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The effect of acetyl on the electronic communication of carbon-bridged diferrocene

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Diferrocenylmethane (**1**) and 2-acetyl(diferrocenyl)methane (**2**) were synthesized and characterized by elemental analysis, FT-IR, and NMR. The molecular structures of **1** and **2** were determined using X-ray single crystal diffraction. The effect of acetyl group on electronic communication between two ferrocenyl units of **2** was investigated through cyclic voltammetry and density functional theory calculation. The acetyl did not influence electronic communication between two ferrocenyl units. The key factor that effected electronic communication of carbon-bridged diferrocenyl derivatives was charge density of the bridged carbon.

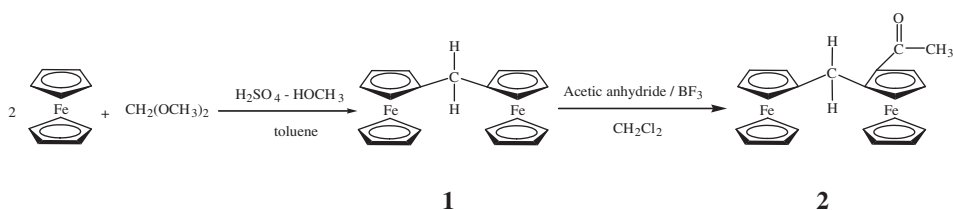
Keywords: Acetyl; Diferrocenylmethane; Crystal structure; Electrochemistry

1. Introduction

Multi-ferrocenyl molecules have attracted attention for redox, non-linear optical, and magnetic properties [1–5]. Interest was concentrated on alkyne [6], ethylene [7], aromatic [8], and chemical bond [9–11] bridged multi-ferrocenyl derivatives. Research concentrated on non-conjugated bridged polyferrocenyl compounds. For example, various “C” [12], “Si” [13, 14], “S, Se, Te” [15], and “Ga” [16] bridged polyferrocenyl derivatives have been synthesized and electronic communication between ferrocenyl units discussed extensively. For carbon-bridged diferrocenyl derivatives, Köhler [17] suggested that electronic communication between two ferrocenyl units was influenced by the dihedral angle of the two bridged Cp rings, while Yuan [18] thought the main factor was Fe–Fe distance. However, our single crystal data do not support their conclusions. Last year, we suggested that the key factor effecting electronic interaction between two ferrocenyl units of diferrocenyl derivatives was the charge density of the bridged carbon from accurate molecular crystal structure analysis, theory calculation, and cyclic voltammetry [19].

To confirm our previous result, 2-acetyl(diferrocenyl)methane (**2**) was prepared through acetylation reaction of diferrocenylmethane (**1**) [20–22] (scheme 1). Initially,

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Scheme 1. The synthesis processes of **1** and **2**.

we supposed the acetyl should influence the charge density of the bridged carbon and change the electronic interaction between two ferrocenyl units. However, an unexpected result is discussed in this article.

2. Experimental

2.1. General procedures

All operations were carried out under an atmosphere of purified argon using standard Schlenk techniques. Solvents were dried and distilled according to standard procedures. Reactions were monitored by thin layer chromatography (TLC). Column chromatographic separations and purification were performed on 200–300 mesh neutral alumina. All other chemicals were obtained from Alfa-Asia Chem. Dimethoxymethane and acetylferrocene (**Afc**) were prepared by the literature method [23, 24]. Infrared (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. ^1H and ^{13}C NMR spectra in CDCl_3 were recorded on a Jeol-Jnm-Al 500 FT-MHz spectrometer. Mass spectra were determined using a Micromass LCT instrument. The crystal structures of **1** and **2** were determined on a Bruker SMART APEX CCD diffractometer with graphite monochromated $\text{Mo-K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation. Data were collected using the φ and ω scan techniques. The structures were solved using direct methods and expanded using Fourier techniques. An absorption correction based on SADABS was applied. Structure solutions and refinements were performed using SHELXSL 97 software [25]. Cyclic voltammetry was performed on a CHI 760C electrochemical analyzer using a platinum disc as working electrode; the electrode surface was polished with $0.05 \mu\text{m}$ alumina before each run. The reference electrode was a $\text{Ag}|\text{AgCl}$ electrode and the auxiliary electrode was a coiled platinum wire. The solvent was dichloromethane and acetonitrile (1 : 1, v/v) containing 0.1 mol L^{-1} supporting electrolyte of tetra-*n*-butylammonium hexafluorophosphate (TBAHFP). Oxygen was purged from the one-compartment cell before electrochemical run. The calculations were carried out on the personal computer with Gaussian 03 program package.

2.2. Synthesis of diferrocenylmethane (**1**)

Toluene (30 mL), methanol (7 mL), sulfuric acid (3.5 mL), and ferrocene (5.6 g, 0.03 mol) were added to a three-neck flask under an atmosphere of pure argon.

Then dimethoxymethane (1.8 mL, 0.02 mol) was added dropwise at 80°C, stirred for 6 h at 80°C, then cooled to room temperature. The reaction mixture was extracted with toluene, the organic phase washed by Na₂CO₃ aqueous solution and distilled water, and desiccated by anhydrous MgSO₄. The solvent was removed *in vacuo*, and the residue subjected to chromatographic separation on a neutral alumina column (Φ 2 × 35 cm). Elution with a mixture of hexane-dichloromethane (10 : 1, v/v) afforded a yellow band for **1**. Yield: 53.3%, m.p. 145–146°C. Anal. Calcd for C₂₁H₂₀Fe₂: C, 65.67; H, 5.25. Found: C, 65.43; H, 5.41. IR(KBr disc): 3085.41 [Cp, ν_{C-H}]; 2925.84, 2886.92 [CH₂, ν_{C-H}]; 1100.54, 1030.49 [Cp, δ_{C-H}]; 816.43 [Cp, γ_{C-H}]. ¹H-NMR (CDCl₃, δ): 4.039–4.156 [Fc, 18H]; 3.388 [CH₂, 2H]. ¹³C-NMR (CDCl₃, δ): 67.33–68.70 [Cp, 20C], 30.09 [CH₂, 1C]. MS (ESI, relative abundance): 384.0 (M⁺, 100%). The single crystal of **1** was obtained by recrystallizing from hexane-dichloromethane (5 : 1, v/v) at room temperature.

2.3. Synthesis of 2-acetyl(diferrocenyl)methane (**2**)

Diferrocenylmethane (1.15 g, 0.003 mol), acetic anhydride (1.0 mL, 0.01 mol), and dichloromethane (30 mL) were added to a three-neck flask under an atmosphere of pure argon at 0°C. Then boron trifluoride ether solution (2.5 mL) was added dropwise at 0°C, stirred for 5 h at room temperature, then hydrolyzed with potassium acetate solution. The reaction mixture was extracted with dichloromethane and the organic phase was washed by Na₂CO₃ aqueous solution and distilled water and desiccated by anhydrous MgSO₄. The solvent was removed *in vacuo* and the residue was subjected to chromatographic separation on a neutral alumina column (Φ 2 × 35 cm). Elution with a mixture of hexane-dichloromethane (5 : 1, v/v) afforded a yellow band for **2**. Yield: 14.0%, m.p. 165–166°C. Anal. Calcd for C₂₃H₂₂Fe₂O: C, 64.83; H, 5.20. Found: C, 64.63; H, 5.12. IR(KBr disc): 3104.86, 3073.73 [Cp, ν_{C-H}]; 2914.16 [CH₂, CH₃, ν_{C-H}]; 1664.86 [ν_{C=O}]; 1100.54, 999.35 [Cp, δ_{C-H}]; 816.43 [Cp, γ_{C-H}]. ¹H-NMR (CDCl₃, δ): 4.044–4.566 [Fc, 17H]; 3.643–3.957 [CH₂, 2H]; 2.407 [CH₃, 3H]. ¹³C-NMR (CDCl₃, δ): 203.59 [CO, 1C]; 67.26–75.73 [Cp, 20C]; 29.33 [CH₂, 1C]; 28.71 [CH₃, 1C]. MS (ESI, relative abundance): 426.1 (M⁺, 100%). The single crystal of **2** was obtained by recrystallizing from hexane-dichloromethane (5 : 1, v/v) at room temperature.

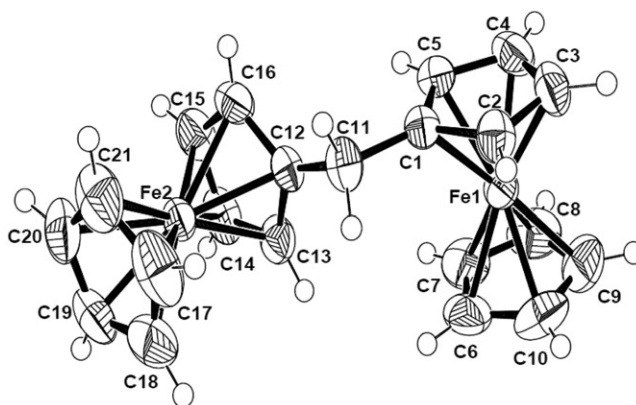
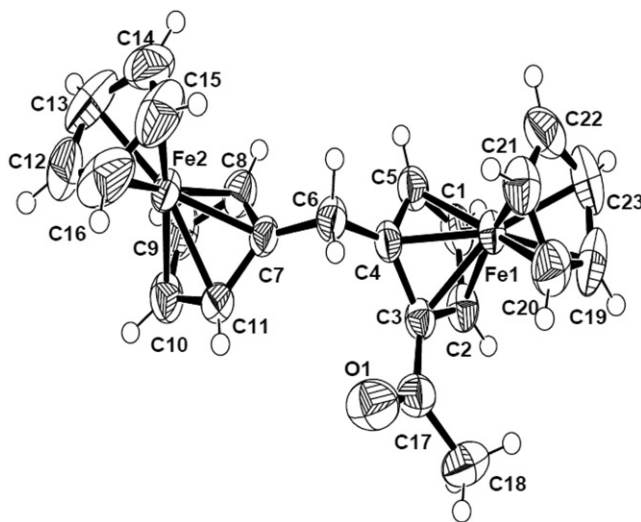
3. Results and discussion

3.1. Reaction and characterization of **1** and **2**

The syntheses are depicted as scheme 1. Compound **1** was prepared *via* acid-catalyzed condensation of ferrocene and dimethoxymethane. Compound **2** was obtained by BF₃-catalyzed reaction of **1** and acetic anhydride. The two compounds were identified by FT-IR, ¹H-NMR, ¹³C-NMR, elemental analysis, and MS.

3.2. Molecular structures of **1** and **2**

The molecular structures of **1** and **2**, determined by X-ray single crystal diffraction, are shown in figures 1 and 2. Compound **1** crystallizes in the monoclinic space group *P21/c*

Figure 1. The molecular structure of **1**.Figure 2. The molecular structure of **2**.

and **2** crystallizes in the triclinic space group $P-1$. Crystal data and relevant structural parameters are enumerated in table 1. Selected bond lengths and angles are listed in table 2. The bond angles around the bridge “C” range from 107.50° to 114.82° , in accord with sp^3 hybridization. The average length of C–C bond in Fc units is 1.41 \AA while the average Fe–C length is 2.04 \AA . The mean length from Fe to cyclopentadiene (Cp) ring plane is 1.65 \AA . The dihedral angle of two Cp ring planes in each ferrocenyl is $1.6\text{--}3.0^\circ$, indicating parallel Cp rings in **1** and **2**. The distance of Cp carbon to bridge carbon is $1.500(2)\text{--}1.509(3) \text{ \AA}$, slightly shorter than C–C single bonds. The dihedral angle of Cp ring plane and acetyl plane is 9.79° , showing the coplanar character of acetyl and Cp ring plane.

Table 1. Crystal data and relevant structural parameters of **1** and **2**.

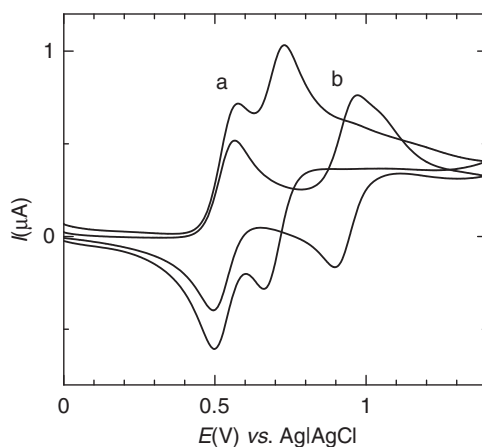
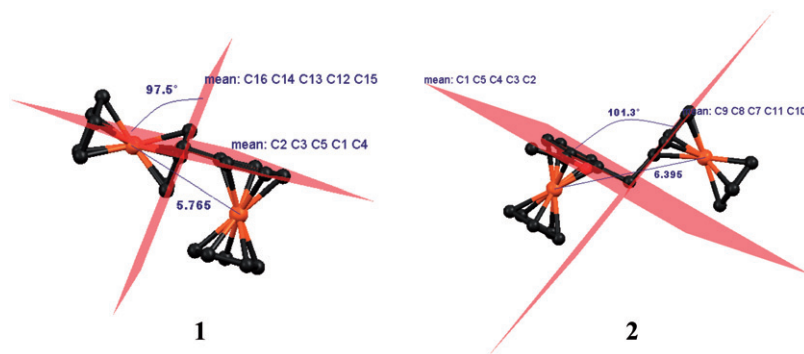
Compounds	1	2
Empirical formula	C ₂₁ H ₂₀ Fe ₂	C ₂₃ H ₂₂ Fe ₂ O
Formula weight	384.08	426.11
Temperature (K)	296(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 21/ <i>c</i>	<i>P</i> -1
Unit cell dimensions (Å, °)		
<i>a</i> (Å)	10.5482(11)	9.6016(13)
<i>b</i> (Å)	7.7605(8)	12.473(3)
<i>c</i> (Å)	20.585(2)	11.5508(15)
α (°)	90.00	111.901(2)
β (°)	103.477(2)	111.424(2)
γ (°)	90.00	92.459(2)
Volume (Å ³), <i>Z</i>	1638.7(3), 8	915.8(2), 2
Calculated density (Mg m ⁻³)	1.557	1.545
Absorption coefficient (mm ⁻¹)	1.766	1.592
<i>F</i> (000)	792	440
Crystal size (mm ³)	0.15 × 0.05 × 0.05	0.20 × 0.20 × 0.20
θ range for data collection (°)	1.99–28.34	2.08–28.35
Limiting indices	–14 ≤ <i>h</i> ≤ 12; –10 ≤ <i>k</i> ≤ 10; –22 ≤ <i>l</i> ≤ 27	–11 ≤ <i>h</i> ≤ 12; –13 ≤ <i>k</i> ≤ 12; –15 ≤ <i>l</i> ≤ 9
Reflections collected	11,644	6816
Independent reflections	4073	4523
Completeness to θ (%)	99.5	98.8
Max. and min. transmission	0.9169 and 0.7776	0.7413 and 0.7413
Data/restraints/parameters	4073/0/208	4523/0/236
Goodness-of-fit on <i>F</i> ²	1.034	1.002
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0301, <i>wR</i> ₂ = 0.0739	<i>R</i> ₁ = 0.0314, <i>wR</i> ₂ = 0.0669
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0409, <i>wR</i> ₂ = 0.0793	<i>R</i> ₁ = 0.0431, <i>wR</i> ₂ = 0.0726
Largest difference peak/hole (e.Å ⁻³)	0.258 and –0.570	0.357 and –0.380

Table 2. Selected bond lengths (Å) and angles (°) of **1** and **2**.

Compound 1					
C1–C11	1.504(2)	C11–C12	1.500(2)	C1–C11–C12	114.82(14)
Compound 2					
C4–C6	1.504(3)	C6–C7	1.509(3)	C3–C17	1.470(3)
C17–C18	1.501(3)	C17–O1	1.210(3)	C4–C6–C7	109.43(16)
C3–C17–C18	117.6(2)	C3–C17–O1	121.7(2)	C18–C17–O1	120.7(2)

3.3. Electrochemistry

The cyclic voltammograms (CVs) of **1** and **2** are depicted in figure 3. Both of the curves display two electrochemically reversible redox waves, each step is one-electron transfer, and are assigned to the two Fe(II)/Fe(III) redox couples. The first oxidation peak potentials of **1** and **2** are $E_{a1} \approx E_{b1}$ (E_{a1} , $E_{b1} \approx 0.570$ V), but the second peak potentials are very different ($E_{a2} = 0.720$ V, $E_{b2} = 0.975$ V). The oxidation potential difference (ΔE) between two oxidation peak potentials of **1** and **2** are $\Delta E_a = 150$ mV and $\Delta E_b = 405$ mV, respectively. Generally, ΔE represents electronic communication ability of two ferrocenyl units. The larger ΔE indicates stronger electronic communication.

Figure 3. CVs of **1** (a) and **2** (b).Figure 4. Dihedral angles of Cp-ring plane of two ferrocenyls and Fe–Fe distances of **1** and **2**.

According to the ΔE values of **1** and **2**, electronic communication ability of the two ferrocenyl units of **2** is larger than that of **1**. The acetyl influences the electronic communication ability of the two ferrocenyl units.

The Fe–Fe distance in **2** (6.395 Å) is longer than that of **1** (5.765 Å), the dihedral angle of the Cp-ring plane of two ferrocenyls of **2** (101.3°) is larger than that of **1** (97.5°) (figure 4). According to Kohler and Yuan's [17, 18] suggestions, the shorter Fe–Fe distance and smaller dihedral angle mean stronger electronic communication of carbon-bridged diferrocenyl derivatives. Hence, the acetyl group should weaken electronic communication ability of two ferrocenyl units, inconsistent with the experimental result.

To understand the effect of acetyl group, cyclic voltammetric experiments of ferrocene (**Fc**) and acetylferrocene (**AFc**) were also performed (figure 5). The oxidation potentials of **Fc** and **AFc** are 0.650 and 0.910 V, respectively, indicating that the oxidation potential of ferrocene increased 260 mV under the electron withdrawing effect of acetyl.

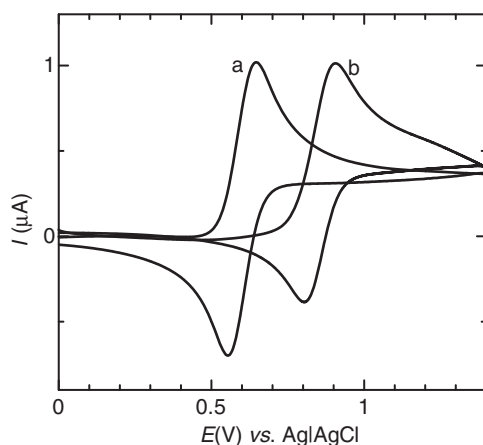


Figure 5. CVs of Fc (a) and AFc (b).

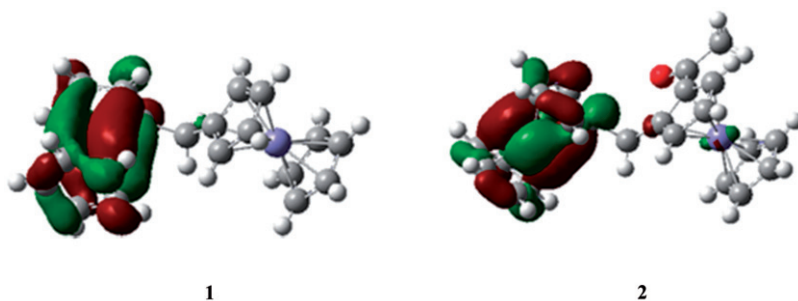


Figure 6. The HOMOs of **1** and **2** calculated by DFT.

If the effect of acetyl on electronic communication of **2** was ignored, the second oxidation potential (E_{b2}) of **2** should be 0.980 V, equal to E_{a2} plus 260 mV ($0.720 \text{ V} + 0.260 \text{ V} = 0.980 \text{ V}$). The predicted potential difference ($\Delta E_{b'}$) of **2** should be 410 mV ($0.980 - 0.570 \text{ mV}$). Interestingly, the predicted potential difference ($\Delta E_{b'}$) was nearly equal to the experimental actual value ($\Delta E_b = 405 \text{ mV}$). The difference of 5 mV ($\Delta E_{b'} - \Delta E_b$) is within the allowable error of the electrochemistry experiment. Hence, the effect of acetyl group on electronic communication between two ferrocenyl units is weak, only increasing the oxidation potential of substituted ferrocenyl unit just like that in AFc.

Because we have suggested charge density of the bridge carbon is important for electronic communication of carbon-bridged diferrocenyl derivatives [19], the electronic structures of the frontier orbitals of **1** and **2** were investigated by computational methods. Based upon a starting geometry from the X-ray structure analyses of **1** and **2**, calculations were carried out using the B3LYP density function and the 6-31G basis set for geometry optimization [26]. The results indicated that the HOMOs of **1** and **2** have similar electron contributions, the HOMO of **1** mainly localized on one ferrocenyl fragment and the HOMO of **2** localized on the non-substituted ferrocenyl fragment (figure 6). The energy of HOMO of **1** and **2** was 0.188 and 0.185 hartress, respectively. Hence, the first oxidation should occur on the more electron-rich ferrocenyl and should have similar oxidation potential ($E_{a1} \approx E_{b1} \approx 0.570 \text{ V}$).

We calculated Mulliken charges of bridged carbon of **1** and **2** as $\mathbf{1} = -0.269$ and $\mathbf{2} = -0.263$, indicating that the charge density of bridged carbon was not changed markedly by acetyl, even if acetyl group was a stronger electron-withdrawing group, further supporting that the charge density of the bridged carbon was the key factor of electronic interaction between two ferrocenyl units of diferrocenyl, acetyl group did not influence the electronic communication of **2**.

4. Conclusion

Two carbon-bridged diferrocenyl compounds, diferrocenylmethane (**1**) and 2-acetyl (diferrocenyl)methane (**2**), were synthesized and characterized by NMR, FT-IR, MS, elemental analysis, and X-ray single crystal diffraction. The effect of acetyl group on the electronic communication of **2** was discussed by comparing CV data of ferrocene to that of acetylferrocene and calculation of **1** and **2**. The results further supported charge density of the bridged carbon being the key factor for electronic communication between two ferrocenyl units of diferrocenyl derivatives.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos 816937 and 816942 for **1** and **2**, respectively. Copies of this information may 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).

Acknowledgments

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