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Communication

Synthesis of a new bis(ferrocenyl)ruthenacyclopentatriene compound with a significant inter-metal electronic communication

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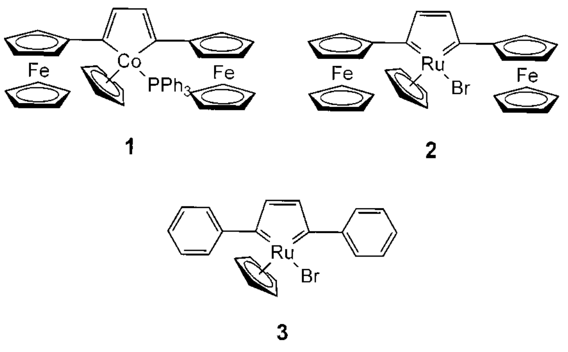
Abstract

A new 2,5-bis(ferrocenyl)ruthenacyclopentatriene complex was synthesized by the metallacycle formation reaction of RuBrCp-(cod) (Cp = η^5-C_5H_5) and ethynylferrocene. Cyclic voltammetry of the complex showed a reversible one-electron reduction due to the ruthenacycle and a two-step one-electron oxidation of the ferrocenyl moieties. Separation of the redox potentials of the ferrocenyl moieties was 0.24 V, and the electronic spectrum of one-electron oxidized species exhibited an intervalence-transfer band at 1180 nm. These results indicate the existence of significant electronic interactions between two ferrocenyl moieties through the ruthenacyclopentatriene ring.

Keywords: Ruthenium; Metallacycle; Ferrocene; Redox; Electronic interaction

1. Introduction

Ferrocene acts as a reversible one-electron redox nucleus, leading to its use as a reference for electrochemistry in organic solvents [1]. Many complexes containing two ferrocenyl moieties have been synthesized to investigate the effectiveness of the bridging groups between the redox nuclei for the internuclear interaction [2]. When two ferrocenyl moieties interact electronically with each other, the redox potential splits into two, and the difference between the two can be used to evaluate the magnitude of the interaction. We have previously synthesized a cobaltacyclopentadiene compound containing two ferrocenyl groups (**1** in Scheme 1) by a metallacycling reaction from ethynylferrocene and $CoCp(PPh_3)_2$, and found that the magnitude of the interaction between the two ferrocenyl moieties was almost as large as that in simple biferrocene [3]. This result prompted us to study the role of the central metal in the metallacycle with regard to the electronic communication between two redox nuclei bound to the metallacycle. In the present study, we synthesized the corresponding ruthenium-containing complex, bis(ferrocenyl)ruthenacyclopentatriene **2**, and investigated the interaction through the ruthenacycle. It should be noted that this is also the first report regarding the redox properties of ruthanacyclopentatriene.



Scheme 1.

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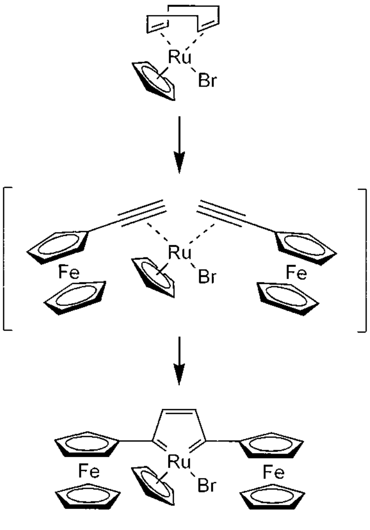

Scheme 2.

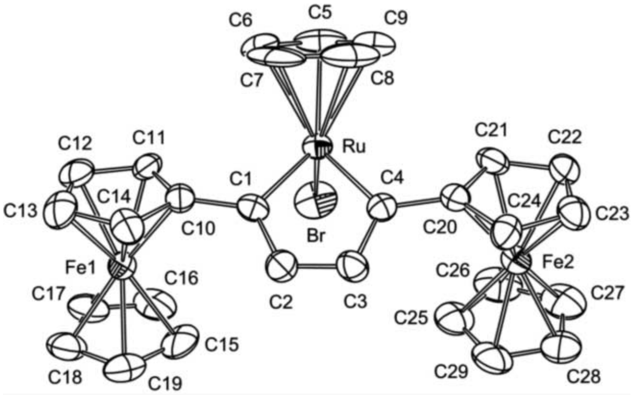

Fig. 1. Crystal structure of **2** (probability level 50%). Selected geometric parameters(Å, °): Ru–Br, 2.4802(9); Ru–C(1), 1.961(5); Ru–C(4), 1.958(4); C(1)–C(2), 1.451(6); C(2)–C(3), 1.363(6); C(3)–C(4), 1.455(6); C(1)–C(10), 1.446(6); C(4)–C(20), 1.454(6); Ru–C(Cp)$_{av}$, 2.298; Fe–C$_{av}$, 2.054; C(1)–Ru–C(4), 80.3(2); Ru–C(1)–C(2), 116.5(4); C(1)–C(2)–C(3), 113.1(5); C(2)–C(3)–C(4), 114.1(4); Ru–C(4)–C(3), 115.9(4).

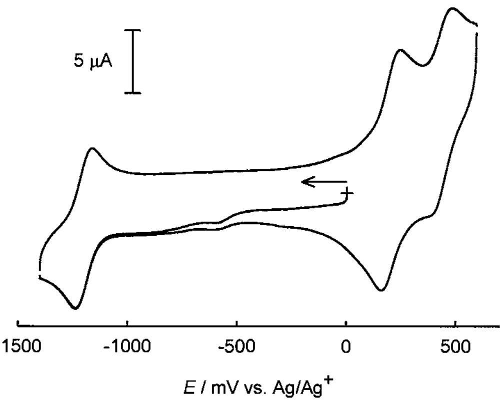

Fig. 2. Cyclic voltammogram of **2** on a glassy carbon disk in 0.1 mol dm^{-3} Bu_4NClO_4–CH_2Cl_2 at a scan rate of 0.1 V s^{-1}.

2. Results and discussion

Bis(ferrocenyl)ruthenacyclopentatriene (**2**) was synthesized by a metallacycling reaction of RuBrCp(cod) and two equivalents of ethynylferrocene based on the synthesis of a 2,5-bis(phenyl)ruthenacyclopentatriene complex **3** by Albers et al. (Scheme 2) [4]. The single crystal suitable for X-ray structure analysis was obtained by recrystallization from toluene/hexane. The crystal structure of **2** is shown in Fig. 1. Two ferrocenyl groups are attached to the 2- and 5-positions of the ruthenacycle. The bond lengths in the ruthenacycle are not significantly different from the corresponding lengths in **3**, which are indicative of the triene nature of the ring [4]. The atoms consisting of the ruthenacycle are almost coplanar, which suggests the existence of aromaticity due to π-delocalization through the ruthenacyclopentatriene moiety as **3** [4].

To examine the redox properties of the ruthenacycle and to evaluate the strength of the interaction between the ferrocenyl moieties, cyclic voltammetry was carried out with **2** in Bu_4NClO_4–dichloromethane, the result of which is shown in Fig. 2. A reversible reduction wave of the ruthenacycle was observed at -1.18 V versus Ag | Ag$^+$, and two quasi-reversible waves of the ferrocene moieties appear at 0.20 and 0.44 V. A similar reversible reduction wave due to the ruthenacycle was also observed in the cyclic voltammogram of **3** at -0.80 V versus Ag | Ag$^+$ in the same electrolyte solution, indicating the role of ruthenacyclopentatriene as a good electron acceptor. This redox property is quite different from those of cobaltacyclopentadiene, for which the oxidation potential is 0–0.5 V versus Ag | Ag$^+$, indicating that it functions as a fine electron donor [5].

The separation of the oxidation waves by the ferrocenyl moieties in **2** indicates the existence of an interaction between the two ferrocene moieties. The difference in potential of the two waves, 0.24 V, is smaller than those for simple biferrocene (0.42 V) [6] and cobaltacyclopentadienyl-bridged complex **1** (0.47 V) [3], whereas the value is larger than those for most bis-ferrocenyl compounds with π-conjugated organic bridges, such as 1,2-diferrocenylethylene (0.17 V) [7] and 1,2-diferrocenylacetylene (0.13 V) [6].

To investigate the delocalization of electron in a mixed-valence state, **2** was oxidized with one equivalent of $[Fe(C_5H_4Cl)_2]PF_6$ [8] in dichloromethane, and the electronic spectrum was measured (Fig. 3). In response to the oxidation, the absorption bands up to 800 nm were blue-shifted, and a new broad band appeared in the near-IR region. Deconvolution of the spectrum into Gaussian functions revealed that the near-IR band was centered at 1180 nm ($= 8484$ cm^{-1}) with FWVH $=$ 3840 cm^{-1}. Further oxidation of the solution up to two equivalents decreased the intensity of the near-IR band.

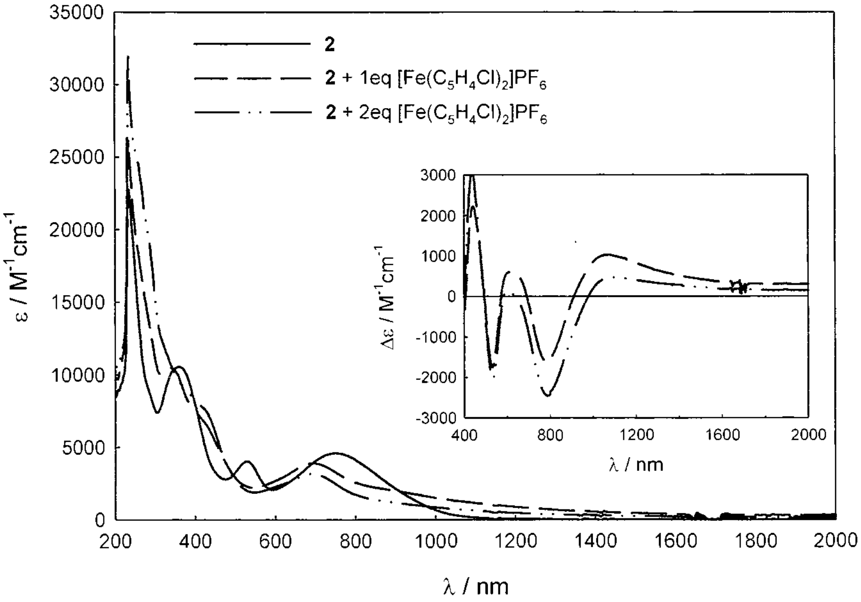

Fig. 3. Electronic spectra of **2** and its oxidized forms generated by addition of one and two equivalents of $[Fe(C_5H_4Cl)_2]PF_6$ in CH_2Cl_2. Inset: differences in the spectra of the oxidized forms from the spectrum of **2**.

There are two possible origins of the near-IR band, one is the LMCT from the cyclopentadienyl to the Fe(III) atom [9–12] and the other is the intervalence-transfer between the Fe(II) and Fe(III) atoms [2]. If the band were due to the LMCT, the intensity should be enhanced by the further oxidation. Thus it is plausible that the absorption is attributed to the intervalence-transfer. Based on Marcus–Hush theory [13], the mixing coefficient was calculated to be 0.06, which is smaller than or comparable to those for biferrocene (0.09) [6], 1,2-diferrocenylethylene (0.09) [7], and 1,2-diferrocenylacetylene (0.07) [6].

From these measurements, the ruthenacyclopentatriene moiety of **2** is found to conduct significant electronic interaction between its 2- and 5-substituents like π-conjugated organic bridges, although the magnitude of this interaction appears to be smaller than that of the cobaltacyclopentadiene analogue **1**. One possible explanation for the larger internuclear interaction in **1** than in **2** is that the stronger donor ability of the cobaltacycle than the ruthenacycle enhances the hole transfer in the electron exchange between the ferrocenyl moieties. However, it may also be due to the difference in the π-conjugation on the carbon atoms as shown in Scheme 2.

3. Experimental

All the manipulations were performed under inert atmosphere. The reagents were prepared according to the literature. Cyclic voltammetry was carried out in a standard one-compartment cell under an argon atmosphere equipped with a 3 mm-o.d. glassy carbon disk working electrode, a platinum-wire counter electrode, and an Ag | Ag^+ reference electrode (10 mmol dm^{-3} $AgClO_4$ in 0.1 mol dm^{-3} Bu_4NClO_4–MeCN, $E^{\circ\prime}$ (ferrocene/ferrocenium in 0.1 mol dm^{-3} Bu_4NClO_4/CH_2Cl_2) = 0.21 V vs. Ag | Ag^+) with a BAS CV-50W voltammetric analyzer. Electronic spectra were measured with a JASCO V-570 spectrometer. NMR spectra were measured with a JEOL A500 spectrometer.

3.1. Synthesis of 2

A mixture of RuBr(Cp)(cod) [14] (86.9 mg, 0.243 mmol) and ethynylferrocene [15] (108.2 mg, 0.528 mmol) in benzene (9 cm^3) was treated under inert atmosphere at room temperature for 13 h, followed by stirring at 50 °C for 2 h. The color was immediately changed from dark orange to dark red, and a black precipitate was gradually generated. After removing the solvent under reduced pressure, the product was dissolved in toluene and purified with preparative GPC, giving the red–purple powder of **2**. Yield: 23.2 mg (14.3%). ^{1}H-NMR (500 MHz, CD_2Cl_2) δ 7.71 (s, 2H), 5.17 (s, 5H), 4.84 (m, 2H), 4.68 (m, 2H), 4.60 (m, 2H), 4.41 (s, 10H), 4.08 (m, 2H). ^{13}C-NMR (125 MHz, CD_2Cl_2) δ 273.0 (s), 151.8 (d), 116.6 (s), 93.6 (d), 74.8 (d), 74.5 (d), 72.4 (d), 70.2 (d), 63.6 (d). Anal. Calc. for $C_{29}H_{25}BrRuFe_2 \cdot 2CH_2Cl_2$: C, 44.54; H, 3.50. Found: C, 44.97; H, 3.71%.

Table 1
Crystal data and refinement parameters for **1**

Empirical formula	$C_{29}H_{25}BrFe_2Ru$
M	666.18
Crystal system	Monoclinic
Space group	$C2/c$ (no. 15)
Unit cell dimensions	
a (Å)	25.99(1)
b (Å)	7.514(2)
c (Å)	25.850(6)
β (°)	110.80(2)
V (Å^3)	4718(3)
Z	8
μ(Mo–K$_\alpha$) (mm^{-1})	35.60
No. reflections measured	5960
No. unique reflections	5419 ($R_{int} = 0.014$)
Transmission factors	0.647–1.000
No. parameters	299
R_1 ($I > 2\sigma(I)$), R_w (all data) [a]	0.036, 0.123
S [b]	1.42
Max. residual density (e Å^{-3})	0.55

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.
[b] $S = [\Sigma w(|F_o| - |F_c|)^2/(N_{reflections} - N_{parameters})]^{1/2}$.

*3.2. X-ray crystallography of **2***

A dark red plate crystal of **2** was attached to a glass fiber and mounted on a Rigaku AFC7R four-circle diffractometer equipped with a rotating anode X-ray generator. The radiation used was Mo Kα monochromated with graphite. Cell constants were determined with 25 diffractions in the range $28.5 < 2\theta < 30.0°$. Intensity data were recorded at 23 °C using the $2\theta - \omega$ scan up to $2\theta = 55.0°$. Three standard reflections were monitored every 150 diffractions, and no decay in intensity was observed. The intensity data were corrected for absorption anisotropy using the standard empirical ψ-scan method. The structure was solved by the direct method with SIR-92 [16] and expanded by successive applications of the least-squares technique and the difference Fourier technique. All the calculations were performed using the TEXSAN software package [17]. The crystallographic data are shown in Table 1.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 154108 for compound **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1233-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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