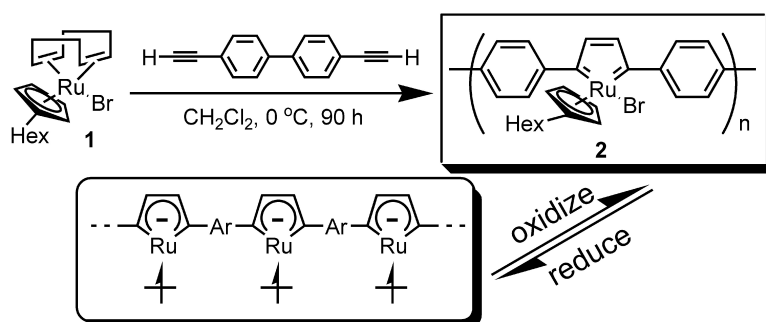## Communication

Synthesis of Poly(biphenylene ruthenacyclopentatrienylene), a New Organometallic Conducting Polymer with Ferromagnetic Interaction in Its Reduced State

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Synthesis of Poly(biphenylene ruthenacyclopentatrienylene), a New Organometallic Conducting Polymer with Ferromagnetic Interaction in Its Reduced State

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π-Conjugated organometallic polymers of transition metals can manifest unique properties by electronic and magnetic interactions between the metal sites through the π-conjugated chain.[1] We previously reported a method to directly prepare a new class of such polymers, "metallacycling polymerization" (MCP), which employs the successive addition of diacetylenylarenes to [CpCo-(PPh$_3$)$_2$], yielding poly(arylene cobaltacyclopentadienylene)s.[2] A problem in this synthesis is unsatisfactory selectivity of the geometric isomers of the cobaltacyclopentadiene moieties. Other groups have reported similar MCP reactions in the synthesis of Co and Zr polymers.[3,4] As the aromatic five-membered heterocycle is isoelectronic to pyrrole and thiophene, an intriguing research subject is the effect of d-block heteroatoms on the physical properties of these compounds. One of the metal candidates to be incorporated into MCP is Ru, because ruthenacyclopentatriene was synthesized recently by the reaction of cyclopentadienyl-Ru complexes with two acetylenes.[5-7] In this paper, we present the first synthesis of the π-conjugated ruthenacyclopentatriene polymer, and we describe its physical properties. This polymer undergoes a reversible reduction ascribed to the Ru sites, and the reduced form exhibits a ferromagnetic interaction between the Ru sites.

The ruthenacyclopentatriene polymer was synthesized as follows. Reaction of [(η^5-C$_5$H$_4$Hex)RuBr(cod)] **1** with 4,4′-diethynylbiphenyl in dichloromethane at 0 °C yielded a reddish-brown polymeric product. This product was purified by washing with ether to remove residual starting materials, and then the residue was extracted with dichloromethane to remove any insoluble component. Evaporation of the solvent under vacuum resulted in a pure product that was a lustrous black film. The product was characterized by elemental analysis, ^{1}H NMR, ^{13}C NMR, IR, and UV−vis spectra, and electrochemical measurements, which together indicated the structure of poly(biphenylene ruthenacyclopentatrienylene), **2** (Scheme 1) (see Supporting Information). Polymer **2** is air-sensitive, and its thermal stability is low. Its solution turned into an insoluble gel after standing for a few days at room temperature, even under nitrogen.

The composition of geometric isomers for ruthenacyclopentatriene units in **2** was examined by ^{1}H NMR spectra. In the spectra of **2** in CDCl$_3$, a signal appeared at δ 7.86, assignable to β-protons of ruthenacyclopentatriene,[8] and no signals due to metallacycle α-protons were detected. Two peaks, one at δ 5.12 and the other at 5.05, both attributed to a cyclopentadienyl ligand, indicate the existence of only one kind of geometric isomers. It is thus concluded that only a 2,5-diaryl derivative of ruthenacyclopentatriene exists in **2**. The result that no geometrical isomer was formed in the polymerization indicates the formation of a fully π-conjugated main chain structure.

Although ruthenacyclopentatriene is known as an intermediate that allows cyclotrimerization of acetylenes to yield a benzene

Scheme 1
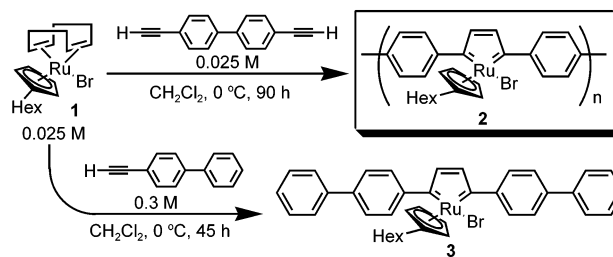
derivative,[8] there was no sign of cyclotrimerization during the polymerization in the conditions of this study. During a reaction of [(η^5-C$_5$Me$_5$)RuCl(cod)] with phenylacetylene, the reaction initially affords ruthenacyclopentatriene, which further reacts with excess acetylene to form [(η^5-C$_5$Me$_5$)Ru(1,2,4-triphenyl)benzene].[6] Although ruthenacycles can react with acetylenes, we found that cyclotrimerization did not occur at 0 °C in the reaction of **1** with 4-ethynylbiphenyl. In the reaction of **1** (0.025 M) with 4-ethynyl-biphenyl (0.3 M) at 0 °C (Scheme 1), which was monitored by ^{1}H NMR spectra in CD$_2$Cl$_2$, ruthenacycle **3** was formed in 100% yield, and the amount of **3** did not decrease. As a result, **3** did not react with excess acetylenes under these conditions.

The GPC of **2** in dichloromethane showed that the molecular weight was up to 2×10^4 (the number of units, $n = 40$). The high solubility of **2** can be attained by the attachment of a hexyl group on Cp. The average molecular weights of **2**, M_n and M_w, were 3400 ($n = 5.9$) and 5800, respectively. It was revealed that these values primarily correspond to the theoretical values by time course GPC analysis of the molecular weight distribution under polymerization at 0 °C. As the polymerization proceeded, M_n and M_w increased at first and became saturated around 90 h, when the M_w/M_n ratio approached the value of 2. In the polycondensation mechanism, the reaction of **1** with 4,4′-diethynylbiphenyl is in equilibrium with the reaction of **2** with COD, which is eliminated from **1**, and both M_n and M_w are maximal when the initial concentrations of **1** and 4,4′-diethynylbiphenyl are equal. The maximal M_n and M_w values depend on the equilibrium constant of the polycondensation. We calculated the equilibrium constant from the time course change in M_n and M_w in the polymerization reaction (see Supporting Information for further discussion). The value obtained was 15, from which M_n and M_w were estimated to be 2800 and 4800, respectively. These values are slightly smaller than those experimentally obtained as noted above. This should be because reprecipitation to purify polymer **2** removed the shorter polymer.

UV−vis−NIR absorption spectra of **2** and **3** in dichloromethane are displayed in Figure 1a. The bands of **3** at 256, 378, and 505 nm are shifted to 296, 400, and 525 nm, respectively, for **2**. These red shifts should be caused by the extension of the conjugated system for the polymer. However, the band at 694 nm remains
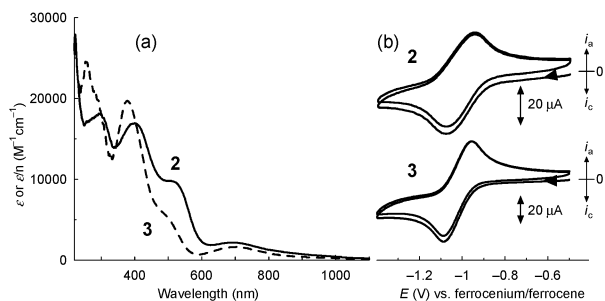
Figure 1. (a) The UV−vis−NIR spectra of **2** (solid line) and **3** (dotted line). (b) Cyclic voltammograms of **2** (top) and **3** (bottom) on a glassy carbon disk in 0.1 M Bu$_4$NClO$_4$−CH$_2$Cl$_2$ at a scan rate of 0.1 V s^{-1}.
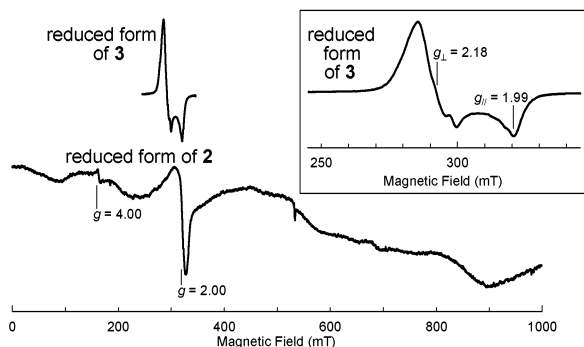

Figure 2. The EPR spectra of reduced forms of **3** (top) and **2** (bottom) at 4 K. Inset: enlarged view of the EPR spectrum of the reduced form of **3**.

unchanged between **2** and **3**. This can be ascribed to LMCT (carbene π → Ru d) at the ruthenacyclopentatriene unit.

Cyclic voltammograms of **2** and **3** indicate that both complexes undergo reversible 1e$^-$ reduction ascribed to the ruthenacyclopentatriene unit at $E^{0'} = -1.01$ V for **2** and -1.03 V for **3** versus ferrocenium/ferrocene (Figure 1b). The peak of **2** is broader than that of **3**, indicating an existence of electronic interaction between ruthenacycle units in **2**. The location of the modestly localized Ru-centered orbital between the π and π* orbitals of the conjugated chain is consistent with the electronic spectra as noted above.

It is interesting to see the magnetic interaction between Ru sites via π-conjugated linker in the reduced form of **2**. We investigated this interaction by comparing the EPR spectra between the reduced forms of **2** and **3**. Reductions of **2** and **3** were carried out under vacuum by treatment with cobaltocene vapor. To confirm whether cobaltocene reduced **2** and **3** successfully, we measured the changes in the UV−vis−NIR spectra of **2** and **3** after adding cobaltocene. We found that the spectrum of **3** was recovered by using iodine vapor to reoxidize the reduced form of **3**. This indicates the reversibility of the chemical redox reaction. For the reduced form of **2**, 20% of spectrum **2** was recovered by oxidation with iodine at room temperature. The changes in the UV−vis−NIR spectra of **2** and **3** showed the same tendency; that is, the band at ca. 500 nm decreased, and the LMCT band at $\lambda_{max} = 694$ nm shifted to ca. 800 nm.

The EPR spectra of the reduced forms of **2** and **3** in frozen THF are displayed in Figure 2. The reduced form of **3** afforded axial symmetry with weak rhombic spectra ($g_\perp = 2.18$, $g_{||} = 1.99$). The spectrum was similar to that of an $S = 1/2$ spin in a low-spin d^5 configuration of Ru(III).[9] The oxidation number of Ru in the

reduced form of **3** is formally V because that in the ruthenacyclopentatriene is VI (carbene counted as dianion). The spin of the Ru in the reduced form of **3** in the d^3 configuration is $S = 1/2$ because the strong ligand field and the low symmetry of the complex structure divides the d-orbitals into nondegenerated components. The instability of the reduced form of **3** as well as that of **2** makes difficult the measurement of magnetic susceptibility to confirm S. Hyperfine interaction with ^{99}Ru and ^{101}Ru isotopes ($I = 5/2$, 12.7% and 17%, respectively) was resolved in the spectra, especially for $g_\perp$ ($a = 3$ mT), indicating that the unpaired electron of the reduced form of **3** localizes in the ruthenacycle moiety and does not interact with other molecules. On the other hand, the EPR spectrum of the reduced form of **2** showed several peaks in a wide magnetic field and was completely different from that of **3**. If there is no interaction between Ru sites, the spectrum should be the same as that of **2**, and if there is antiferromagnetic interaction between Ru sites, the signals should diminish. However, neither occurred in this case. We attribute this inconsistency to the ferromagnetic interaction between Ru sites. The interaction was not intermolecular but intramolecular, because the concentration of the reduced form of **2** (0.03 mM, converted to ruthenacycle unit concentration) was much lower than that of **3** (0.27 mM). The signal at $g = 2$ was caused mainly by isolated spin in the ruthenacycle, but it should be the sum of this state and the triplet state, indicated by a signal at $g = 4$. Broad signals at 50, 205, 553, and 855 mT indicated interactions between more than two ruthenacyclopentatriene units. To clarify this phenomenon, we are now investigating the synthesis of low oligomers and their magnetic properties.

Supporting Information Available: General methods, materials, synthesis details of **1**−**3**, reaction analysis of the polymerization process, electrochemical measurements, changes in the UV−vis−NIR spectra with redox reaction, and temperature dependence of the EPR spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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