Synthesis and Properties of 1,1-Diferrocenylethylenes and Their Mono- and Dications

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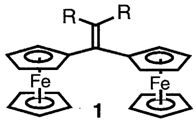
(Received September 9, 1996)

1,1-Diferrocenylethylenes have been synthesized efficiently by palladium-catalyzed cross-coupling reaction. The interaction of the two ferrocene units has been investigated in the neutral, monocationic and dicationic states using spectroscopic analyses.

Conjugated systems containing two ferrocene units can be expected to show intramolecular and intermolecular interactions of the ferrocenyl groups either in solution or in solid state. Thus, the two ferrocenyl groups at 1,1-position of ethylene bonds like **1** can show the cross-conjugation in the neutral state. When one of two ferrocenyl groups is oxidized to the monocation **2**, the delocalization of the cationic charge between the ferrocene and ferrocenium ions in **2** may occur to give a mixed-valence state.[1] In addition, the dication **3** derived from **1** is expected to show a triplet ground state, because the topological symmetry of the π-conjugated systems in **3** leads to the ferromagnetic interaction between two ferrocenium cations.[2] We now report here the convenient synthesis of **1** and properties of the mono- and di-cations **2** and **3**.



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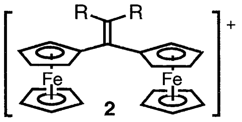

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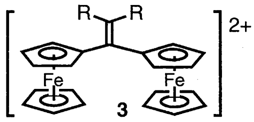

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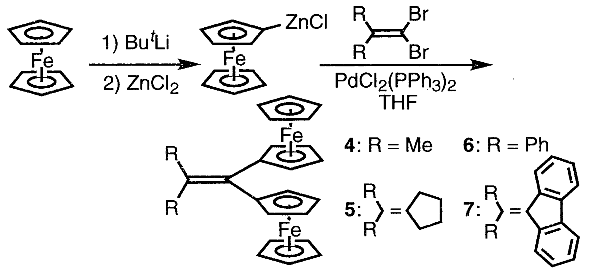
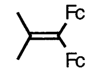
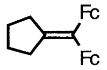
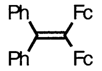
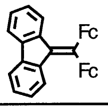
In order to construct the framework of the title compounds, we applied the palladium-catalyzed coupling reaction as shown in Scheme 1. Ferrocene can be easily converted into its lithio derivative by treatment with *t*-butyllithium.[3] Thus, we obtained ferrocenylzinc chloride by successive treatment of ferrocene with 1.2 equiv. of *t*-butyllithium and 1.28 equiv. of zinc chloride. The reaction of 2,2-disubstituted 1,1-dibromo-ethylenes with ferrocenylzinc chloride (3 equiv.) in THF in the presence of $PdCl_2(PPh_3)_2$ (10 mol%) gave the desired 1,1-diferrocenylethylenes **4**-**7** in a one-pot procedure in 55, 50, 75, and 67% yields, respectively.[4,5]



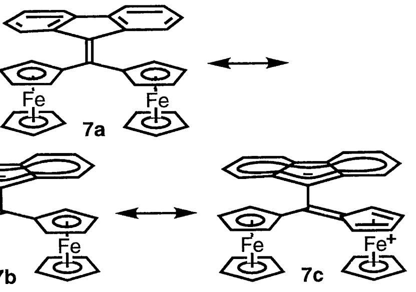
Scheme 1.

The cyclic voltammetric analysis of the 1,1-diferrocenylethylenes **4**-**7** shows two one-electron oxidations, reflecting the interaction of the two ferrocenyl groups in **4**-**7**. As shown in Table 1, the first oxidation potentials of the 1,1-diferrocenylethylenes **4**-**6** are lower than that of ferrocene, whereas the second oxidation potentials of **4**-**6** are higher. In the case of **7**, the crystals of this molecule have a deep violet color, because the fluorenide structure **7b** and **7c** make a contribution to 9,9-diferrocenylmethylenefluorene **7**. The contribution of the structure **7b** and **7c** increases the positive charge of the ferrocenyl groups, and hence the oxidation potentials of **7** are shifted to more positive.

Table 1. Redox potentials of 1,1-diferrocenylethylenes (**4**-**7**)[a]

Compounds		$E^1_{1/2}$	$E^2_{1/2}$	ΔE
	4	-0.10	0.06	0.16
	5	-0.09	0.05	0.16
	6	-0.05	0.10	0.15
	7	0.03	0.19	0.16

[a] V *vs*. Fc/Fc$^+$ measured by cyclic voltammetry with Bu_4NClO_4 (0.1 M) as the supporting electrolyte in PhCN.



Scheme 2.

The molecular structures of **6** and **7** were determined by X-ray crystallographic analysis.[6] The two ferrocenyl groups of **6** are located at opposite sides of the central ethylene plane with torsional angles of 35° and 17°. Two phenyl groups are also twisted with angles of 54° and 59°. Furthermore, these bulky substituents distort the central double bond with a torsion angle of about 15°. In the case of **7**, the corresponding double bond is more twisted (29°) and elongated as the result of the resonance shown in Scheme 2.

The diferrocenylethylenes **4**-**7** were oxidized easily by the treatment with molecular iodine to afford mono- and dication depending on the substituents at 2-position. Thus, 2,2-dimethyl derivative **4** gave the corresponding dication $4^{2+}{\bullet}2I_3^-$ in 91%

yield and 2,2-diphenyl derivative **6** gave the corresponding monocation $\mathbf{6}^{+}\bullet I_3^-$ in 93% yield.

These cations were characterized by the ^{57}Fe-Mössbauer spectroscopy as shown in Table 2. The spectrum of dication $\mathbf{4}^{2+}\bullet 2I_3^-$ shows only a ferrocenium signal, which means all ferrocene nuclei were completely oxidized. The Mössbauer spectrum of $\mathbf{6}^{+}\bullet I_3^-$ was observed as a four-line spectrum which showed the separated system of ferrocene and ferrocenium. This localized structure was also supported by the X-ray crystallography as shown in Figure 3.[6] The averaged bond length of Fe(II)-C was observed to be 0.06 Å longer than that of [illegible](III)-C.

Table 2. ^{57}Fe-Mössbauer parameters of $\mathbf{4}^{2+}\bullet 2I_3^-$ and $\mathbf{6}^{+}\bullet I_3^-$

Compound	*T* (K)	δ (mm/s)	ΔE_Q (mm/s)	Γ (mm/s)
$\mathbf{4}^{2+}\bullet 2I_3^-$	298	0.46	0.30	0.29, 0.30
	80	0.55	0.33	0.43, 0.36
$\mathbf{6}^{+}\bullet I_3^-$	298	0.43	2.20	0.32
		0.48	0.35	0.31
	80	0.53	2.28	0.25, 0.26
		0.60		0.65

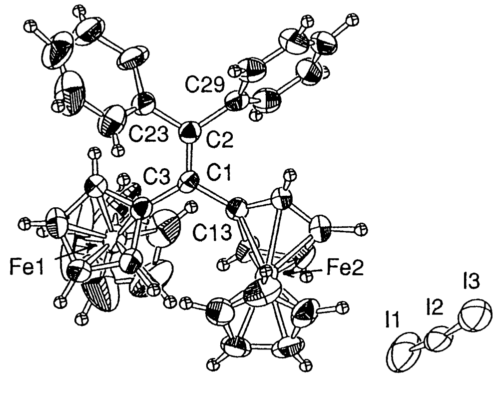


Figure 3. Molecular structure of $\mathbf{6}^{+}\bullet(I_3)^-$. The selected bond distances (Å): C1-C2 1.365(10), C1-C3 1.459(10), C1-C13 1.491(9), C2-C23 1.493(10), C2-C29 1.500(10), Fe1-C(average) 2.02, Fe2-C(average) 2.08.

Magnetic susceptibility of the dication $\mathbf{4}^{2+}\bullet 2I_3^-$ was measured by SQUID susceptometer in the range 2-270 K under 5000 Oe of the magnetic field. The results are shown in Figure 4, where the paramagnetic susceptibility and effective magnetic moment vs. temperature are plotted. The temperature dependence of magnetic susceptibility followed Curie-Weiss law with -2.6 K of Weiss constant. On the other hand, the effective magnetic moment of $\mathbf{4}^{2+}\bullet 2I_3^-$ showed constant value (3.49 μ_B) above 30 K and decreased at lower temperatures. Usually, the effective magnetic moment of ferrocenium salts are largely deviated from the spin only value (1.73 μ_B) due to the orbital contribution and reported to be 2.3-2.6 μ_B.[8] If such magnetic properties of ferrocenium salts applicable to $\mathbf{4}^{2+}\bullet 2I_3^-$, the two ferrocenium groups of $\mathbf{4}^{2+}\bullet 2I_3^-$ are concluded to be magnetically independent above 30 K and the decrease of the effective magnetic moment below 30 K would be interpreted as intra- and/or intermolecular antiferromagnetic interactions.[9]

We believe that our experiments have disclosed interesting inter-actions of two ferrocene units at 1,1-diferrocenylethylenes in the neutral, monocationic and dicationic states, although these interactions are weak. The synthesis of 1,1-metallocenylethylenes having stronger interactions are now under investigation.

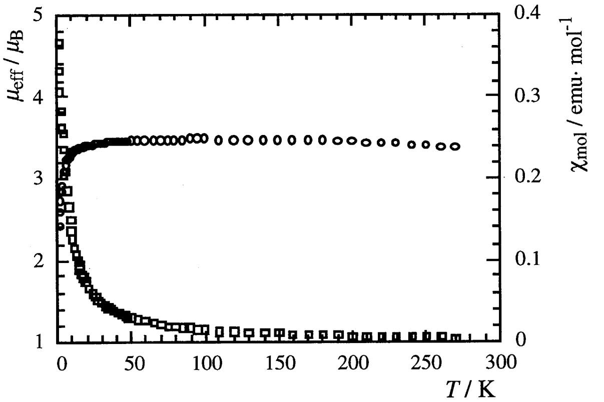


Figure 4. Magnetic susceptibility and effective magnetic moment of $\mathbf{4}^{2+}\bullet 2I_3^-$.

We thank to Professor T. Nogami and Dr. T. Ishida, Department of Applied Physics and Chemistry, The University of Electro-Communications for the measurements of the magnetic susceptibility of $\mathbf{4}^{2+}\bullet 2I_3^-$.

References and Notes

1 C. L. Vanda, K. Bechgaard, D. O. Cowan, U. T. Mueller-Westerhoff, P. Eilbracht, G. A. Candela, and R. L. Collins, *J. Am. Chem. Soc.*, **98**, 3181 (1976); J. A. Kramer and D. N. Hendrickson, *Inorg. Chem.*, **19**, 3330 (1980); T.-Y. Dong, D. N. Hendrickson, K.Iwai, M. J. Cohn, S. J. Geib, A. L. Rheingold, H. Sano, I. Motoyama, and S. Nakashima, *J. Am. Chem. Soc.*, **107**, 7996 (1985); S. Barlow, V. J. Murphy, J. S. O. Evans, and D. O'Hare, *Organometallics*, **14**, 3461 (1995).

2 T. Matsumoto, N. Koga and H. Iwamura, *J. Am. Chem. Soc.*, **114**, 5448 (1992); T. Matsumoto, T. Ishida, N. Koga and H. Iwamura, *J. Am. Chem. Soc.*, **114**, 9952 (1992).

3 F. Rebiere, O. Samuel, and H. B. Kagan, *Tetrahedron Lett.*, **31**, 22 (1990).

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5 Selected spectral data are as follows: **4**: orange needles, mp 140-1 °C, ^{1}H NMR ($CDCl_3$) δ 4.30-4.28 (m, 4H), 4.20-4.17 (m, 4H), 4.01 (s, 10H), 2.12 (s, 6H); MS (EI) *m/z* 424 (M^+). **5**: orange crystals, mp 143-4 °C, ^{1}H NMR ($CDCl_3$) δ 4.54-4.52 (m, 4H), 4.20-4.18 (m, 4H), 4.03 (s, 10H); 2.64-2.58 (m, 4H), 1.73-1.67 (m, 4H); MS (EI) *m/z* 450 (M^+). **6**: red crystals, mp 250 °C (decomp.), ^{1}H NMR ($CDCl_3$) δ 7.27-7.18 (m, 6H), 7.10-7.05 (m, 4H), 4.60-4.59 (m, 4H), 4.18-4.16 (m, 4H), 4.16 (s, 10H); MS (EI) *m/z* 548 (M^+). **7**: purple crystals, mp 263 °C (decomp.), ^{1}H NMR ($CDCl_3$) δ 7.73 (d, J = 7.4 Hz, 2H), 7.65 (d, J = 4.3 Hz, 2H), 7.24 (dd, J = 8.4, 7.4 Hz, 2H), 7.06 (dd, J = 8.4, 4.3 Hz, 2H), 4.68-4.44 (brs, 8H); 4.16 (s, 10H); MS (EI): *m/z* 546 (M^+).

6 X-ray analysis of **6** and **7**: S. Sasaki, Y. Kuwatani, T. Okabe, and M. Iyoda, to be published.

7 Crystal data for $\mathbf{6}^{+}\bullet I_3^-$: $C_{34}H_{28}Fe_2I_3$, FW = 929.00, monoclinic, Space group: $P2_1/n$, a = 10.235(2), b = 10.271(3), c = 29.812(2) Å, β = 90.07(1) °, V = 3134.1(9) Å^3, Z = 4, D_{calc} = 1.969 g/cm^3. The structure was solved by a direct method using SIR88. Full matrix least-squares refinement yielded the final R value of 0.046 (Rw = 0.030) for 3513 independent reflections [$2\theta \le 55.1°$, $I > 3.00\sigma(I)$] measured on a Rigaku AFC7R diffractometer using Mo-Kα radiation (λ = 0.71069 Å) and ω-2θ scan.

8 D. N. Hendrickson, Y. S. Sohn, and H. B. Gray, *Inorg. Chem.*, **10**, 1559 (1971).

9 Although ESR measurment of $\mathbf{4}^{2+}\bullet 2I_3^-$ was carried out at 290 and 77 K, $\mathbf{4}^{2+}\bullet 2I_3^-$ did not display any signal.