단 신

π-다리로 연결된 디-페로센의 전기화학적 특성

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Electrochemical Properties of Di-ferrocenes Linked by π-Bridge

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Ferrocene ($C_{10}H_{10}Fe$: bis(η^5-cyclopentadienyl)iron: **Fc**) is known as a good electron donor molecule showing one reversible redox cycle.[1] This is one of the reasons why ferrocene is widely used as the main component of electronic, optical and biologically-active materials. Especially, multi-ferrocenyl compounds are frequently studied in the research field of intra-molecular electron-transfer processes. Di-ferrocene compounds linked by a polyethylene moiety (Fc(CH = CH)$_m$Fc: **dFcE$_m$**) are the typical system studied by many researchers.[2] The number and the geometry of ethylene linkage are the critical factors which control the efficiency of electron-transfer in this system. In this study, we prepared and spectroscopically characterized a di-ferrocenyl compound in which two ferrocenyl groups are linked by an enone moiety (Fc-C(O)CH = CH-Fc: **Fc-Fc**). The electron-transfer behavior of this compound was investigated electrochemically and compared with that of 1,2-diferrocenylethylene (**dFcE**). This is a part of series of studies of ferrocenyl chalcones.[3]

EXPERIMENTAL

General Methods

Acetylferrocene (**ActFc**), ferrocenecarboxaldehyde (**FcAld**) and HPLC-grade organic solvents were commercially purchased (Aldrich) and used as received.

The FT-IR spectra were recorded on a MIDAC FT-IR spectrometer within the range of 4000 ~ 400 cm^{-1}. The UV-Vis spectra were measured on an HP 8452A diode array spectrophotometer. The ^{1}H NMR spectra were obtained on a Bruker Avance 500 using CDCl$_3$ as a solvent. The mass spectra were obtained on a JMS-700 Mstation by fast atom bombardment (FAB). The electrochemical studies were carried out at room temperature with a CHI 620A Electrochemical Analyzer (CHI Instrument Inc.) under the following conditions: 1.0 mM samples in MeCN containing 0.1 M n-Bu$_4$N·BF$_4$ using a Pt-button (r = 1 mm) working electrode. Ag/AgCl reference electrode and Pt-wire (ϕ = 1 mm) counter electrode at a scan rate of 50 mV s^{-1}. The potentials were referenced to that of Fc/Fc$^-$ ($E_{1/2}$ = +0.464 V *vs.* Ag/AgCl).

Preparation of Fc-Fc

A mixture of **ActFc** (1 mmol, 228 mg), **FcAld** (1 mmol, 214 mg) and NaOH (5 mmol, 200 mg) was ground with an agate mortar and a pestle. This mixture was allowed to stand in a water bath (85 °C) for 30 min. The final product was extracted

with CH_2Cl_2 and the solution was dried with $MgSO_4$. After filtration, the solvent was removed at reduced pressure and the final product was separated from the residue by column chromatography (SiO_2, CH_2Cl_2). Yield: 63% (267 mg). Wine-red colored powder. Mp: 208~209°C. Elemental analysis: Cal. (Obs.) for $C_{23}H_{20}Fe_2O$: C, 65.14 (65.28); H, 4.75 (4.75). FAB-MS(m/z, %): 424.1 (M^+, 100), 359.1 ([$M-C_5H_5$]$^+$, 17), 307.3 ([$M-Fe(C_5H_5)-4H$]$^+$, 10). FT-IR (KBr, cm^{-1}): 3089 (Cp C-H), 1664, 1641 (C=O), 1574, 1448, 1290, 1248 (C=C), 826 (Cp C-H), 674 (C-H), 512, 481 (Cp-Fe). ^{1}H NMR (500 MHz, CDCl$_3$, ppm): 7.71 (1H, CH, d, J = 15.4 Hz), 6.75 (1H, CH, d, J = 15.4 Hz), 4.88 (2H, C$_5$H$_4$, t, J = 1.9 Hz), 4.60 (2H, C$_5$H$_4$, t, J = 1.8 Hz), 4.56 (2H, C$_5$H$_4$, t, J = 1.9 Hz), 4.47 (2H, C$_5$H$_4$, t, J = 1.8 Hz), 4.20 (5H, C$_5$H$_5$, s), 4.19 (5H, C$_5$H$_5$, s). UV-vis (nm): 314, 382, 492 (MeCN); 250, 316, 386, 500 (CHCl$_3$); 320, 386, 510 (EtOH); 322, 394, 488, 512 (MeOH).

Preparation of dFcE

1,2-Diferrocenylethylene (dFcE) was synthesized by the McMurry coupling method[1] using FcAld and a low-valence titanium compound prepared in a TiCl$_4$ and Zn powder mixture, as described in a previous report.[5] This compound was characterized spectroscopically and confirmed to be identical with that prepared before.[5]

RESULTS AND DISCUSSION

Synthesis and Characterization

Fc-Fc was synthesized by solvent-free aldol condensation using ActFc and FcAld with NaOH as a base catalyst. The purification of Fc-Fc was easily achieved by column chromatography using CH$_2$Cl$_2$ as the eluent, giving rise to a moderate yield (63%). In this reaction, using stoichiometric amounts of the reactants is important to reduce the amount of side products. For example, the product (Fc-Fc) can react further with an excess of the acetyl reactant to produce 1,5-pentadione derivatives via Michael addition reaction.[6] The purified product was characterized by elemental analysis to-
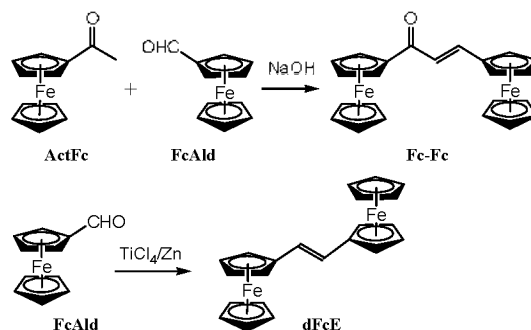
Scheme 1. Syntheses of **Fc-Fc** and **dFcE**.

gether with the FAB-mass, FT-IR, ^{1}H-NMR and UV-Vis spectroscopic methods. The FAB-MS data show the mother peak (M^+) at 424.1 for Fc-Fc with 100% intensity and the successive loss of the Cp and FeCp moieties at m/z = 359.1 and 307.3, respectively. The ν(C=O) of ActFc was observed at 1663 cm^{-1}, which shifts to a lower frequency (1641 cm^{-1}) for Fc-Fc. This is due to the delocalization of the π-electrons on the carbonyl and ethylene moieties in the enon linkage. The NMR spectra measured at room temperature show two doublets at 7.71 ppm (J = 15.4 Hz) and 6.75 ppm (J = 15.4 Hz) together with other peaks from the ferrocenyl moieties, indicating that the ethylene moiety in the enon linkage is in the *trans*-conformation.

Statistically, four isomers (two s-*cis* and two s-*trans* conformational isomers) are possible as the reaction product, among which the minimized energy structures of Fc-Fc with the s-*cis* conformation[8] are shown in *Fig.* 1. This may be one of the reasons why the Fc-Fc compound was precipitated as a reddish-brown powder, rather than being grown as single crystals, when it was recrystallized in many appropriate solvent pairs such as CH$_2$Cl$_2$/n-Hx, CH$_2$Cl$_2$/ether, CH$_2$Cl$_2$/EtOH, etc. Furthermore, the techniques of electrochemical

Fig. 1. Energy-minimized structures of Fc-Fc with s-*cis* conformation calculated by using DMol3 method.

oxidation using an n-Bu$_4$N·PF$_6$ electrolyte and chemical oxidation with I$_2$, TCNQ or F$_4$TCNQ were not effective to obtain a single crystal of the **Fc-Fc** charge-transfer salt, for the same reason.

Electrochemical Study

The cyclic voltammetry (CV) and differential pulse voltammetry (DPV) results for **Fc-Fc** and **dFcE** are shown in *Fig.* 2 and 3, respectively. The electrochemical parameters are listed and compared with those of the reactants in *Table* 1. Both complexes show two reversible and reproducible cycles on a repeated scan between 0~1.3 V, irrespective of the working electrodes (Pt, Au or glassy carbon), corresponding to the two redox processes of the ferrocenyl moieties (Fc$^+$ ↔ Fc). The first

half-wave potential of **dFcE** ($E_{1/2}^1$ = 0.404 V) is smaller than that of **Fc-Fc** ($E_{1/2}^1$ = 0.581 V) and even smaller than those of **ActFc** ($E_{1/2}^1$ = 0.712 V) and **FcAld** ($E_{1/2}^1$ = 0.752 V). Based on the results of the MO calculation[9] on the simplified compounds (*Fig.* 4), in which the ferrocenyl moieties were replaced with cyclopentadienyl rings, the electrons in the HOMO are mainly located on the Cp-C(O)CH–CH- part of Cp-C(O)CH–CH-Cp, while they are on the Cp part of Cp-CH–CH-Cp. It can be inferred from this result that the $E_{1/2}^1$ value of **dFcE** is smaller than that of **Fc-Fc**. On the contrary, the difference between $E_{1/2}^1$ and $E_{1/2}^2$ for **dFcE** (ΔE^0 = 173 mV) is slightly larger than that for **Fc-Fc** (165 mV). As the ΔE^0 value is closely related to the measure of repulsive energy between
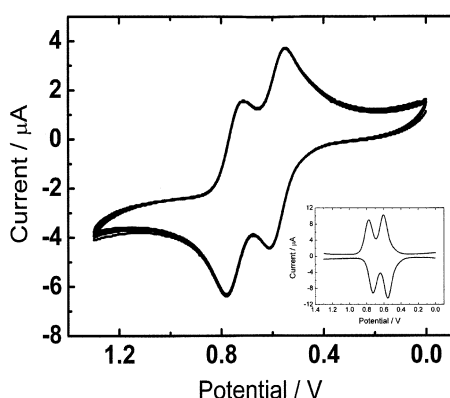

Fig. 2. The cyclic voltammogram (CV) scanned 10 times repeatedly between 0 V and 11.3 V and corresponding differential pulse voltammograms (DPV; inset) of the **Fc-Fc** compound (vs. Ag/AgCl).
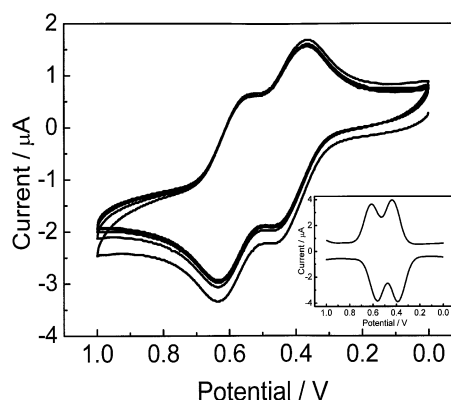

Fig. 3. The cyclic voltammogram (CV) scanned 5 times repeatedly between 0 V and 11.0 V and corresponding differential pulse voltammograms (DPV; inset) of the **dFcE** compound (vs. Ag/AgCl).

Table 1. The cyclic voltammetry parameters for **Fc-Fc**, **dFcE** and their reactants.[a]

Compound	Anodic		Cathodic		$E_{1/2}$[b]	ΔE^0[c]
	E_{pa}^1	E_{pa}^2	E_{pc}^1	E_{pc}^2		
ActFc	0.745		0.679		0.712	
FcAld	0.787		0.717		0.752	
Fc-Fc	0.611			0.551	0.581	0.165
		0.781	0.711		0.746	
dFcE	0.456			0.351	0.404	0.173
		0.621	0.532		0.577	

[a]The samples are dissolved in MeCN containing 0.1 M n-Bu$_4$N·BF$_4$ electrolyte, and the potentials (in volt) are referenced to Fc/Fc$^+$ ($E_{1/2}$ = +0.464 V vs. Ag/AgCl). [b]$E_{1/2}$ = (E_{pa} + E_{pc})/2. [c]ΔE^0 = $E_{1/2}^2$ - $E_{1/2}^1$.
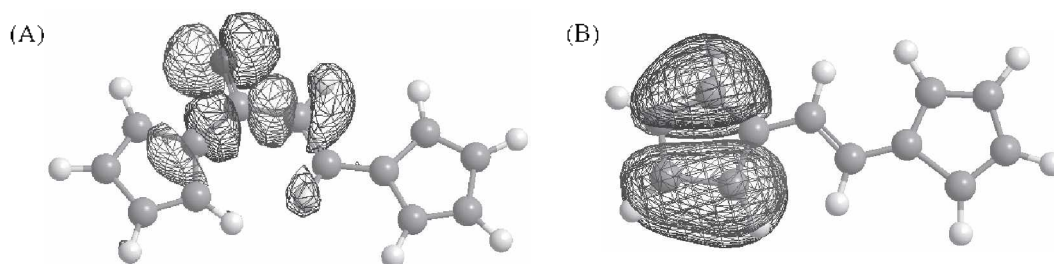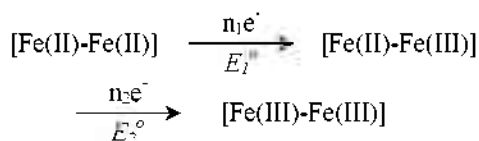
(A)　　　　　　　　　　　　　　　　　　　　(B)

Fig. 4. HOMO of (A) Cp-C(O)CH=CH-Cp (N = 34, -11.920 eV) and (B) Cp-CH=CH-Cp (N = 29, -12.408 eV). These are the model compounds in which the ferrocenyl moieties in **Fc-Fc** and **dFcE** are replaced with cyclopentadienyl rings for the simplification of the calculation.

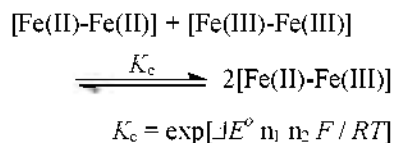*Table* 2. The comparison of ΔE° (mV) and K_c values of the diferrocenyl compounds.

	Compound	No. C(sp^2)	ΔE° (mV)	Solvent	$K_c{}^a$	ref
dFcE	Fc(CH=CH)Fc	2	173	CH$_3$CN	841	This work
		2	170	CH$_2$Cl$_2$	748	2b
Fc-Fc	FcCO(CH=CH)Fc	3	165	CH$_3$CN	616	This work
dFcE$_2$	Fc(CH=CH)$_2$Fc	4	129	CH$_2$Cl$_2$	151	2b
dFcE$_3$	Fc(CH=CH)$_3$Fc	6	100	CH$_2$Cl$_2$	49	2b

$^a \Delta E^{\circ} = (RT/F) \ln K_c = (25.69) \ln K_c$ at 298K.

the two charged centers (that is, the Coulomb repulsion energy), it can be expressed by the comproportionation constant (K_c) of the successive redox processes of the di-ferrocenyl system, as described below:[10]

$$[\text{Fe(II)-Fe(II)}] \xrightarrow[E_1^{\circ}]{n_1 e^-} [\text{Fe(II)-Fe(III)}]$$

$$\xrightarrow[E_2^{\circ}]{n_2 e^-} [\text{Fe(III)-Fe(III)}]$$

At equilibrium,

$$[\text{Fe(II)-Fe(II)}] + [\text{Fe(III)-Fe(III)}]$$

$$\xrightarrow{K_c} 2[\text{Fe(II)-Fe(III)}]$$

$$K_c = \exp[\Delta E^{\circ} n_1 n_2 F / RT]$$

where $n_1 = n_2 = 1$, $\Delta E^{\circ} = E_2^{\circ} - E_1^{\circ}$ and $K_c = \exp[\Delta E^{\circ}/25.69]$ at 298K. This gives $K_c = \exp(165/25.69) \approx 616$ for **Fc-Fc** and $K_c = \exp(173/25.69) \approx 841$ for **dFcE**. These K_c values are compared with those of **dFcE$_m$** (m = 1, 2 and 3)[2b] in *Table* 2. The results clearly show that the number of sp^2 carbon atoms

between the redox active ferrocenyl centers of the **dFcE$_m$** system is inversely proportional to the K_c value. It is noteworthy that the K_c value for **Fc-Fc** (No. C(sp^2) = 3) is closer to that of **dFcE** (No. C(sp^2) = 2), than that of **dFcE$_2$** (No. C(sp^2) = 4), even though the enone bridge contains an additional ketone moiety. In other words, we can surmise that the additional antibonding π-orbital on the ketone moiety does not significantly inhibit the intramolecular electron-transfer process. Moreover, it should also be pointed out that the solvents used in the CV measurement (CH$_3$CN and CH$_2$Cl$_2$) do not affect the results seriously enough to cause a deviation from this trend.

In conclusion, it is demonstrated herein that the enone is as effective a bridging group as the ethylene moiety, in terms of its accommodation of electronic communication between the two redox active ferrocenyl groups.

REFERENCES

1. Hayashi, T.; Togni, A. (eds.), *Ferrocenes*, VCH, Weinheim, 1995.
2. (a) Tolbert, L. M.; Zhao, X.; Ding, Y.; Bottomley, L. A. *J. Am. Chem. Soc.*, **1995**, *117*, 12891. (b) Ribou, A. C.; Launay, J. P.; Sachtleben, M. L.; Li, H.; Spangler, C. W. *Inorg. Chem.*, **1996**, *35*, 3735-3740. (c) Dong, T. Y.; Lin, P. J.; Lin, K. J. *Inorg. Chem.*, **1996**, *35*, 6037. (d) Dong, T. Y.; Chang, C. K.; Lee, S. H.; Lai, L. L.; Chiang, M. Y.; Lin, K. J. *Organomet.*, **1997**, *16*, 5816. (e) Heigl, O. M.; Herker, M. A.; Hiller, W.; Kohler, F. H.; Schell, A. *J. Organomet. Chem.*, **1999**, *574*, 94.
3. (a) Jung, Y. J.; Son, K.-I.; Oh, Y. E.; Noh, D.-Y. *Polyhedron*, **2008**, *27*, 861. (b) Son, K.-I.; Noh, D.-Y. *J. Korean Chem. Soc.* **2007**, *51*, 591.
4. (a) McMurry, J. E. *Acc. Chem. Res.*, **1974**, *7*, 281. (b) McMurry, J. E.; Fleming, M. P.; Kees, K. L.; Krepski, L. R. *J. Org. Chem.*, **1978**, *43*, 3255. (c) Takimiya, K.; Shibata, Y.; Ohnishi, A.; Aso, Y.; Otsubo, T.; Ogura, F. *J. Mater. Chem.*, **1995**, *5*, 1539.
5. Lee, H. J.; Noh, D. Y. *J. Mater. Chem.* **2000**, *10*, 2167.
6. Yang, J.-X.; Tao, X.-T.; Yuan, C. X.; Yan, Y. X.; Wang, L.; Liu, Z.; Ren, Y.; Jiang, M. H. *J. Am. Chem. Soc.*, **2005**, *127*, 3278.
7. Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectroscopic Identification of Organic Compounds*, 5th ed., John Wiley, Singapore, 1991.
8. MS Visualizer 4.3, Accelrys.
9. Chem3D Ultra, ver. 10.0, ChemOffice, CambridgeSoft.
10. Richardson, D. E.; Taube, H. *Inorg. Chem.*, **1981**, *20*, 1278.