Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Masahiko Iyoda [a] , Toshitaka Okabe [a] , Terumasa Kondo [a] , Shigeru Sasaki [a] , Haruo Matsuyama [a] , Yoshiyuki Kuwatani [a] & Motomi Katada [b]

[a] Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Hachioji, Tokyo, 192-03, Japan

[b] Radioisotope Research Center, Tokyo Metropolitan University, Hachioji, Tokyo, 192-03, Japan

Version of record first published: 04 Oct 2006.

To cite this article: Masahiko Iyoda , Toshitaka Okabe , Terumasa Kondo , Shigeru Sasaki , Haruo Matsuyama , Yoshiyuki Kuwatani & Motomi Katada (1996): Synthesis and Properties of Mono- and Dications of 1,1 -Diferrocen Yleth Ylenes, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 286:1, 65-70

To link to this article: http://dx.doi.org/10.1080/10587259608042266

Mol. Cryst. Liq. Cryst., 1996, Vol. 286, pp. 65–70
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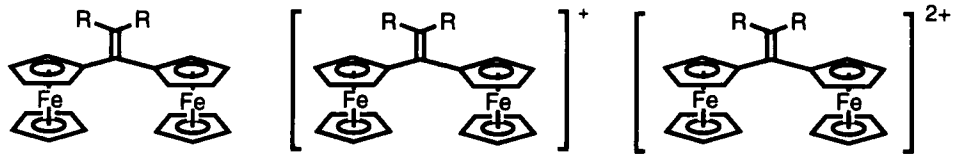
SYNTHESIS AND PROPERTIES OF MONO- AND DICATIONS OF 1,1-DIFERROCENYLETHYLENES

MASAHIKO IYODA,[1]* TOSHITAKA OKABE,[1] TERUMASA KONDO,[1] SHIGERU SASAKI,[1] HARUO MATSUYAMA,[1] YOSHIYUKI KUWATANI,[1] MOTOMI KATADA,[2]

[1]Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Hachioji, Tokyo 192-03, Japan; [2]Radioisotope Research Center, Tokyo Metropolitan University, Hachioji, Tokyo 192-03, Japan

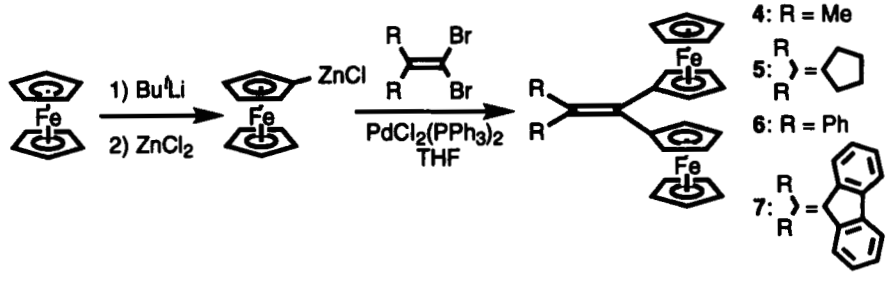
Abstract 1,1-Diferrocenylethylenes have been synthesized efficiently by palladium-catalyzed cross-coupling reaction. The interaction of the two ferrocene units has been investigated in the neutral, monocationic and dicationic states using spectroscopic analyses.

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** occurs 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 1,1-diferrocenylethylenes **1** and properties of the mono- and dications **2** and **3**.



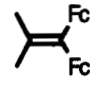
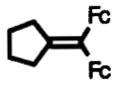
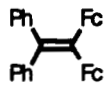
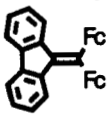
1 **2** **3**

In order to construct the framework of the title compounds, we applied the palladium-catalyzed cross-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-dibromoethylenes 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 moderate to good yields (Table 1).[4,6]



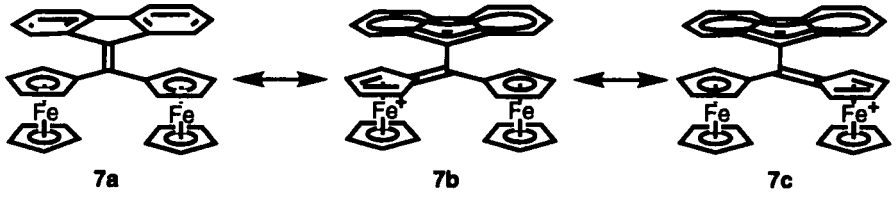
Scheme1

Table 1. Redox potentials of 1,1-diferrocenylethylenes *vs.* Fc/Fc^+ measured by cyclic voltammetry with Bu_4NClO_4 (0.1 M) as the supporting electrolyte in PhCN.

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

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.



7a **7b** **7c**

Scheme 2

The molecular structures of **6** and **7** were determined by X-ray crystallographic analysis.[5] As shown in Figure 1, 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 and the lack of the distortion of the phenyl groups (Figure 2).

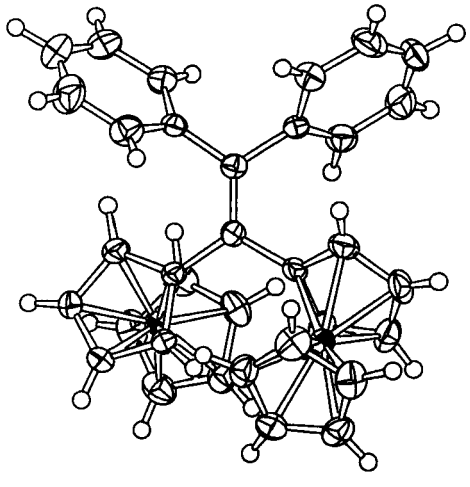


Figure 1. Molecular structure of **6**

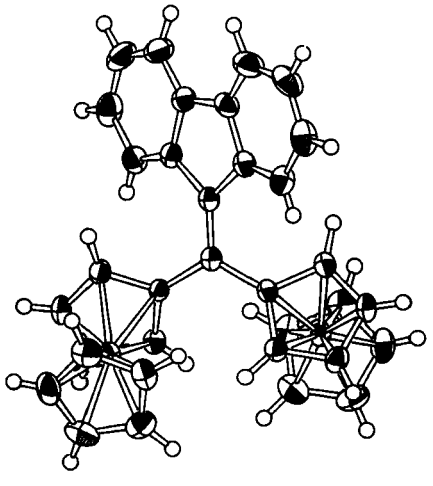


Figure 2. Molecular structure of **7**

These diferrocenylethylenes 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 $\mathbf{4}^{2+}\bullet 2I_3^-$ 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.[5] The averaged bond length of Fe(II)-C was observed to be 0.06 Å longer than that of Fe(III)-C.

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

Compounds	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
	77	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
	77	0.53	2.28	0.25, 0.26
		0.60		0.65

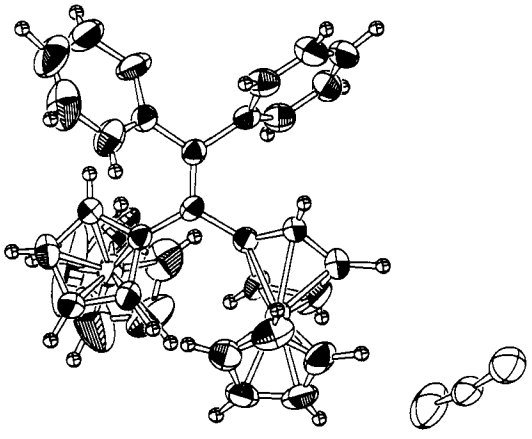


Figure 3. Molecular structure of $\mathbf{6}^{+}\bullet I_3^-$

Magnetic susceptibility of the dication $4^{2+}\bullet 2I_3^-$ 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 $4^{2+}\bullet 2I_3^-$ 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[7]. If such magnetic properties of ferrocenium salts applicable to $4^{2+}\bullet 2I_3^-$, the two ferrocenium groups of $4^{2+}\bullet 2I_3^-$ are concluded to be magnetically independent above 30 K and the decrease of the effective magnetic moment below 30 K would be interpreted as inter- and/or intramolecular antiferromagnetic interaction. Although ESR measurment of $4^{2+}\bullet 2I_3^-$ was carried out at 290 and 77 K, $4^{2+}\bullet 2I_3^-$ did not display any signal. ESR study of $4^{2+}\bullet 2I_3^-$ at lower temperatures and crystal structure analysis are in progress for further discussion.

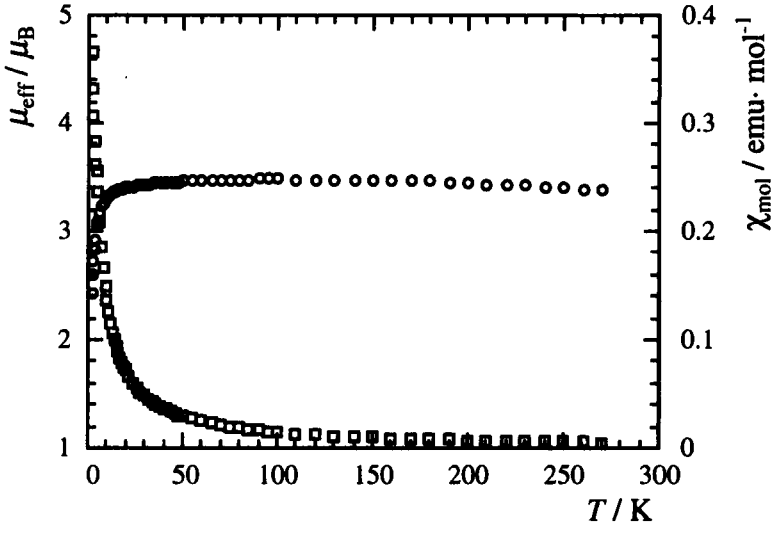


Figure 4. Magnetic susceptibility and effective magnetic moment of $4^{2+}\bullet 2I_3^-$

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Hendrickson, *Inorg. Chem.* **1980**, *19*, 3330; 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.* **1985**, *107*, 7996; S. Barlow, V. J. Murphy, J. S. O. Evans, D. O'Hare, *Organometallics* **1995**, *14*, 3461.

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4. A. Minato, K. Suzuki, and K. Tamao, *J. Am. Chem. Soc.* **1987**, *109*, 1257.
5. The crystallographic parameters of **6**, **7**, and $\mathbf{6}^{+}\bullet I_3^{-}$ were as follows: **6**: $C_{34}H_{28}Fe_2$, triclinic, Space group: P-1(No. 2), a = 9.950(2), b = 14.451(1), c = 9.745(2) Å, α = 106.17(1), β = 112.30(1), γ = 89.87(1) °, V = 1236.7(4) Å^3, Z = 2, D_{calc} = 1.472 g/cm^3, Observed ($F > \sigma(F)$): 4628, R: 0.030, R_w: 0.027; **7**: $C_{34}H_{26}Fe_2$, orthorhombic, Space group: Fdd2(No. 43), a = 18.247(7), b = 15.91(1), c = 16.835(8) Å,V = 4888(7) Å^3, Z = 8, D_{calc} = 1.484 g/cm^3, Observed ($F > \sigma(F)$): 1323, R: 0.023, R_w: 0.016; $\mathbf{6}^{+}\bullet I_3^{-}$: $C_{34}H_{28}Fe_2I_3$, monoclinic, Space group: $P2_1/n$(No. 14), 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, Observed ($F > \sigma(F)$): 3513, R: 0.046, R_w: 0.030.
6. Selected spectral data are as follows: **4**: orange needles, mp 140-1 °C, ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 4.30-4.28 (m, 4H), 4.20-4.17 (m, 4H), 4.01 (s, 10H), 2.12 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ = 133, 126, 90.5, 70.8, 69.1, 66.2, 24.6, MS (EI) m/z = 424 (M^+); Anal. Calcd for $C_{24}H_{24}Fe_2$: C, 67.96%; H, 5.70%; Found: C, 67.50%; H, 5.80%. **5**: orange crystals, mp 143-4 °C, ^{1}H-NMR (400 MHz, $CDCl_3$) 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); ^{13}C-NMR (100 MHz, $CDCl_3$) δ = 144, 123, 89.5, 70.1, 69.1, 66.4, 35.0, 26.8; MS (EI) m/z = 450 (M^+); Anal. Calcd for $C_{26}H_{26}Fe_2$: C, 69.37%; H, 5.82%; Found: C, 69.12%; H, 5.82%. **6**: red crystals, mp = 250 °C (decomp.), ^{1}H-NMR (400 MHz, $CDCl_3$) 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); ^{13}C-NMR (100 MHz, $CDCl_3$) δ = 147, 140, 134, 131, 128, 126, 86.7, 71.7, 69.7, 67.7; MS (EI) m/z = 548 (M^+); Anal. Calcd for $C_{34}H_{28}Fe_2$: C, 74.48%; H, 5.15%; Found: C, 74.02%; H, 4.88%. **7**: purple crystals, mp 263 °C (decomp.), ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.73 (d, J = 7.4 Hz), 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); ^{13}C-NMR (100 MHz, $CDCl_3$) δ = 146, 141, 138, 133, 125, 125, 124, 119, 85.3, 71.1, 70.6, 70.1; MS (EI): m/z = 546 (M^+); Anal. Calcd for $C_{34}H_{26}Fe_2$: C, 74.76%; H, 4.80%; Found: C, 74.91%; H, 4.72%.
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