Bull. Chem. Soc. Jpn., **72**, 2557—2562 (1999)

1 : 2 Polycondensation of 3,3′,4,4′-Biphenyltetramine and 1,1′-Ferrocenedimethanol Catalyzed by [RuCl$_2$(PPh$_3$)$_3$] to Give Polybenzimidazole Containing Ferrocenylene Groups

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(Received May 10, 1999)

The 1 : 2 polycondensation of 3,3′,4,4′-biphenyltetramine and 1,1′-ferrocenedimethanol catalyzed by [RuCl$_2$(PPh$_3$)$_3$] gives ferrocenylene-containing polybenzimidazole **1**, (Im–Fc–CH$_2$–O–CH$_2$–Fc)$_n$ (Im = [5,5′-bi(benzimidazole)]-2,2′-diyl, Fc = 1,1′-ferrocenediyl). The reaction involves 1 : 2 condensation of 3,3′,4,4′-biphenyltetramine and 1,1′-ferrocenedimethanol to make two imidazole rings and subsequent intermolecular dehydrating coupling of two CH$_2$OH groups to form the CH$_2$–O–CH$_2$ linkage. Polymer **1** is soluble in DMF and DMSO and has molecular weights, $M_n = 2.1\times10^4$ and $M_w = 4.5\times10^4$, determined by GPC (polystyrene standards). Extremely broad ^{1}H NMR signals and results of SQUID measurements showing paramagnetism of **1** suggest the presence of Fe(III) centers in the polymer. The content of Fe(III) is estimated as approximately 20% based on the Mössbauer spectrum of **1**. An equimolar reaction of 1,2-diaminobenzene and 1,1′-ferrocenedimethanol in the presence of the Ru(II) catalyst gives bis[1′-(benzimidazol-2-yl)ferrocen-1-ylmethyl] ether. The model compound shows reversible oxidation and reduction peaks assigned to the Fe(II)/Fe(III) redox, whereas the Polymer **1** undergoes oxidation and subsequent irreversible deprotonation to give the electrochemically inert polymer.

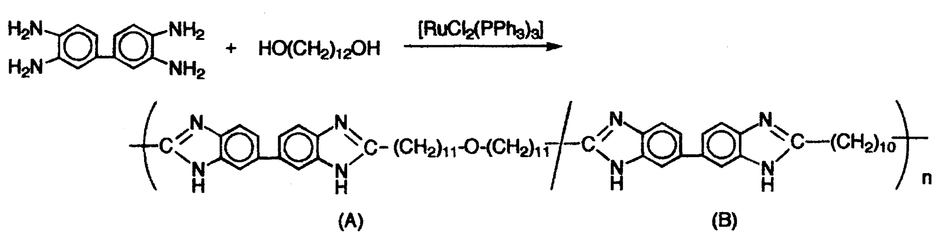
Recently, organometallic polymers have emerged as an important category of polymeric materials since they are expected to show some properties which are rarely found in conventional organic polymers.[1—9] The polymers whose main chain contains π-systems such as cyclopentadienyl (Cp) and cyclobutadiene ligating to transition metals have rigid structures and show π–π* or charge transfer absorption in the visible region.[10—44] Ferrocene-containing polymers[45—48] are most common among the metallocene polymers owing to high stability of the ferrocenylene unit. A wide variety of functionalized ferrocene derivatives could be available as starting materials of the organometallic polymers. On the other hand, they show a redox behavior owing to facile oxidation of Fe(II) to Fe(III) in the ferrocenylene unit as well as a number of properties such as electrical conductivity,[49—56] unique magnetic character,[57] thermal stability,[58—61] and high nonlinear optical susceptibility[62—67] which depend on the structure. They are regarded as promising materials for modified electrodes[68—72] and liquid crystals[73,74] also. Polybenzimidazole containing ferrocenylene unit was obtained from melting polycondensation of 3,3′,4,4′-biphenyltetramine and diphenyl 1,1′-ferrocenedicarboxylate,[75] but it showed low solubility in organic solvents, which prevented further investigations from being carried out.

On the other hand, we recently reported [RuCl$_2$(PPh$_3$)$_3$] catalyzed polycondensation of 3,3′,4,4′-biphenyltetramine and 1,12-dodecanediol to give a polyalkylenebenzimidazole.[76,77] The reaction, based on the Ru complex-catalyzed condensation of 1,2-diaminobenzene with primary alcohol,[78] gave the product containing structural units (A) and (B) randomly, as shown in Scheme 1. [RuCl$_2$(PPh$_3$)$_3$] catalyzes both condensation of 1,2-diaminophenyl and CH$_2$OH groups to give imidazole ring and self-condensation of CH$_2$OH groups to form CH$_2$–O–CH$_2$ linkage, affording the polymer whose structural unit ratio ((A) : (B)) depends on molar ratios of the monomers used.

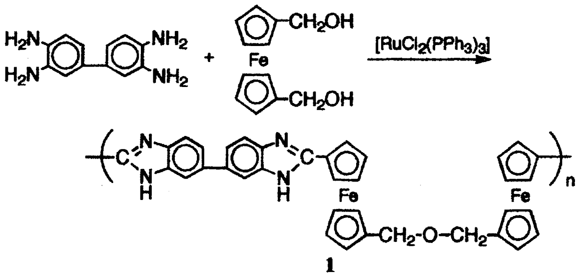
Here we report the polycondensation of 3,3′,4,4′-biphenyltetramine and 1,1′-ferrocenedimethanol to give a new class of polymer containing [5,5′-bi(benzimidazole)]-2,2′-diyl units and 1,1′-ferrocenediyl units in a 1 : 2 ratio.

Results and Discussion

The reaction of 3,3′,4,4′-biphenyltetramine and 1,1′-ferrocenedimethanol in a 1 : 2 molar ratio in the presence of [RuCl$_2$(PPh$_3$)$_3$] catalyst gives Polymer **1** as a brown solid in 98% yield (Eq. 1).



Scheme 1.



1 (1)

An equimolar reaction also produces **1** in a lower yield (38%). The polymer derived from 1 : 1 condensation of the monomers is not observed in the product. Elemental analyses of **1** agree with the proposed structure rather than that of a 1 : 1 polycondensation product. The Polymer **1** prepared from the reaction of the monomers in a 1 : 2 molar ratio has molecular weights, $M_n = 2.1\times10^4$ and $M_w = 4.5\times10^4$, as determined by GPC, and a reduced viscosity, $\eta_{red} = \eta_{sp/c}$, of 0.08 $dL\,g^{-1}$ (at $c = 1$ $mg\,cm^{-3}$ in DMSO at 30 °C, 1 dL = 0.1 dm^3). TGA measurement shows the decomposition starting at 280 °C and a 70% weight decrease at 500 °C. The IR spectrum of **1** indicates the presence of the imidazole group which gives rise to peaks due to ν(N–H), ν(C=N), and ν(C–N) vibrations at 3340, 1610, and 810 cm^{-1}, respectively. Absorption peaks at 1250 and 1080 cm^{-1} are observed at positions close to those of the previously reported polyalkylenebenzimidazole containing $(CH_2)_{11}$–O–$(CH_2)_{11}$ group (1280 and 1060 cm^{-1})[76,77] and assigned to asymmetric and symmetric ν(C–O–C) vibrations of the CH_2–O–CH_2 group between two ferrocenylene groups, respectively.

The ^1H NMR spectrum of **1** contains two very broad signals at $\delta = 4.2$ and 6.8 in an approximately 10 : 3 peak area ratio. They are assigned respectively to CH_2 and Cp hydrogens and hydrogens of the benzene rings. The half peak widths of the signals are 400—420 Hz. The broad ^1H NMR signals suggest the presence of paramagnetic Fe(III) centers in the polymer backbone. In order to confirm this, the polymer was subjected to Mössbauer spectroscopy and SQUID (Superconductive Quantative Interference Devices) measurements. The Mössbauer spectrum of **1** shows two doublets whose isomer shifts and quadropole splittings are IS = 0.42 $mm\,s^{-1}$ and QS = 2.34 $mm\,s^{-1}$, and IS = 0.13 $mm\,s^{-1}$ and QS = 0.56 $mm\,s^{-1}$, respectively, as shown in Fig. 1. The outer and inner doublets are reasonably assigned to Fe(II) and low spin Fe(III) nuclei in the polymer chain, respectively.[79] The ratio of the Fe(II) and Fe(III) nuclei is estimated as approximately 80 : 20. SQUID measurement shows magnetic susceptibility of **1** of 2.0×10^{-2} $emu\,mol^{-1}$ at 300 K. The ESR spectrum of **1** shows an intense symmetrical signal with a very large peak-to-peak width of 180 mT. A small amount of oxidizing chemicals such as Ru(III) complexes generated under polycondensation conditions are responsible for oxidation of a part of Fe(II) centers and formation of Fe(III) centers in the product. Oxygen contained as an impurity in the inert gas used in the polycondensation reaction seems to be much less related to the oxidation since Polymer **1** prepared under air gives the identical ^1H NMR spectrum with that prepared under N_2 atmosphere and does not show a higher degree of oxidation than that obtained in the inert atmosphere.

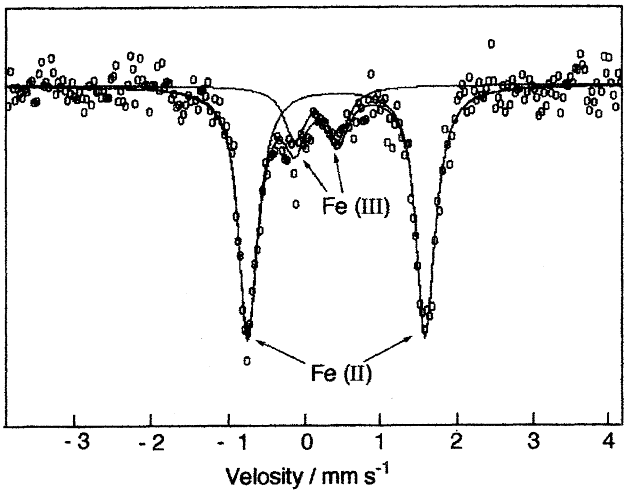
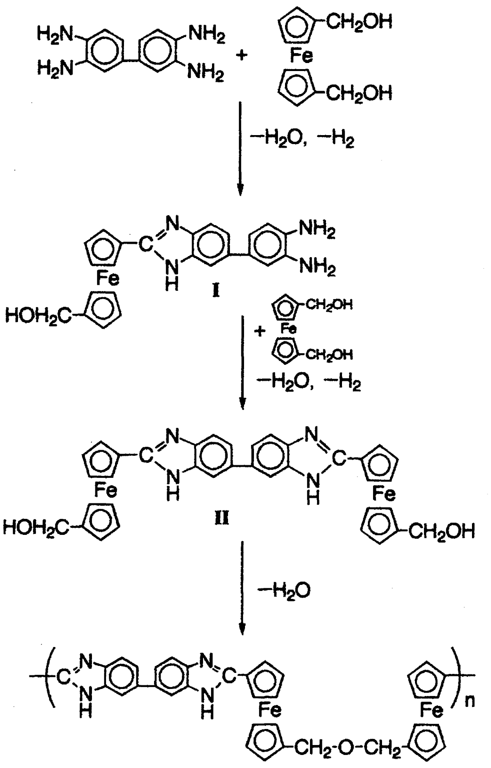


Fig. 1. Mössbauer spectrum of **1** at 298 K.

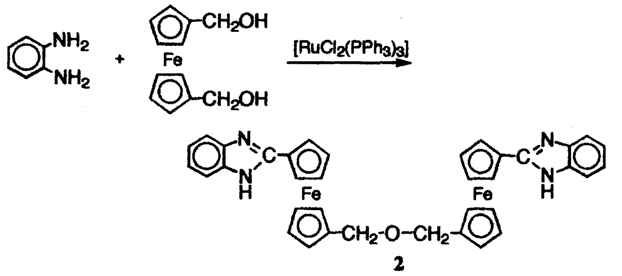
Scheme 2 depicts a plausible polycondensation pathway that involves an intermediate **II** formed via the 1 : 2 condensation of 3,3′,4,4′-biphenyltetramine and 1,1′-ferrocenedimethanol. Subsequent dehydrating condensation of the CH_2OH groups of **II** leads to the CH_2–O–CH_2 bond. Formation of **1** containing two 1,1′-ferrocenediyl groups for each [5,5′-bi(benzimidazole)]-2,2′-diyl unit implies that diaminophenyl group of **I** reacts with CH_2OH group of ferrocenedimethanol to form **II** more readily than with CH_2OH group of **I**. Polycondensation of 3,3′,4,4′-biphenyltetramine with 1,12-dodecanediol caused formation of the polymer having the two structural units via 1 : 2 and 1 : 1 polycondensation reactions.[76,77] In the reaction (Eq. 1), formation of an Im–Fc–Im linkage (Im = [5,5′-bi(benzimidazole)]-2,2′-diyl, Fc = 1,1′-ferrocenediyl) from self-condensation of **I** occurs much more slowly than the reaction of **I** with 1,1′-ferrocenedimethanol, due to steric reasons.

Reaction of *o*-diaminobenzene with 1,1′-ferrocenedimeth-



Scheme 2.

anol was conducted to reveal detailed processes of the polycondensation. The reaction gave bis[1′-(benzimidazol-2-yl)ferrocen-1-ylmethyl] ether (**2**) in 60% (Eq. 2).



(2)

Another product expected from the 2 : 1 condensation, $\overline{HN-C_6H_4-N=C}-Fc-\overline{C=N-C_6H_4-NH}$, was not formed at all. The IR spectrum of **2** shows absorbance due to ν(N–H), ν(C=N), ν_{as}(C–O–C), ν_s(C–O–C), and ν(C–N) at 3426, 1603, 1260, 1028, and 799 cm^{-1}. Figure 2(a) shows the ^1H NMR spectrum of **2** giving rise to peaks due to CH_2 hydrogens at $\delta = 3.35$ and hydrogens of the Cp ring at $\delta = 4.15$ and 4.20, respectively. The $^{13}C\{^1H\}$ spectrum shows peaks due to C=N carbon of the imidazole ring and $CH_2–O–CH_2$ carbons at $\delta = 141.9$ and 51.7, respectively (Fig. 2(b)). The results indicate that $[RuCl_2(PPh_3)_3]$ catalyzes both imidazole ring formation and dehydrative coupling of CH_2OH groups.

Figure 3(a) exhibits cyclic voltammograms of Polymer **1** in a film cast on a Pt plate. A peak due to Fe(II)/Fe(III) oxidation is observed at 0.21 V (vs. Ag/Ag^+) in the first scan. Reduction of the resultant Fe(III) to Fe(II) is not observed

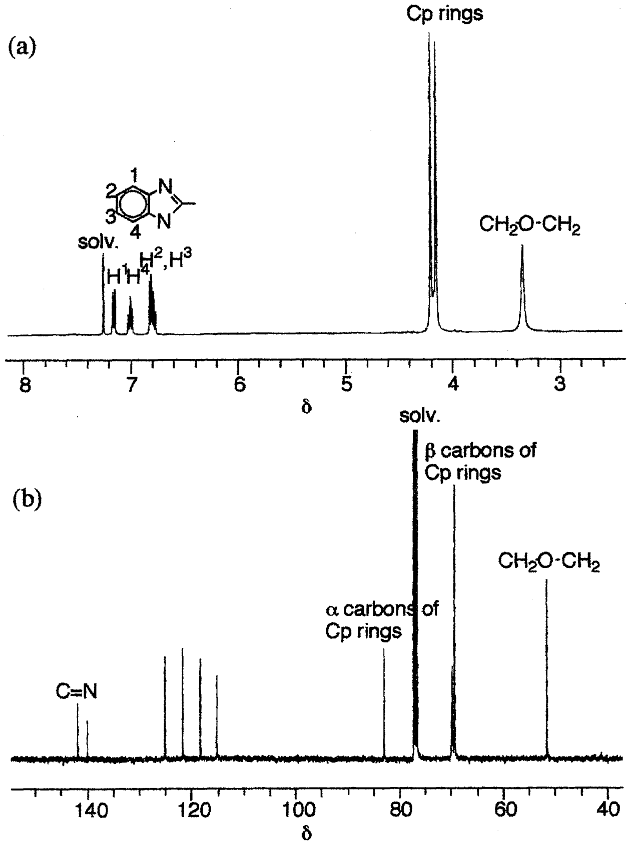


Fig. 2. (a) ^1H (400 MHz) and (b) $^{13}C\{^1H\}$ (100 MHz) NMR spectra of **2** in $CDCl_3$.

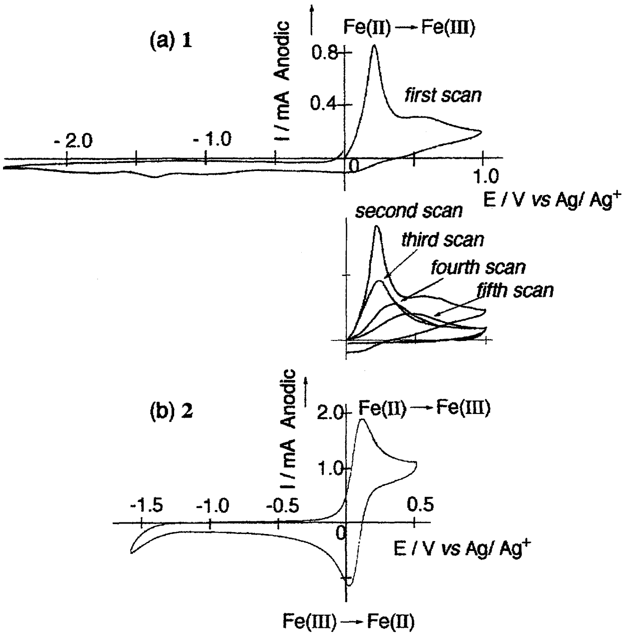
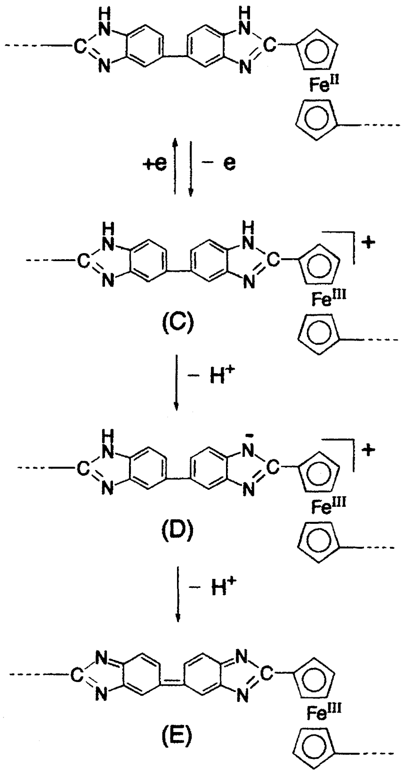


Fig. 3. Cyclic voltammograms of (a) **1** in a film cast on a Pt electrode and (b) **2** in MeCN solution of 0.10 mol dm^{-3} $[N(C_4H_9)_4][ClO_4]$ with scan rates (a) 20 mV s^{-1} and (b) 100 mV s^{-1}. Measurement was carried out under N_2 atmosphere.



Scheme 3.

during the scan. Further repeated scans cause a shift of the oxidation potential center to a higher potential region, accompanied by a decrease in the electrical current corresponding to the oxidation. The electrochemical behavior can be interpreted by assuming the irreversible structural change of Polymer **1** caused by electrochemical oxidation, as depicted in Scheme 3. The oxidation of a ferrocenylene group leads to an intermediate (C) containing a ferricenium cation in the polymer chain. Subsequent elimination of H$^+$ occurs to leave zwitterionic species (D), which is further turned into a neutral species (E). The stable π-conjugated quinonoid structure in (E) prevents protonation of the imidazolate group and reduction of the Fe(III) center to regenerate the Fe(II) containing structural units. IR spectrum of electrochemically oxidized **1** shows no peak due to ν(N–H) vibration, although IR spectrum of **1** before the oxidation shows a clear peak due to ν(N–H) vibration, as mentioned above. Figure 3(b) shows a cyclic voltammogram of **2** and a pair of redox waves at $E_{1/2} = 0.07$ V (vs. Ag/Ag$^+$). The electrochemically active cycles are stable after repeated scanning.

Polycondensation of two monomers gives the polymer product only when equimolar monomers are used.[80] The exceptional 1 : 2 polycondensation of the two monomers in Eq. 1 can be ascribed to unique characteristics of the bond-forming reactions catalyzed by transition metal complexes. The CH_2OH group could react with 1,2-diaminophenyl groups to form a benzimidazole ring or undergoes self-condensation, making a CH_2–O–CH_2 bond in the presence of [$RuCl_2(PPh_3)_3$] catalyst. The intermediate **II** in Scheme 2 is formed selectively since condensation of two diaminophenyl groups of a 3,3′,4,4′-biphenyltetramine molecule with CH_2OH groups of the diol occurs much faster than either the similar coupling reaction with CH_2OH group of **I** in Scheme 2 or the condensation reaction between two CH_2OH groups.

The present work has provided clear 1 : 2 polycondensation of 3,3′,4,4′-biphenyltetramine and 1,1′-ferrocenedimethanol to give a new class of poly(benzimidazole) having ferrocenylene groups in the polymer backbone. The polycondensation with unique stoichiometry has been achieved by combination of proper reaction conditions and structures of the monomers suited for the transition metal complex-catalyzed bond-forming reactions.

Experimental

Materials and Measurements. All the manipulations were performed under nitrogen using standard Schlenk techniques. Solvents were distilled by usual methods and stored under nitrogen. [$RuCl_2(PPh_3)_3$] and 1,1′-ferrocenedimethanol were prepared according to the literature procedures.[81,82] Other organic chemicals were purchased and used as received. IR spectrum was recorded on a JASCO-IR 810 spectrophotometer. NMR and ESR spectra were obtained on JEOL EX-400 and JES-RE3X spectrometers, respectively. Elemental analyses were carried out by a Yanagimoto Type MT-2 CHN autocorder. GPC traces were obtained by a Toso HLC 8020 equipped with polystyrene gel columns (TSK gel G2500, G4000, and G5000), using a DMF solution of LiBr (0.01 mol dm^{-3}) as the eluent with a flow rate of 1.0 cm^3 min^{-1} and with RI and UV detectors. Cyclic voltammetry was carried out with a Hokuto Denko HA-151 galvanostat/potentiostat. SQUID measurement was performed with a Quantum Design MLPM-2. TGA analyses were performed on a Shimadzu TGA-50 under N_2 at a heating rate of 10 °C min^{-1}. Mössbauer spectra were recorded on a transducer-driven Mössbauer Spectrometer (Wissel) in constant acceleration mode at room temperature and 80 K. A 925 MBq ^{57}Co(Rh) source was used. The velocity scale was calibrated by using an enriched iron foil. The isomer shift was referred to metallic iron at room temperature. The spectra were fitted to Lorenzian line shapes using a standard least-square procedure.

Polymerization. To an NMP (1-methyl-2-pyrrolidone, 2 cm^3) solution of [$RuCl_2(PPh_3)_3$] (19 mg, 0.020 mmol) was added 3,3′,4,4′-biphenyltetramine (110 mg, 0.50 mmol) and 1,1′-ferrocenedimethanol (250 mg, 1.0 mmol) at room temperature. After the reaction mixture was stirred at 180 °C for 5 h under nitrogen the solvent was removed by evaporation under high vacuum. The resulting brown paste was washed with methanol (50 cm^3) three times and dried in vacuo to give Polymer **1** as a brown solid (0.32 g, 98% based on 3,3’-diaminobenzidine). IR (KBr) 3340(w), 3110(w), 2920(s), 2850(s), 1610(m), 1540(m), 1450(s), 1410(s), 1250(m), 1080(m), 810(m) cm^{-1}. ^{1}H NMR (400 MHz in DMSO-d_6) $\delta = 6.8$ ($\nu_{1/2} = 420$ Hz, hydrogens of benzene rings), 4.2 ($\nu_{1/2} = 400$ Hz, hydrogens of Cp rings and CH_2). Found: C, 66.6; H, 5.4; N, 8.5%. Calcd for $(C_{36}H_{28}N_4OFe_2)_n$: C, 67.1; H, 4.4; N, 8.7%.

Equimolar reaction of 3,3′,4,4′-biphenyltetramine with 1,1′-ferrocenedimethanol was carried out in a similar manner (yield = 38%). IR (KBr) 3340(w), 3111(w), 2922(s), 2850(s), 1609(w), 1541(m), 1453(s), 1410(s), 1280(m), 1080(w), 810(w) cm^{-1}. ^{1}H NMR (400 MHz in DMSO-d_6) $\delta = 6.8$ ($\nu_{1/2} = 160$ Hz, hydrogens of benzene rings), 4.2 ($\nu_{1/2} = 140$ Hz, hydrogens of Cp rings and CH_2).

Model Reaction. To an NMP (3 cm^3) solution of

[$RuCl_2(PPh_3)_3$] (34 mg, 0.036 mmol) were added 1,2-diaminobenzene (110 mg, 1.0 mmol) and 1,1′-ferrocenedimethanol (250 mg, 1.0 mmol) at room temperature. After the reaction mixture was stirred at 180 °C for 6 h under nitrogen, the solvent was removed by evaporation under high vacuum. The resulting dark brown paste was purified by column chromatography (neutral alumina, hexane–ethyl acetate (5 : 1), $R_f = 0.39$) to give **2** (190 mg, 60% based on 1,2-diaminobenzene). Mp 136—137 °C. IR (KBr) 3426(w), 3024(w), 2962(w), 2870(w), 2814(w), 1603(m), 1496(s), 1260(s), 1093(m), 1028(s), 799(s), 741(s), 511(m) cm^{-1}. ^1H NMR (400 MHz in DMSO-d_6) $\delta = 7.16$ (H^1, dd, 2H, $J = 1$ and 8 Hz), 7.00 (H^4, dt, 2H, $J = 1$ and 8 Hz), 6.78—6.83 (H^2 and H^3, m, 4H), 4.15 and 4.20 (Cp ring, t, 16H, $J = 2$ Hz), 3.35 (CH_2O, br, 4H). $^{13}C\{^1H\}$ NMR (100 MHz in DMSO-d_6) $\delta = 141.9$ (C=N), 140.1, 125.2, 121.8, 118.4, 115.2 (carbons of benzene rings), 83.0, 69.9, 69.4 (carbons of Cp rings), 51.7 (CH_2–O–CH_2). Found: C, 67.6; H, 5.4; N, 8.6%. Calcd for $C_{36}H_{30}N_4OFe_2$: C, 66.9; H, 4.7; N, 8.7%.

The authors are grateful to Mr. Y. Takenaka of our laboratory for experimental assistance. This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture.

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