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Syntheses and Properties of 1',1'''-Diphenylbiferrocene and Its Mixed-valence Salt

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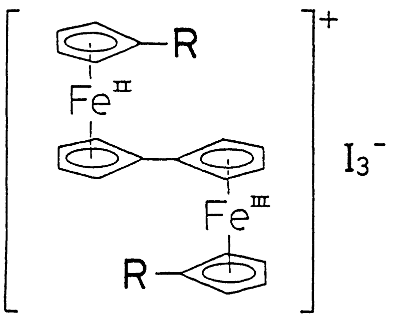
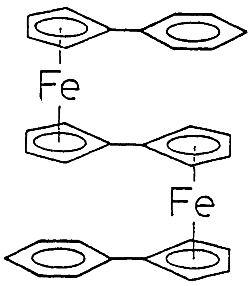
A binuclear ferrocenyl derivative with phenyl groups and its mixed-valence triiodide salt were prepared. The ^{57}Fe-Mössbauer spectra of the triiodide salt show that the temperature dependence of mixed-valence state is different from that of biferrocenium triiodide but rather similar to those of dialkylbiferrocenium salts which show an averaged-valence state at high temperatures.

Some mixed-valence binuclear ferrocenes, in which the valence state of iron atoms depends upon temperature, have attracted much attention in recent years. In the ^{57}Fe-Mössbauer spectra of 1',1'''-diethyl- (1), 1',1'''-di-n-propyl- (2),[1] and 1',1'''-di-n-butylbiferrocenium triiodides (3),[2] for instance, it is known that the two doublets ascribed to Fe(II) and Fe(III) at 78 K approach to each other with increasing temperature to converge into one doublet of an averaged-valence state at 275, 260, and 259 K, respectively. On the other hand, it is also known that the third doublet of an averaged-valence state appears in the Mössbauer spectra of biferrocenium triiodide (4) before the two doublets ascribed to Fe(II) Fe(III) disappear at 350 K.[3] The latter type of temperature dependence is explained by assuming that the intermolecular interaction between the biferrocenium cations through the cyclopentadienyl-cyclopentadienyl groups plays a predominant role in determining the valence state.[4,5] The former type is



1: R=CH_2CH_3
2: R=$CH_2CH_2CH_3$
3: R=$CH_2CH_2CH_2CH_3$
4: R=H
6: R=C_6H_5



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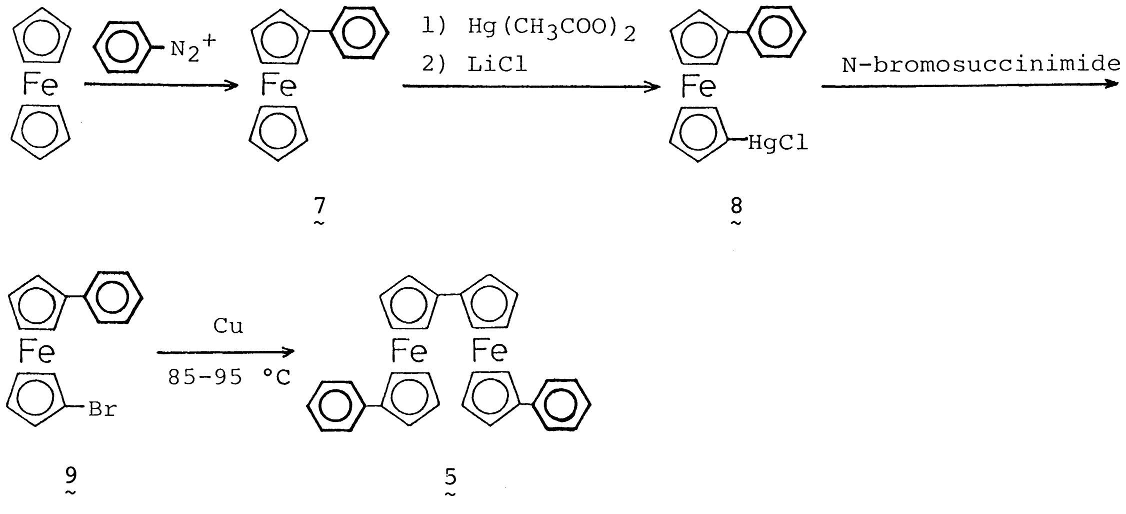

explained by assuming that the interaction between the cations and its nearest-neighbor anions should be more important.[4-7] A binuclear ferrocenyl derivative with phenylcyclopentadienyl groups, 1',1'''-diphenylbiferrocene (5), was prepared in order to clarify if the valence state would be more affected by a π-π interaction between the cations. The preparation of 5 and the valence state of the iron atoms in its mono-oxidized mixed-valence salt, 1',1'''-diphenylbiferrocenium triiodide (6), are reported in the present studies.

Phenylferrocene (7) was prepared by the method reported previously.[8] A solution of 28.5 g (89.4 mmol) of mercuric acetate in 340 ml of absolute methanol was added to a solution of 45.0 g (0.179 mol) of 7 in 500 ml of dry benzene with stirring. The reaction mixture was stirred under nitrogen for 19 hours. A solution of 7.6 g (0.179 mol) of lithium chloride in 80 ml of a 1:1 mixture of ethanol and water was added dropwise at the end of this period. Orange precipitates were immediately formed. After stirring the solution for two hours and refluxing for an hour, the orange products were filtered, washed with benzene, and dried in air. After removal of phenylferrocene, 7, by extraction with hexane, 1-phenyl-1'-chloromercuryferrocene (8) was extracted with dichloromethane. A solution of 2.3 g (12.9 mmol) of N-bromosuccinimide in 200 ml of dry N,N-dimethylformamide was added dropwise to a stirred cold solution of 1.8 g (3.6 mmol) of 8 in 250 ml of the same solvent. Reaction was continued at 0 °C under nitrogen for four hours, then 400 ml of a 10% sodium thiosulfate solution was added. The resulting dark colored solution was poured into 450 ml of cold water. From the aqueous solution 1-phenyl-1'-bromoferrocene (9) was extracted with petroleum ether. A mixture of 0.5 g of 9 and 20 g of copper bronze was heated at 90-95 °C under nitrogen for 18 hours and cooled. After removal of 7 by extraction with hexane, 0.3 g of crude 1',1'''-diphenylbiferrocene, 5, was extracted repeatedly with benzene. Recrystallization of the products from benzene solution gave red needles of 5: ^1H NMR ($CDCl_3$) $\delta = 4.01$ (4H, q), 4.10 (2H, t), 4.36 (2H, t), and 7.2 (5H, m). Found: C, 73.62; H, 5.04%. Calcd for $C_{32}H_{26}Fe_2$: C, 73.56; H, 4.98%.

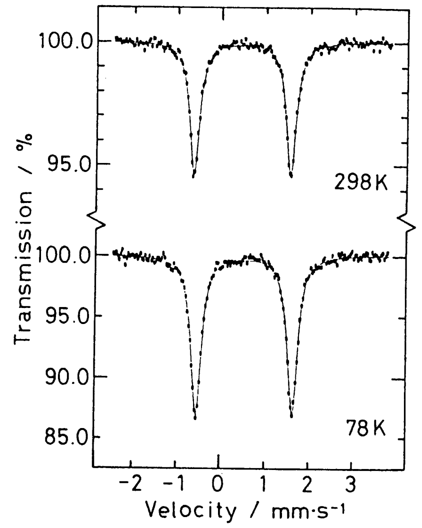

Fig. 1. ^{57}Fe-Mössbauer spectra of 1',1'''-diphenylbiferrocene, **5**.

Table 1. ^{57}Fe-Mössbauer Parameters

Compd.	Temp K	I.S. mm s^{-1}	Q.S. mm s^{-1}	Γ mm s^{-1}
5	298	0.43	2.23	0.27, 0.28
	78	0.52	2.23	0.29, 0.29
6	298	0.42	1.14	0.25, 0.27
	200	0.46	1.16	0.34, 0.34
	185	0.47	1.42	0.30, 0.31
		0.47	0.94	0.28, 0.28
	170	0.48	1.50	0.28, 0.29
		0.48	0.87	0.27, 0.27
	150	0.48	1.58	0.28, 0.28
		0.49	0.81	0.26, 0.26
	78	0.52	1.72	0.36, 0.35
		0.53	0.74	0.35, 0.35

I.S.: Isomer Shift (relative to iron foil).
Q.S.: Quadrupole Splitting. Γ: Half-width.

The triiodide salt, **6**, was prepared as follows. A solution of 80 mg (0.32 mmol) of iodine in 10 ml of dry benzene was added to a stirred solution of 101 mg (0.19 mmol) of **5** in 80 ml of the same solvent. The resulting black precipitates were filtered, washed with cold benzene, and dried in vacuo, giving 170 mg of **6**. Found: C, 42.28; H, 2.76%. Calcd for $C_{32}H_{26}Fe_2I_3$: C, 42.67; H, 2.89%.

As illustrated in Fig. 1, the ^{57}Fe-Mössbauer spectra of the neutral 1',1'''-diphenylbiferrocene, **5**, consist of one doublet ascribed to ferrocene-like Fe(II). The Mössbauer parameters estimated by a least-squares fitting with Lorentzian line shapes are given in Table 1. The quadrupole splitting (Q.S.) values are 2.23 mm s^{-1} at both 298 and 78 K. The Q.S. values are a slightly smaller than that of biferrocene at 78 K, 2.36 mm s^{-1},[9)] and presumably are interpreted in terms of the effect of a phenyl group.

The Mössbauer spectra of 1',1'''-diphenylbiferrocenium triiodide, **6**, were determined at temperatures between 78 and 298 K. As seen in Fig. 2, the spectrum at 78 K consists of two doublets ascribed to ferrocene-like Fe(II) and ferricinium-like Fe(III) valence states. The two doublets in the spectra approach to each other with increasing the temperature above ca. 100 K as well as do those in the spectra of 1',1'''-dialkylbiferrocenium triiodides, such as **1**, **2**,[1)] and **3**.[2)] Without any additional doublets appearing below 200 K, the two doublets finally converge into one doublet ascribed to an averaged-valence state at 200 K. Since the valence-averaged temperature is found to be lower than those of 1',1'''-dialkylbiferrocenium triiodides (275 K for **1**, 260 K for **2**,[1)] and 259 K for **3**[2)]), the phenyl groups introduced to cyclopentadienyl rings may have rather larger effect than an alkyl group on the valence state of the iron atoms. This type of temperature dependence is different from that of **4**, suggesting that the π-π

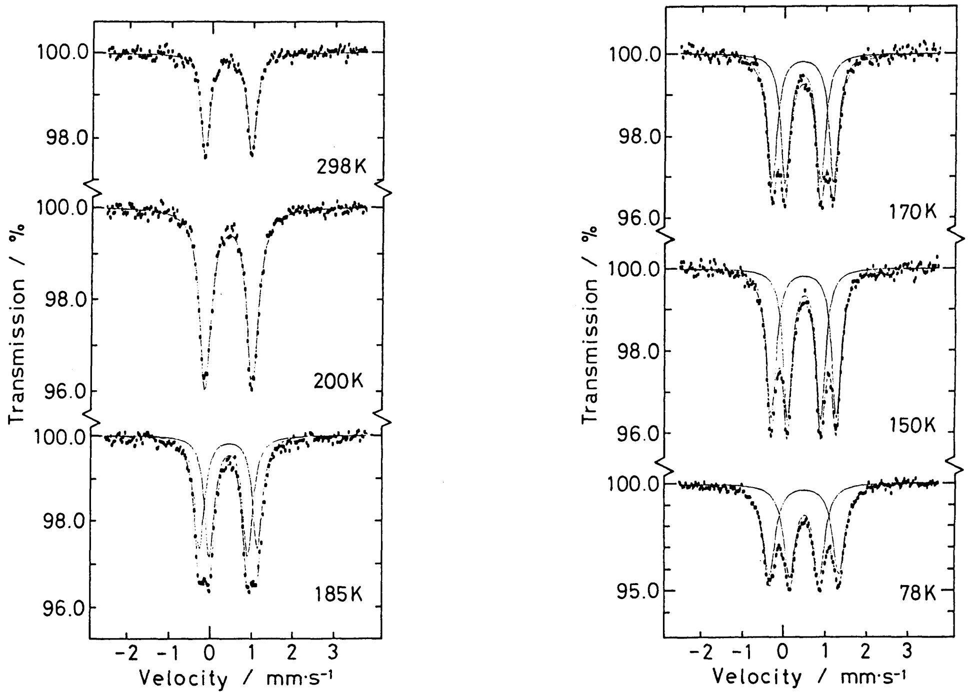

Fig. 2. ^{57}Fe-Mössbauer spectra of 1',1'''-diphenylbiferrocenium triiodide, 6.

intermolecular interaction between the cations which has been proposed for biferrocenium triiodide, 4,[4,5] may not play a predominant role in determining the valence state of the salt 6.

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