -0.269329, 0.288454 and 0.020845, respectively, which indicate the bridged carbon show different polarity degree in order of **C** < **A** < **B**. Fortunately, the distribution of the Mulliken charges of the bridged carbon of the compounds **A**, **B** and **C** were consistent with the order of the electron communication of the compounds **A**, **B** and **C**. Therefore, the compound **B** exhibit the strongest electron communication ($\Delta E_B = 210$ mV) and the compound **C** exhibit the weakest electron communication ($\Delta E_C = 158$ mV).

Conclusion

Three diferrocenyl compounds: $\text{FcC(H)}_2\text{Fc}$ (**A**), FcC(O)Fc (**B**) and FcC(H)C(OH)Fc (**C**) were synthesized and determined by X-ray single crystal diffraction, elemental analysis, FT-IR, NMR and MS. The electrochemical interactions between the two ferrocenyl units of these compounds were investigated by cyclic voltammetry, molecular structure analysis and theory calculation and we found that the polarity degree of the bridged carbon was the pivotal factor for the electron communication of the two ferrocenyl units in **A**, **B** and **C**.

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Fig. 5. DFT computed frontier orbitals of compounds **A**, **B** and **C**

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