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Syntheses of [1.1]Ferrocenylruthenocenophanes and ^{57}Fe-Moessbauer Spectroscopic Studies of Their Reaction Products with Benzoquinone and BF_3-Et_2O

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[1.1]Ferrocenylruthenocenophane was prepared by the reduction of [1.1]ferrocenylruthenocenophane-1,12-dione. [1.1]Ferrocenylruthenocenophane and [1.1]ferrocenylruthenocenophane-1,12-dione react with BF_3-Et_2O containing benzoquinone and give black monocationic salts analyzed as [1.1]ferrocenylruthenocenophanium$^+BF_4^-$ and [1.1]-ferrocenylruthenocenophane-1,12-dionium$^+BF_4^-$, respectively. ^{57}Fe-Moessbauer spectroscopic studies of the salts suggest the presence of an intramolecular electron transfer between the Ru and Fe atoms.

A great number of the studies of trapped and averaged valence states have been reported about the mixed-valence ferrocene derivatives, such as [0.0]ferrocenophane, [1.1]ferrocenophane, and dialkyl- and dihalobiferrocenes. Most of them are prepared by partially oxidizing the original neutral materials to their monocation salts in an appropriate condition.$^{1-6)}$ The results of the ^{57}Fe-Moessbauer spectroscopic studies show that some of the monocation salts are in either an averaged or a trapped valence state not depending on temperature,$^{1,2)}$ while others are in a temperature-dependent trapped to averaged valence state in a pertinent temperature range.$^{3-6)}$ On the other hand, it has recently been discovered for ferrocenylruthenocene and ferrocenylruthenocenylmethane, that the e_{2g} electrons of the metal atoms in the metallocenes (Fe and Ru) are ligated to Lewis acids, such as $HgCl_2$, I_2, and $SnCl_4$, giving their stable adducts with chemical bonds (Ru-Hg, Ru-I, Ru-Sn, and Fe-Hg) based on the results of the ^{57}Fe- and ^{119}Sn-Moessbauer and ^{13}C-CP-MAS NMR spectroscopic studies.$^{7-9)}$

[1.1]Ferrocenylruthenocenophane was first prepared from the reaction of dianion of 1,1'-bis(cyclopentadienylmethyl)ferrocene and ruthenium dichloride in 1982 by Westerhoff et al.$^{10,11)}$ This compound has a structure favorable to the studies of the interaction between the Fe and Ru atoms, because the intramolecular distance between the Fe and Ru atoms leaves a possibility of intramolecular electron transfer between both the atoms in the [1.1]ferrocenylruthenocenophanium salt. The present studies were planned to show an improved method in the preparation of [1.1]ferrocenylruthenocenophane and to provide information about the chemical state of the Fe atoms in the [1.1]ferrocenylruthenocenophanium cation by means of ^{57}Fe-Moessbauer spectroscopy and other physicochemical measurements.

^{57}Fe-Moessbauer spectroscopic measurements were carried out by using a ^{57}Co(Rh) source moving in a constant acceleration mode. The isomer shift (I. S.)

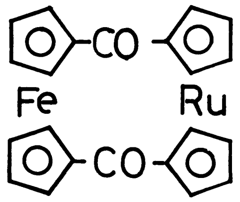
value for ^{57}Fe was taken with respect to metallic iron and the experimental error of the I. S. and quadrupole splitting (Q. S.) values was estimated within ± 0.02 mm s^{-1}. Cyclic voltammograms were obtained by using a Hokuto Denko HB-107A function generator and a Hokuto Denko HA-201 potentiostat combined with a standard three-electrode configuration. A working electrode of platinum button (Beckman) and an Ag/AgCl reference electrode were connected via a salt bridge of CH_3CN containing (0.1 mol dm^{-3})$[(C_4H_9)_4N]ClO_4$. The scan rate was 200 mV/s. [1.1]Ferrocenylruthenocenophane-1,12-dione was first prepared in the present study by the reaction of ruthenocene and dichlorocarbonylferrocene in CH_2Cl_2 containing $AlCl_3$ by the following method. A solution of ruthenocene (17.3 g, 0.075 mol) in CH_2Cl_2 (100 ml) was added to a solution of $AlCl_3$ (52 g) in CH_2Cl_2 (600 ml) at 0 °C and then a solution of 1,1'-bis-(chlorocarbonyl)ferrocene (23.3 g, 0.064 mol) in CH_2Cl_2 (200 ml) was added as in the case of preparation of [1.1]ferrocenophane-1,12-dione.$^{12)}$ The crude products were separated by column chromatography on alumina. A purple-red band eluted by CH_2Cl_2-$CH_3COOC_2H_5$ (9:1) was determined to be [1.1]ferrocenylruthenocenophane-1,12-dione. Purple-red products were crystallized from $CHCl_3$ (10.6 g, 30%). Found: C, 56.46; H, 3.60%. Calcd for $C_{22}H_{16}O_2FeRu$; C, 56.30; H, 3.44%. [1.1]Ferrocenylruthenocenophane was prepared in the present study by reducing [1.1]ferrocenylruthenocenophane-1,12-dione, because the yield of [1.1]ferrocenylruthenocenophane by the Westerhoff's method is poor (less than 25%). [1.1]-Ferrocenylruthenocenophane-1,12-dione (4.7 g, 0.01 mol) was treated with $LiAlH_4$ (7.6 g, 0.2 mol) and $AlCl_3$ (26.8 g, 0.2 mol) in diethyl ether (400 ml) as described in the previous report for the preparation of [1.1]ferrocenophane from [1.1]ferrocenophane-1,12-dione.$^{13)}$ The mixture was diluted with water, filtered, and extracted with ether and hexane. The crude products were separated by column

Table 1. Q. S., I. S., and intensity ratios of [1.1]ferrocenylruthenocenophane and related compounds in the ^{57}Fe-Moessbauer spectra

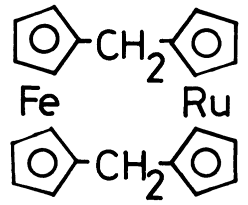
Compounds	Temp K	Q. S. mm s^{-1}	I. S. mm s^{-1}	I(II)/I(III)$^{a)}$
Ferrocene	78	2.41	0.49	-
[1.1]Ferrocenylruthenocenophane	78	2.41	0.49	-
	300	2.40	0.45	-
[1.1]Ferrocenylruthenocenophane-1,12-dione	78	2.21	0.51	-
	300	2.20	0.45	-
[1.1]Ferrocenylruthenocenophanium$^+BF_4^-$	78	2.23	0.51	
		0.32	0.47	1.96
	140	2.20	0.50	
		0.29	0.46	1.71
	190	2.21	0.48	
		0.30	0.44	1.09
	238	2.20	0.45	
		0.27	0.40	0.79
	300	2.21	0.44	
		0.27	0.38	0.54
[1.1]Ferrocenylruthenocenophane-1,12-dionium$^+BF_4^-$	78	2.17	0.46	
		0.34	0.45	0.38
	190	2.17	0.44	
		0.33	0.42	0.32
	300	2.13	0.42	
		0.29	0.40	0.21

a) I(II) and I(III) stand for the relative areal intensities of spectral components assigned to Fe(II) and Fe(III) state.

chromatography on alumina. [1.1]Ferrocenylruthenocenophane was eluted as a yellow band by a mixture of hexane and benzene (1:1). The products were crystallized from hexane mixed with benzene as yellow precipitates (4.1 g, yield; 92%). Found: C, 60.30; H, 4.82%. Calcd for $C_{22}H_{20}FeRu$; C, 59.87; H, 4.57%. [1.1]Ferrocenylruthenocenophane reacts with a stoichiometric amount of benzoquinone and BF_3-Et_2O in dry hexane mixed with benzene, and gives black products. The products were recrystallized from acetonitrile and analyzed as [1.1]ferrocenylruthenocenophanium$^+$ BF_4^-. Found: C, 50.68; H, 3.88%. Calcd for $C_{22}H_{20}FeRuBF_4$; C, 50.03; H, 3.82%. [1.1]Ferrocenylruthenocenophane-1,12-dionium$^+BF_4^-$ salt was prepared by the same conditions as in the case of [1.1]-ferrocenylruthenocenophanium$^+BF_4^-$. Found: C,47.91; H, 3.57%. Calcd for $C_{22}H_{16}O_2FeRuBF_4$; C, 47.51; H, 2.90%.



[1.1]Ferrocenylruthenocenophane-1,12-dione



[1.1]Ferrocenylruthenocenophane

Typical ^{57}Fe-Moessbauer spectra of [1.1]ferrocenylruthenocenophane and its BF_4 salt are shown in Fig. 1. ^{57}Fe-Moessbauer parameters are listed in Table 1. A relatively smaller Q. S. value observed for [1.1]ferrocenylruthenocenophane-1,12-dione (2.21 mm s^{-1} at 78 K) is ascribed to the effect of electron-attractive carbonyl groups attached to the cyclopentadienyl rings and the value of [1.1]ferrocenylruthenocenophane (2.41 mm s^{-1} at 78 K) well corresponds with the value of ferrocene itself (2.41 mm s^{-1} at 78 K). The fact shows that the ruthenocene moiety has little effects on the electronic state of ferrocene moiety in [1.1]ferrocenylruthenocenophane.

Studies of the cyclic voltammography of [1.1]ferrocenylruthenocenophane show a reversible one-electron oxidation peak ($E_{1/2}$; 0.35 V) and irreversible two-electron oxidation peak ($E_{1/2}$; 0.78 V), while [1.1]ferrocenophane gives two reversible one electron oxidation peaks ($E_{1/2}$; 0.35 and 0.57 V). The fact shows that the former value (0.35 V) of [1.1]ferrocenylruthenocenophane is ascribed to the oxidation of ferrocene-type Fe atoms since the effect of ruthenocene moiety on the electronic

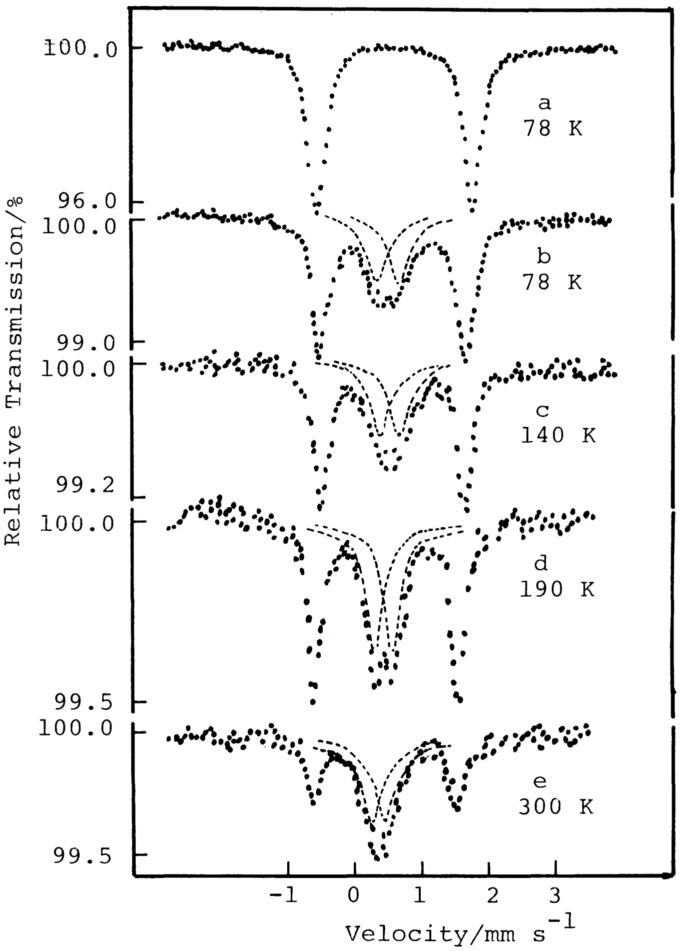


Fig. 1. ^{57}Fe-Moessbauer spectra of [1.1]-ferrocenylruthenocenophane (a) and its BF_4^- salt (b-e) at indicated temperatures.

state may be neglected because ruthenocene moiety gives little change to the I. S. Q. S. values of ferrocene moiety. The latter value (0.78 V) is ascribed to that of ruthenocene-type Ru atoms; i.e., the Ru atoms are found to be oxidized less easily than the Fe atoms in this compound. The results of the ^{57}Fe-Moessbauer study of [1.1]ferrocenylruthenocenophanium^{+}BF$_4^{-}$ salt show that two kinds of chemical state of the Fe atoms are observed, as seen in Table 1 and Fig 1-b; i.e., the component with a larger Q. S. value (2.23 mm s^{-1} at 78 K; which is a little smaller than that of [1.1]ferrocenylruthenocenophane) is ascribed to a low-spin Fe(II) species and the other component with a smaller Q. S. value (0.32 mm s^{-1} at 78 K) is to a low-spin Fe(III) species, although all the mononuclear ferrocene and ferrocenium derivatives are known to show only single spectral component in their spectra. The results indicate that there is a kind of electronic effect of ruthenocene moiety on iron atoms in the salt. Moreover, the decreasing intensity in the larger Q. S. component and the increasing intensity in the smaller Q. S. component are observed with increasing temperature. A similar temperature dependence of the intensities of both the components are found in [1.1]ferrocenylruthenocenophane-1,12-dionium^{+} BF$_4^{-}$, although the temperature dependence of the intensity ratio is smaller than in the case of [1.1]ferrocenylruthenocenophanium^{+}BF$_4^{-}$. The temperature dependence of the intensities of the components lead us to the conclusion that there is an intramolecular electron transfer or redox process between the Ru and Fe atoms; i.e., the electrons located at the Fe atoms giving a low-spin Fe(II) and Ru(III) states at lower temperatures are transferred to the Ru atoms giving a low-spin Fe(III) and Ru(II) states at higher temperatures in the BF$_4^{-}$ salts.

References

1) W. H. Morrison, Jr. and D. N. Hendrickson, J. Chem. Phys., 59, 380 (1973).
2) W. H. Morrison, Jr. and D. N. Hendrickson, Inorg. Chem., 14, 2331 (1975).
3) S. Nakashima, M. Katada, I. Motoyama, and H. Sano, Bull. Chem. Soc. Jpn., 59, 2923 (1986).
4) 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).
5) S. Iijima, I. Motoyama, and H. Sano, Bull. Chem. Soc. Jpn., 53, 3180 (1980).
6) S. Iijima, R. Saida, I. Motoyama, and H. Sano, Bull. Chem. Soc. Jpn., 54, 1375 (1981).
7) M. Watanabe, I. Motoyama, and H. Sano, Chem. Lett., 1986, 1699.
8) M. Watanabe, Y. Masuda, I. Motoyama, and H. Sano, Chem. Lett., 1987, 1669.
9) M. Watanabe, I. Motoyama, and H. Sano, Chem. Lett., 1987, 309., M. Watanabe, Y. Masuda, I. Motoyama, and H. Sano, Bull. Chem. Soc. Jpn., 61, 827 (1988).
10) U. T. Mueller-Westerhoff, A. Nazzal, and M. Tanner, J. Organomet. Chem., 236, C41 (1982).
11) A. F. Diaz, U. T. Mueller-Westerhoff, A. Nazzal, and M. Tanner, J. Organomet. Chem., 236, C45 (1982).
12) T. H. Barr, H. L. Lenzner, and W. E. Watts, Tetrahedron, 25, 6001 (1969).
13) W. E. Watts, J. Organomet. Chem., 10, 191 (1967).

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