Introduction of FeCp$^+$ to *o*-, *m*-, *p*-terphenyl and the structures of mononuclear and dinuclear complexes

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Abstract

FeCp$^+$ complexes of *o*-, *m*-, and *p*-terphenyl were synthesized. Mass spectra showed the existence of mononuclear and dinuclear complexes in all isomers. Mononuclear and dinuclear complexes were separated by using the difference in solubility to CH_2Cl_2. X-ray structural analyses revealed that the FeCp$^+$ was introduced to the central benzene in the mononuclear complexes, while they were introduced to the terminal benzenes in the dinuclear complexes. ^{57}Fe Mössbauer spectra showed arene-type Fe^{II} doublet.
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1. Introduction

A great number of studies concerning metal–metal interactions in mixed-valence biferrocene derivatives have been carried out for a long time [1–3]. The property of electron transfer in a molecule is greatly important in studying superconductive materials and biological system. By introducing an iron atom to the benzene ring in organic compounds, it becomes possible to study the electron transfer process in organic compounds by using ^{57}Fe Mössbauer spectroscopy. The mixed-valence state for arene-type complex such as $[(FeCp^*)_2(diphenyl)]^{m+}$, $[(FeCp^*)_2(pentalene)]^{m+}$, or $[(FeCp^*)_2(indacene)]^{m+}$ has been reported [4,5]. It is already known that mononuclear and dinuclear derivatives are obtained by introducing FeCp$^+$ to *p*-terphenyl [6]. Although its dinuclear complex has been assigned by ^{13}C NMR spectrum [7,8], the separation of mononuclear and dinuclear derivatives and their X-ray structural analyses are not reported. The introduced number and position of transition metal to cyclophanes are also an interesting problem [6,9]. The introduction of FeCp$^+$ to the carbon hexagonal plane of the sp^2-carbon has a possibility to provide a novel property to carbon materials [10]. The chemistry of organo-iron complexes of aromatic compounds is interesting from the point of redox reaction [6]. Arene complexes are also important in the synthesis of metallodendrimers [11].

In the present study, the introduction of FeCp$^+$ to *o*-, *m*-, and *p*-terphenyl is examined and we confirmed the introduced number and position by using single crystal X-ray structural analysis. The electronic state is also discussed by using ^{57}Fe Mössbauer spectroscopy.

2. Experimental

2.1. Preparations

24.2 g (130 mmol) of ferrocene, 17.3 g (130 mmol) of AlCl$_3$, 0.235 g (8 mmol) of Al powder, and 2 g (8.7 mmol) of *o*-, *m*-, or *p*-terphenyl were stirred under

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nitrogen atmosphere. The mixture was heated at 80 °C under nitrogen atmosphere for 16 h. The reaction mixture was hydrolyzed slowly with 100 ml of degassed ice water and then concentrated NH_4OH was added to become pH 9 and to precipitate $Al(OH)_3$. After filtration, a yellow solid was obtained by adding 20 ml of an aqueous HPF_6. The precipitation was filtered, and dried in vacuo. The dried crude product was treated with 50 ml of CH_2Cl_2. The CH_2Cl_2 solution was filtered and concentrated to 5 ml by evaporation. Then a large amount of ether was added to give yellow microcrystals (*o*-complex: 0.881 g, 20.4%. *m*-complex: 1.02 g, 23.6%. *p*-complex: 0.915 g, 21.2%.). The insoluble product to CH_2Cl_2 was treated with a large amount of acetone until all yellow residue was dissolved and then filtered. The acetone solution was evaporated to give yellow microcrystals (*o*-complex: 3.15 g, 47.6%. *m*-complex: 2.35 g, 35.4%. *p*-complex: 2.11 g, 31.8%.). *Anal.* mononuclear *o*-complex: ^1H NMR(δ/ppm, CD_3CN) 5.14(5H), 6.15–6.44(4H), 6.81–8.16(10H). FAB Mass 351 ([CpFe-(*o*-terphenyl)]$^+$). Dinuclear *o*-complex: ^1H NMR(δ/ppm, CD_3CN) 4.95(10H), 6.04(4H), 6.21(6H), 7.78(2H), 8.00(2H). FAB Mass 617 ([[(CpFe)$_2$(*o*-terphenyl)]$^{2+}$-PF$_6^-$]$^+$). Mononuclear *m*-complex: ^1H NMR(δ/ppm, CD_3CN) 4.88(5H), 6.54–6.83(4H), 7.26–7.91(10H). FAB Mass 351 ([CpFe(*m*-terphenyl)]$^+$). Dinuclear *m*-complex: ^1H NMR(δ/ppm, CD_3CN) 4.99(10H), 6.38(2H), 6.47(4H), 6.78(4H), 7.78(1H), 8.04(2H), 8.16(2H). FAB Mass 617 ([[(CpFe)$_2$(*m*-terphenyl)]$^{2+}$PF$_6^-$]$^+$). Mononuclear *p*-complex: ^1H NMR(δ/ppm, CD_3CN) 5.12(5H), 6.83–7.14(4H), 7.61–7.90(10H). FAB Mass 351 ([CpFe-(*p*-terphenyl)]$^+$). Dinuclear *p*-complex: ^1H NMR(δ/ppm, CD_3CN) 4.98(10H), 6.38(2H), 6.47(4H), 6.74(4H), 8.03(4H). FAB Mass 617 ([[(CpFe)$_2$(*p*-terphenyl)]$^{2+}$PF$_6^-$]$^+$).

2.2. X-ray crystal structural analyses

Single crystals for X-ray crystallography of mononuclear and dinuclear *o*-, *m*-, and *p*-terphenyl complexes except for mononuclear *m*-isomer were obtained by the following method. The mononuclear complexes were dissolved in dichloromethane, while the dinuclear complexes were in acetone and then they were put in the hexane atmosphere at −15 °C. After several weeks single crystals for X-ray structural analysis were obtained as yellow column-shape crystals. They were cut so that the longest side was less than 0.5 mm. All measurements were made on Mac Science DIP 2030 imaging plate area detector using graphite-monochromated Mo Kα radiation. The cell parameters and intensities for the reflection were estimated by program package of Mac DENZO [12]. The crystal structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically, while hydrogen atoms were refined isotropically. All calculations were performed with the CrystalStructure crystallographic software packages of Rigaku and Molecular Structure Corporation [13]. Table 1 summarizes crystallographic data and experimental details.

2.3. ^{57}Fe Mössbauer spectroscopic measurements

A $^{57}Co(Rh)$ source moving in a constant-acceleration mode was used for ^{57}Fe Mössbauer spectroscopic measurements. ^{57}Fe Mössbauer spectra at 78 K were obtained by using a Wissel spectrometer. The ^{57}Fe Mössbauer parameters were obtained by least-squares fitting to Lorentzian peaks. The isomer shift values are referred to metallic iron.

Table 1
Details of crystal structure determinations

	Mononuclear *o*-complex	Dinuclear *o*-complex	Dinuclear *m*-complex	Mononuclear *p*-complex	Dinuclear *p*-complex
Formula	$C_{23}H_{19}FePF_6$	$C_{31}H_{30}Fe_2P_2F_{12}O$	$C_{31}H_{30}Fe_2P_2F_{12}O$	$C_{23}H_{19}FePF_6$	$C_{28}H_{24}Fe_2P_2F_{12}$
Formula weight	496.21	820.2	820.2	496.21	762.12
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$(#14)	$C2/c$(#15)	$P2_1/c$(#14)	Pn(#7)	$P2_1/n$(#14)
T (K)	296	296	296	296	296
a (Å)	10.7100(4)	26.6550(5)	12.7670(2)	9.8310(3)	10.5720(3)
b (Å)	10.7160(3)	10.4660(2)	16.9570(3)	10.6700(4)	12.9810(4)
c (Å)	19.0790(9)	23.0270(6)	15.1310(3)	10.3780(3)	10.8340(4)
β (°)	102.5260(10)	107.9020(10)	92.9480(10)	105.968(3)	100.9000(10)
V (Å^3)	2187.25(12)	6112.9(2)	3271.38(9)	1046.61(6)	1459.98(7)
Z	4	8	4	2	2
D_{calc}	1.542	1.782	1.665	1.574	1.733
μ	8.39	11.54	10.78	8.56	11.98
R^a	0.119	0.054	0.078	0.036	0.100
R_w^b	0.177	0.121	0.095	0.042	0.116

^{a} $R = \sum ||F_o| - |F_c||/\sum |F_o|$.
^{b} $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.