

Synthesis, structure, and electrochemical properties of biferrocenes annulated with 1,2-dithiin and 1,2-dithiin 1,1-dioxides

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Abstract—2,2''-Bis(*N,N*-dimethylaminosulfonyl)-1,1''-biferrocene (**6**), a precursor of biferrocenes annulated with 1,2-dithiin and 1,2-dithiin 1,1-dioxides, was prepared by a sequence of selective *ortho*-lithiation and dimerization reaction from *N,N*-dimethylaminosulfonylferrocene. New biferrocenes annulated with 1,2-dithiin (**1**) and 1,2-dithiin 1,1-dioxides (**2**) and (**3**) were successfully synthesized in satisfactory yields by the reaction of compound **6** with lithium aluminum hydride followed by treatment with chlorotrimethylsilane. The electrochemical properties of the biferrocenes (**1**)–(**3**) were furnished by voltammetric studies.
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Much attention has been lately devoted to the chemistry of ferrocenes because of the facility for organic functionalization and the chemical stability of both ferrocene and ferrocenium species. These unique properties make complexes having ferrocenes good candidates for the preparation of new materials with applications in organic synthesis and material science.¹ Moreover, complexes in which two or more metal centers are simultaneously coordinated to a bridging ligand interact between the metal centers, and are models for organometallic polymers.² Since the first designed mixed-valence complexes, the Creutz–Taube ion³ and the biferrocenium cation,⁴ were reported, there were numerous reports on the synthesis and properties of mixed-valence compounds on the basis of their electrochemical, spectroscopic, and magnetic measurements.⁵ Now, we have designed *anti*- and *syn*-biferrocenes in which the fulvalene fragments are fixed by disulfanyl or thiosulfonyl moieties. We report here the synthesis, structural characterization, and electrochemical properties of *anti*-biferrocenes (**1**) and (**2**) and *syn*-biferrocene (**3**).

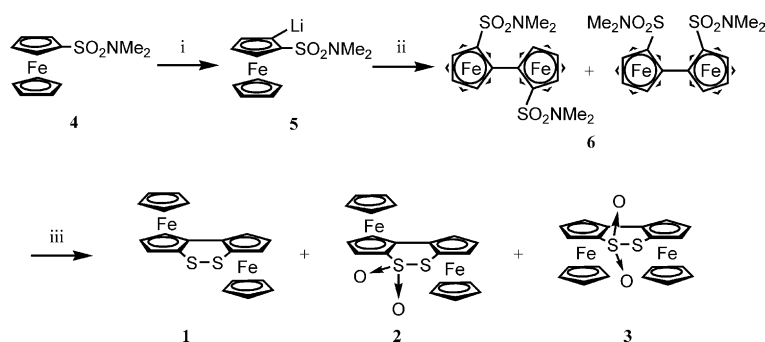
Treatment of *N,N*-dimethylaminosulfonylferrocene⁶ (**4**) with an equimolar amount of *n*-butyllithium in THF at 0 °C followed by treatment of the resulting *ortho*-lithioferrocene (**5**) with copper(I) chloride gave 2,2''-bis(*N,N*-dimethylaminosulfonyl)-1,1''-biferrocene (**6**) as a mixture of diastereomers in 62% isolated yield (Scheme 1). To a solution of a diastereomeric mixture of **6** in THF at 0 °C was added lithium aluminum hydride. The reaction mixture was heated under reflux condition for 48 h and cooled to 0 °C. Then, chlorotrimethylsilane was added to the reaction mixture at 0 °C and it was stirred at room temperature for 1 h. After usual work-up, purification of the reaction mixture by column chromatography on silica gel with chloroform as the eluent gave *anti*-biferrocene **1** fixed by a disulfanyl unit in 10% isolated yield, and *anti*- and *syn*-biferrocenes **2** and **3** fixed by thiosulfonyl moieties in 19% and 17% isolated yields, respectively.⁷ Upon treatment of the reaction mixture with aqueous hydrochloric acid instead of chlorotrimethylsilane, the isolated yields of these biferrocenes **1**–**3** decreased to less than 1% and oligomeric mixtures were obtained without solubility in common organic solvents. No formation of the corresponding *syn* isomer to biferrocene derivative **1** was observed in the same condition. All of these biferrocenes (**1**–**3**) were quite stable toward day light and were thermally stable up to 300 °C under air. Although it had been reported that many 1,2-dithiins were sensitive to light-induced extrusion reaction of a sulfur atom to form the corresponding thiophenes,⁸ the structure of **1** could be kept

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Scheme 1. Reagents and conditions: (i) *n*-BuLi, THF, 0 °C, 2 h; (ii) (a) CuCl, 0 °C to room temperature, (b) under an oxygen atmosphere, 1 h; (iii) (a) LiAlH₄, THF, reflux, 24 h, (b) Me₃SiCl, 0 °C to room temperature.

in a chloroform solution for 24 h at 15 °C under photoirradiation using a high-pressure mercury lamp and for several months at room temperature under day light. The prominent stability of **1** is similar to those of previously reported 1,2-dithiins annulated with bicycloalkenes, that is, 1,7,7-trimethylbicyclo[2.2.1]hept-2-ene⁹ and bicyclo[2.2.2]oct-2-ene.¹⁰ Thus, a cyclopentadienyl ring of a ferrocene of **1** may prevent the formation of 2-butenedithial derivative as an acyclic tautomer form generating under these conditions in analogy of the case of the bicycloalkenes.^{9,10}

The structural characterization of new biferrocenes **1–3** has been performed by the ¹H and ¹³C NMR spectroscopies and X-ray crystallographic analyses. The features of the ¹H and ¹³C NMR spectra for **1** indicated a C₂ symmetric conformation in a solution. In the ¹H and ¹³C NMR spectra of **1**, the singlet signals for the unsubstituted cyclopentadienyl ring were 4.17 and 70.9 ppm, respectively. Furthermore, the infrared spectrum of **1** exhibited neither a sulfinyl nor a sulfonyl group. As shown in Figure 1, the X-ray crystallographic analysis for **1** revealed that two ferrocene units were located in an *anti*-conformation, the torsion angle of which was ca. 17°. The structural parameters of the ferrocene moieties for **1** should be the usual values, which were comparable to those for the previously reported ferrocenes.² In addition, the structure of the six-membered 1,2-dithiin ring of **1** showed that the sulfur–sulfur bond length (2.0710(12) Å) was similar to those of the reported 1,2-dithiins (2.06–2.07 Å),¹² and the C–S–S–C torsion angle (–48.54(6)°) lay in a range of the typical torsion angles (46.6–54.6°) of the reported 1,2-dithiins.¹²

The features of the ¹H and ¹³C NMR spectra for **2** and **3** are in sharp contrast to **1**. It was indicated that the signals for the two ferrocene units of both **2** and **3** were not equivalent, which should be C₁ symmetric structures in solution. Then, the signals for the unsubstituted cyclopentadienyl ring of the ¹H NMR spectra for **2** and **3** in chloroform-*d*₁ solution were 4.20 and 4.21 ppm and 4.41 and 4.55 ppm, respectively. In the NOESY spectrum of **3**, an enhancement between the unsubstituted cyclopentadienyl ring protons for **3** was exclusively observed through the cross-peaks. However, it was not observed for **2** under the same conditions. These results indicated that the conformations of two ferrocene

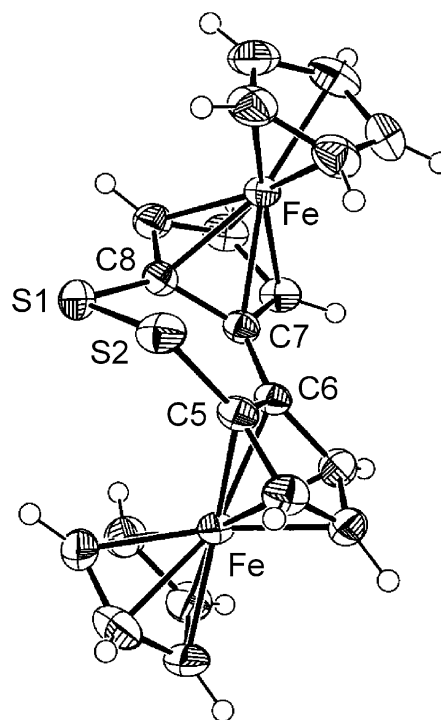


Figure 1. ORTEP drawing of **1** with thermal ellipsoid plots (50% probability). Selected bond distances (Å) and torsion angles (°): S1–S2 2.0710(12), S1–C8 1.755(3), S2–C5 1.759(3), C5–C6 1.426(4), C7–C8 1.438(4), C6–C7 1.466(4), C5–S2–S1–C8 –48.54(6), C5–C6–C7–C8–17.23(5).

moieties of **2** and **3** are located in *anti*- and *syn*-conformations, respectively. Moreover, the infrared spectra of **2** and **3** showed characteristic resonances at 1309 and 1127 (**2**) and 1306 and 1122 (**3**) cm^{–1}, which should be the stretching vibration of the sulfonyl group, respectively, in analogy of the case of the reported 1,2-dithiin 1,1-dioxides.¹³ Single crystals of **3** were successfully obtained by slow crystallization from a chloroform solution at room temperature. The crystal structure of **3** was determined by X-ray crystallographic analysis and revealed that two ferrocene units were located in a *syn*-conformation having the twist angle of ca. 28° (Fig. 2).¹⁴ Thus, the molecular structure of **3** was supported by not only the spectroscopic data but also the solid-state structure. The structural parameters of the

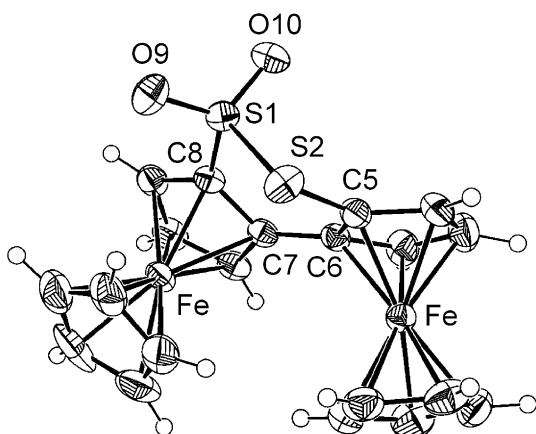


Figure 2. ORTEP drawing of **3** with thermal ellipsoid plots (50% probability). Selected bond distances (Å) and torsion angles (°): S1–S2 2.0882(15), S1–C8 1.742(4), S2–C5 1.765(4), C5–C6 1.739(5), C6–C7 1.455(5), C7–C8 1.444(5), C8–S1–S2–C5 53.72(7), C8–C7–C6–C5 27.61(4).

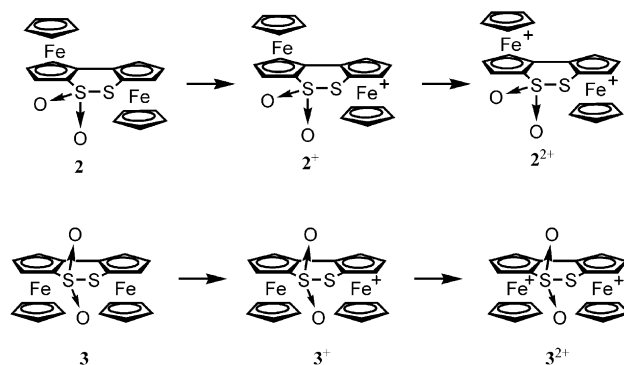
ferrocene moieties for **3** should be the usual values, which were comparable to those for the previously reported ferrocenes.² The distance between two iron atoms for **3** was 4.52 Å which was closer than that for **1** (5.13 Å). In addition, the structure of the six-membered 1,2-dithiine ring of **3** showed that the sulfur–sulfur bond length was 2.0882(15) Å which lay in a range of the reported typical bond lengths (2.01–2.11 Å),¹⁵ and the C–S–S–C torsion angle was 53.72(7)° due to repulsion between the oxygen atoms and the lone-pair electrons on the neighboring sulfur atoms.

The redox behavior of **1–3** has been furnished by cyclic and differential pulse voltammetric studies. As shown in Figure 3, the cyclic voltammograms of **1–3** were measured in benzonitrile (in the case of **1**) and acetonitrile (in the case of **2** and **3**) containing 0.1 mol dm^{−3} *n*-Bu₄NPF₆ as a supporting electrolyte at room temperature under an argon atmosphere and their redox potentials were summarized in Table 1. Biferrocene derivative **1** displayed two reversible one-electron redox waves as Fe(II)/Fe(III) and Fe(III)/Fe(III) processes. The difference between the half-potentials ($\Delta E_{1/2}$) for **1** was 0.35 V and implied a comproportionation constant $K_c = 8.2 \times 10^5$ for the Fe(II)–Fe(III) mixed-valence state, indicating a reasonably strong electronic interaction as

Table 1. Redox potentials [V vs Ag/Ag⁺] of biferrocenes **1**, **2**, and **3**

	1		2		3	
	First	Second	First	Second	First	Second
E_{pa}	+0.12	+0.47	+0.19	+0.65	+0.26	+0.62
E_{pc}	+0.03	+0.38	+0.12	—	+0.18	—
$E_{1/2}$	+0.08	+0.43	+0.16	—	+0.22	—

well as that for the previously reported biferrocene ($\Delta E_{1/2} = 0.33$ V and $K_c = 3.8 \times 10^5$ in *n*-Bu₄NClO₄–CH₃CN).¹⁶ Biferrocene derivatives **2** and **3** showed reversible and subsequent irreversible waves, both of which corresponded to one-electron processes as judged by their differential pulse voltammograms. Considering the strong electron-withdrawing effect of the sulfonyl groups in **2** and **3**, the oxidation pathways are expected to involve mixed-valence states in which charge distribution is roughly expressed as mono-cationic forms **2**⁺ and **3**⁺ as shown in Scheme 2. The irreversible redox behavior for **2** and **3** implies that thermodynamic instabilities of the dicationic forms **2**²⁺ and **3**²⁺ are in contrast to the stability of **1**²⁺ under this condition. The separation between the first and second oxidation potentials (ΔE_{pa}) for **2** and **3** were 0.46 and 0.36 V, which gave comproportionation constants $K_c = 5.9 \times 10^7$ and 1.2×10^6 for the Fe(II)–Fe(III) mixed-valence states, respectively. The latter was similar to that of the previously reported *syn*-biferrocene ($\Delta E_{1/2} = 364$ mV and $K_c = 1.4 \times 10^6$ in CH₃CN).¹⁷ Interestingly, it was found that the structural difference between **2** and **3** should cause the differences in their redox behavior and thermodynamic stability in mixed-valence intermediates **2**⁺ and **3**⁺.



Scheme 2. Plausible oxidation processes for **2** and **3**.

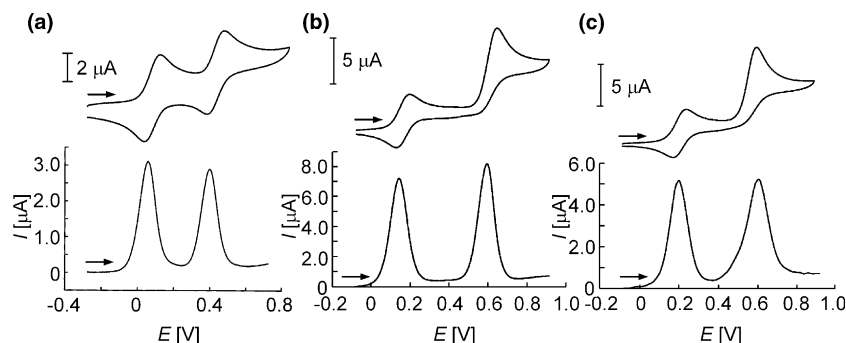


Figure 3. Cyclic (top) and differential pulse (bottom) voltammograms of **1** (a), **2** (b), and **3** (c).

In summary, we have succeeded in the synthesis of *anti*-biferrocene annulated with 1,2-dithiin (fixed by a disulfanyl group) **1** and *anti*- and *syn*-biferrocenes annulated with 1,2-dithiin 1,1-dioxides (fixed by a thiosulfonyl group) **2** and **3** by the reactions of biferrocene **6** bearing two *N,N*-dimethylaminosulfonyl groups. The crystal structures of **1** and **3** were confirmed by X-ray crystallographic analyses. The electrochemical properties of **1–3** were furnished by cyclic and differential pulse voltammetric studies which were indicative of the metal–metal interactions between two iron centers in the homometallic systems having the fulvalene fragments fixed by disulfanyl or thiosulfonyl moieties. It was found that the structural difference between **2** and **3** enabled improvement in their electrochemical behavior. Further studies on chemical oxidations of biferrocenes **1–3** are in progress.

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