

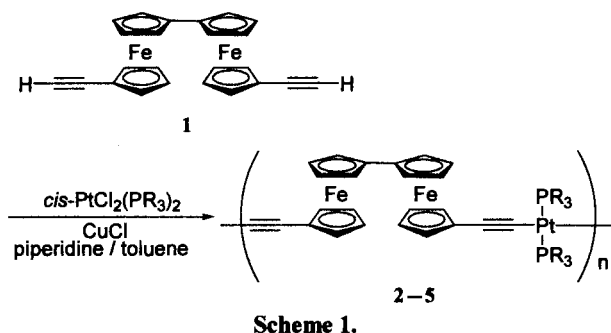
Synthesis and Redox Property of Cyclic Mixed-Metal Complexes from Diethynylbiferrocene

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The reaction of 6,6'-diethynylbiferrocene (**1**) with *cis*-PtCl₂(PR₃) (R= ⁿBu and Me) or (η⁵-C₅H₅)Co(PR₃)₂ gave novel cyclic mixed metal complexes, which show a rich oxidative electrochemistry.

The redox active π-conjugated system has potential application for the molecular electronic devices such as molecular wires and molecular sensors.¹ Linear π-conjugated ferrocenyl polymers and metal poly-yne polymer have been extensively studied,^{2,3} though the examples of cyclic π-conjugated ferrocenyl systems are relatively scarce. The cyclic π-conjugated ferrocenyl systems are attractive from the following viewpoints; (1) the amount of charge delocalization within the ring for different redox states, (2) redox switching of the inclusion to the inner space by the change of ferrocene–ferrocinium redox states and (3) a potential candidate for a molecular unit toward quantum-dot cellular automata.⁴ In the course of synthetic studies on π-conjugated mixed metal polymers containing biferrocenyl groups, the combination between 6,6'-diethynylbiferrocene (**1**)⁵ and Pt complex leads to the formation of cyclic mixed-metal complexes, which is now presented in this paper.



The reaction of **1** (0.82 g, 2 mmol) with *cis*-PtCl₂(PⁿBu₃)₂ (0.66 g, 1.0 mmol) in the presence of CuI in piperidine/toluene (1/1) at reflux temperature for 48 h gave a dark brown solution (Scheme 1). After concentration, the residue was chromatographed on alumina. The pale yellow eluate by benzene/hexane (1/4), the orange eluate by benzene/hexane (1/1) and the orange eluate by benzene were evaporated in vacuo to provide orange solids (**2**) (0.094 g), (**3**) (0.077 g) and (**4**) (0.443 g), respectively. An elemental analysis revealed that they had the same composition, [C₄₈H₇₀P₂Fe₂Pt]_n. A GPC analysis suggested that their molecular weight increased in this order. Although the IR spectra show nearly the same ν(C≡C) band at 2100 cm⁻¹, the ¹H NMR spectra clearly exhibited a different set of four triplets in the region of the cyclopentadienyl protons from each other suggesting that the complexes are cyclic oligomers. We obtained a single crystal of **2** suitable

for X-ray and the structure was unequivocally determined as a cyclic dimer complex.⁶ For the disorder problem of this crystal, we attempted to prepare a trimethylphosphine analogue of **2** and successfully obtained brown crystals of the required complex (**5**, 22% yield).⁷ The X-ray structure of **5** showed an overall planar rhomboidal shape consisting of four ferrocene, two platinum and four acetylene units (Figure 1). The dimensions of the rhomboid defined by the centers of the cyclopentadienyl groups connected with acetylenic carbons is 7.68 × 11.64 (Å) with angles at Cp(cent) of 116.7 and 63.3°. The ethynyl linkage is nearly linear with angles at C(1), C(2), C(23) and C(24) of 172(1), 176(1), 178(1) and 177(1)°, respectively. However, the distance between the platinum is slightly smaller than the shorter edge of the rhomboid although the reverse is observed in the structure of **2**.

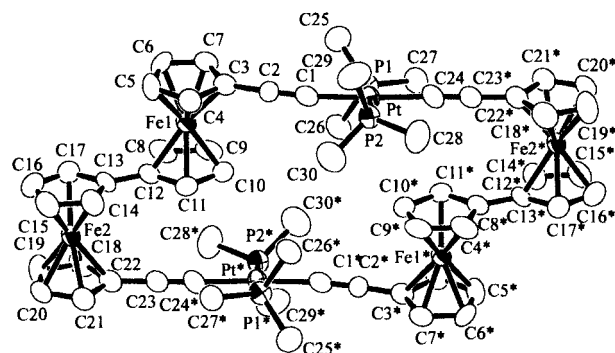


Figure 1. ORTEP view of **5**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Pt(1)–P(1) 2.285(3), Pt(1)–P(2) 2.282(3), Pt(1)–C(1) 1.99(1), Pt(1)–C(24) 1.99(1), C(1)–C(2) 1.21(1), C(2)–C(3) 1.42(1), C(22)–C(23) 1.46(1), C(23)–C(24) 1.18(1).

The geometry at the platinum is a slightly distorted square planar with angles in the ranges of 85.8(3)–92.4(3) and 172.0(1)–177.1(5)°. The plane of the substituted cyclopentadienyl ring is rotated by ca. 21.9° out of the platinum coordination plane. The bicyclopentadienyl units are nearly coplanar with each other within 0.05 Å. Previously, Long et al. reported that the reaction of **1** with *trans*-PtCl₂(PⁿBu₃)₂ in the presence of CuI in diethylamine at room temperature gave oligomeric species of up to 12 units.⁸ Successful isolation of the dimeric species in our case may be due to the employment of a higher reaction temperature.

The cyclic and differential pulse voltammograms of **5** in CH₂Cl₂ is shown in Figure 2. Two well-separated ferrocene–ferrocinium oxidation waves i and ii are observed at E_{1/2} = 0.33 and 0.65 V vs Ag/Ag⁺ at the scan rate of 100 mVs⁻¹, each of which involves two-electrons. The peak-to-peak separations for the 1st and 2nd waves are 70 and 83 mV, respectively, which indicates that each wave consists of two closely spaced one-electron processes and further the electronic interaction between biferrocenes through Pt complexes is relatively weak. The oxidation potentials of **5** exhibit large negative potential

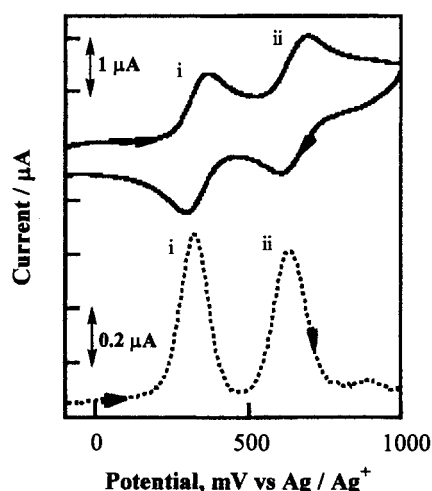
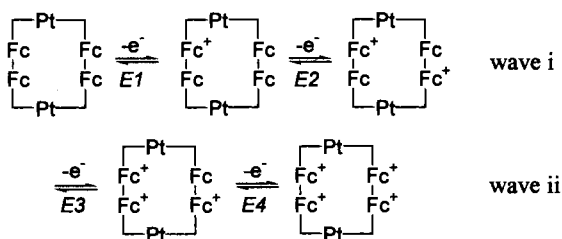


Figure 2. Cyclic (solid line) and differential pulse voltammograms (broken line) of **5** vs Ag/Ag^+ in $0.1\text{M } t\text{Bu}_4\text{NClO}_4/\text{CH}_2\text{Cl}_2$ at a scan rate of 100mVs^{-1} .



Scheme 2.

shifts compared to those of starting complex **1** ($E_{1/2} = 0.55$ and 0.88 V), which suggests a strong electron-donating property of Pt-PR_3 moieties. The whole oxidation processes are schematically described as Scheme 2. In this cyclic system, several mixed-valent oxidation isomers are possible during the consecutive oxidations, and further study for these mixed-valent states is currently under way.

Recently, the reaction of diacetylene and $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{PPh}_3)_2$ was reported to give rigid-rod organocobalt polymers with cobaltacyclopentadiene or η^4 -cyclobutadiene cobalt units in the main chain.⁹ In order to obtain a similar mixed metal polymer having ferrocene and cyclopentadienyl cobalt units, the reaction of **1** (0.213 g, 0.67 mmol) and $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{PPh}_3)_2$ (0.38 g, 0.55 mmol) was carried out in benzene at room temperature for 2 h. After concentration of the reaction mixture, the residue was chromatographed on alumina. From the orange band eluted by the hexane/benzene (4/1) mixture, orange-brown crystals were obtained (0.025 g, 7% yield). The elemental analysis and ^1H NMR spectrum suggested the formation of the cyclic $(\eta^5\text{-C}_5\text{H}_5)\text{Co}[(\eta^4\text{-C}_4\text{H}_2)\{(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{-}\eta^5\text{-C}_5\text{H}_4\}\text{Fe}(\eta^5\text{-C}_5\text{H}_4)]$ (**6**).¹⁰ The unequivocal structure was obtained by the X-ray crystallographic analysis (Figure 3). One of the edges of the cyclobutadiene, which are substituted by ferrocenyl groups on either side, is slightly elongated ($1.468(7)$ vs $1.438(7)$ Å of the opposite edge). The ferrocenyl carbons, C(10) and C(20), deviate from the plane of cyclobutadiene and occupy the position outside of the plane by 0.15 and 0.29 Å, respectively. The cyclopentadienyl rings of Fc(1) and Fc(2) (abbr. of ferrocene moieties of Fe(1) and Fe(2))

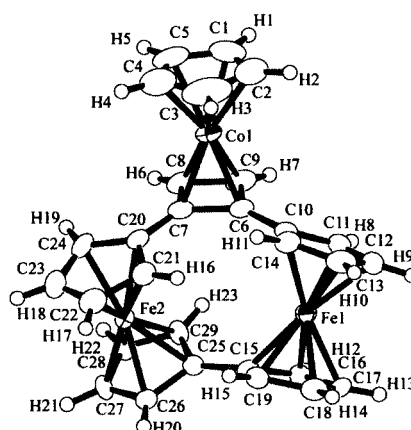


Figure 3. ORTEP view of **6**. Selected bond lengths (Å) and Angles (deg): Co(1)-C(6) $1.992(4)$, Co(1)-C(7) $1.977(5)$, Co(1)-C(8) $1.954(5)$, Co(1)-C(9) $1.961(5)$, C(6)-C(7) $1.468(7)$, C(6)-C(9) $1.453(6)$, C(6)-C(10) $1.451(6)$, C(7)-C(8) $1.457(7)$, C(7)-C(20) $1.456(7)$, C(8)-C(9) $1.438(7)$, C(6)-C(7)-C(8) $89.5(4)$, C(7)-C(6)-C(10) $137.9(4)$, C(6)-C(9)-C(8) $90.8(4)$, C(7)-C(6)-C(9) $89.4(4)$, C(6)-C(7)-C(20) $135.9(4)$, C(7)-C(8)-C(9) $90.3(4)$.

are slightly tilted by 7.8 and 3.8° , respectively. The substituents of Fc(1) and Fc(2) are each rotated by 9.8 and 67.5° , respectively. The bicyclopentadienyl ligand is significantly twisted by ca. 45° , so as to minimize the ring strain.

Further study to prepare macrocyclic mixed metal complexes using diethynylbiferrocene is in progress.

References and Notes

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- 6 Crystallographic data for **2**: $\text{C}_{96}\text{H}_{140}\text{P}_4\text{Fe}_4\text{Pt}_2$, fw = 2031.62; triclinic, $P\bar{1}$ (#2), $a = 18.0650(3)$ Å, $b = 19.0635(3)$ Å, $c = 15.119(2)$ Å, $\alpha = 109.36(1)^\circ$, $\beta = 107.08(1)^\circ$, $\gamma = 99.35(1)^\circ$, $V = 4780(1)$ Å³; $Z = 2$; $R = 0.053$, $R_w = 0.043$.
- 7 **5**: ^1H NMR (CDCl_3 , 400MHz): δ 4.33 (t, 8H, Fc), 4.21 (t, 8H, Fc), 3.90 (t, 8H, Fc), 3.30 (t, 8H, Fc), 1.87 (t, 36H, CH_3). IR (KBr): $\nu(\text{C}\equiv\text{C})$ 2097 cm^{-1} . Crystallographic data of **5**: $\text{C}_{60}\text{H}_{68}\text{P}_4\text{Fe}_4\text{Pt}_2$, fw = 1526.66; monoclinic, $P2_1/a$ (#14); $a = 11.529(4)$ Å, $b = 10.634(2)$ Å, $c = 21.583(2)$ Å, $\beta = 100.063(9)^\circ$, $V = 2831.5(8)$ Å³; $Z = 2$; $R = 0.040$, $R_w = 0.027$.
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- 10 **6**: ^1H NMR (CDCl_3 , 400 MHz): δ 4.66 (m, 2H, Fc), 4.61 (s, 5H, Fc), 4.35 (m, 2H, Fc), 4.26 (m, 4H, Fc), 4.22 (m, 2H, Fc), 4.15 (m, 2H, Fc), 4.02 (m, 2H, Fc), 4.02 (s, 2H, Cb), 3.93 (m, 2H, Fc). Mp >225 °C. MS: $[\text{M}]^+$, m/z 542. Crystallographic data: $\text{C}_{20}\text{H}_{23}\text{Fe}_2\text{Co}$, fw = 542.13; monoclinic, $P2_1/a$ (#14); $a = 11.529(4)$ Å, $b = 11.179(5)$ Å, $c = 16.865(3)$ Å, $\beta = 91.57(2)^\circ$, $V = 2172(1)$ Å³; $Z = 4$, $R = 0.039$, $R_w = 0.038$.