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# A Novel Coordination Mode of the Fulvalene Ligand in Binuclear Ruthenium Complexes. Synthesis, Structure, and Some Reactivities of $[(\eta^5\text{-Cp})Ru(\mu_2\text{-}\eta^6{:}\eta^6\text{-}C_{10}H_8)Ru(\eta^5\text{-Cp})](BF_4)_2$

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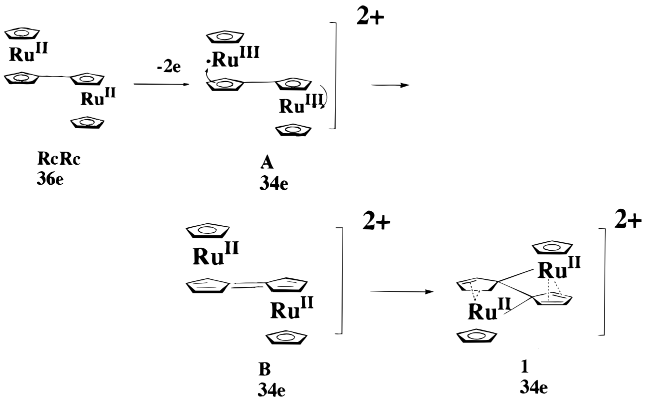
*Summary: The reaction of biruthenocene with excess p-benzoquinone and boron trifluoride−diethyl ether produced the title complex (**1**) in good yield. Single-crystal X-ray analysis revealed that **1** is the Ru−fulvalene complex with the novel coordination mode* $\mu_2$-$\eta^6$:$\eta^6$. *The reaction of **1** with* $Br_2$ *and* $PPh_3$ *in* $CH_3NO_2$ *gave cations formulated as* $[BrCpRu^{IV}FvRu^{IV}CpBr]^{2+}$ *(**2**) and* $CpRu^{II}FvRu^{II}$ $(C_5H_4P^+Ph_3)$ *(**3**), respectively.*

The fulvalene (abbreviated as Fv) ligand is interesting because it provides the possibility of the simultaneous coordination of two metals. Thus, many M−Fv complexes have been reported.[1−6] In M−Fv complexes reported to date, two coordination modes have been found; one is the $\mu_2$-$\eta^5$:$\eta^5$ form, which is the most typical, and the other is the $\mu_2$-$\eta^4$:$\eta^4$ form, found in $[Fe_2Fv(CO)_6]^{2+}$ and related cations.[7,8] Here, we report the synthesis and structure of the Ru−Fv complex **1**, which contains a third type of coordination mode ($\mu_2$-$\eta^6$:$\eta^6$) for the Fv ligand. Reactions of **1** with $Br_2$ or $PPh_3$ are also described.[9]

When a benzene−hexane solution containing $BF_3\cdot Et_2O$ was added to a solution of biruthenocene (abbreviated as RcRc) and *p*-benzoquinone in benzene, a black precipitate was obtained immediately.[10] Recrystallization of the precipitate from nitromethane−diethyl ether gave well-formed orange-yellow crystals of **1**. The $^1H$ NMR spectrum of **1** in $CD_3NO_2$ showed signals assigned to the Cp ligand at $\delta$ 5.79 (s) and two triplets due to the Fv ligand at $\delta$ 6.82 (t) and 4.96 (t). The signal pattern suggests a symmetric structure for the molecule and is quite different from that of the mixed-valence ($Ru^{II}Ru^{IV}$) biruthenocenium cation, formulated as $[CpRu^{II}FvRu^{IV}CpL]^{2+}$ (L = $CH_3CN$, $C_2H_5CN$).[10] The remarkable difference of the chemical shift between the α- and *β*-protons of the Fv ligand suggests that the Fv ligand is coordinated in an unusual manner. The $^{13}C$ NMR spectrum of **1** showed four signals at $\delta$ 89.7, 95.7, 87.0, and 74.8, which are assigned to the Cp ligand, the Fv ligand, and the ipso carbon of the Fv ligand, respec-

**Scheme 1**



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(9) **1** was prepared by the addition of RcRc (100 mg; 0.217 mmol) and *p*-benzoquinone (108 mg; 1.0 mmol) in benzene (100 mL) to a solution of $BF_3\cdot Et_2O$ (0.06 mL) in benzene−hexane (10 mL). The resulting black crude product was washed with tetrahydrofuran to remove the hydroquinone and was recrystallized from nitromethane and diethyl ether to give **1** (121 mg, 0.191 mmol, 88% yield). Orange-yellow planar single crystals were formed by the recrystallization from nitromethane and diethyl ether on standing at 260 K for several days. Anal. Calcd for $C_{20}H_{18}B_2F_8Ru_2$: C, 37.88; H, 2.86. Found: C, 37.95; H, 2.90. **2** was prepared by the addition of **1** (50 mg; 0.079 mmol) in $CH_3NO_2$ (10 mL) to a solution of $Br_2$ (13 mg; 0.081 mmol) in $CH_3NO_2$ (5 mL). A green precipitate (50.4 mg; 0.065 mmol, 82% yield) was formed by the addition of diethyl ether. Single crystals were obtained by diffusion of diethyl ether into a solution of **2** in $CH_3NO_2$ for several days at 270 K. $^1H$ NMR (400 MHz, $CD_3NO_2$): $\delta$ 6.19 (s, Cp), 6.51 (t, $C_5H_4$), 6.26 (t, $C_5H_4$). Anal. Calcd for $C_{20}H_{18}B_2Br_2F_8Ru_2$: C, 30.96; H, 2.34. Found: C, 30.56; H, 2.52. **3** was prepared by the reaction of a solution of **1** (50 mg; 0.079 mmol) in $CH_3NO_2$ (10 mL) with a solution of $PPh_3$ (26 mg; 0.162 mmol) in $CH_3NO_2$ (5 mL). From the yellow solution, yellow crystals (59.9 mg; 0.068 mmol, 87% yield) precipitated by the addition of diethyl ether at 270 K. $^1H$ NMR (400 MHz, $CD_3NO_2$): $\delta$ 7.9−7.6 (m, Ph), 5.16 (t), 4.88 (t), 4.79 (t), 4.68 (t), 4.56 (t), 4.49 (t), 4.48 (s). $^{13}C$ NMR (100 MHz, $CD_3NO_2$): $\delta$ 134.2 (d, $J_{CP} = 2.8$ Hz, *p*-Ph), 133.0 (d, $J_{CP} = 13.0$ Hz, *o*-Ph), 129.0 (d, $J_{CP} = 10.0$ Hz, *m*-Ph), 119.4 (d, $J_{CP} = 92.3$ Hz, ipso-Ph), 91.1 (ipso-$C_5H_4$), 83.6 (ipso-$C_5H_4$), 76.3 (d, $J_{CP} = 10.2$ Hz, $C_5H_4$ of $C_5H_4PPh_3$), 75.6 (d, $J_{CP} = 14.1$ Hz, $C_5H_4$ of $C_5H_4PPh_3$), 72.6 ($C_5H_4$), 72.4 ($C_5H_4$), 70.1 ($C_5H_5$), 69.4 ($C_5H_4$), 69.1 ($C_5H_4$), 63.3 (d, $J_{CP} = 103$ Hz, ipso-$C_5H_4$ of $C_5H_4PPh_3$). $^{31}P$ NMR ($CH_3CN$, 162 MHz, referenced to 85% $H_3PF_6$): $\delta$ 25.08 ($PPh_3$). Anal. Calcd for $C_{38}H_{32}BF_4PRu_2$: C, 56.45; H, 3.99. Found: C, 56.25; H, 3.86.

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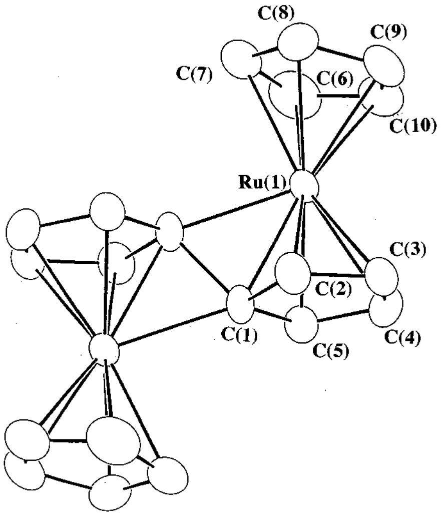

**Figure 1.** ORTEP drawing of the cation of [CpRuFvRuCp]-$(BF_4)_2$. Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) and angles (deg) are as follows: Ru(1)−C(1) = 2.18(1), Ru(1)−C(2) = 2.19(1), Ru(1)−C(3) = 2.24(1), Ru(1)−C(4) = 2.22(2), Ru(1)−C(5) = 2.17(2), Ru(1)−C(6) = 2.28(2), Ru(1)−C(7) = 2.21(2), Ru(1)−C(8) = 2.20(2), Ru(1)−C(9) = 2.15(2), Ru(1)−C(10) = 2.17(2), Ru(1)−C(1)* = 2.13(2), C(1)−C(1)* = 1.62(2); Ru(1)−C(1)−C(1)* = 69.6(8), Ru(1)−C(1)*−C(1) = 66.4(7), C(1)−Ru(1)−C(1)* = 44.1(6), Ru(1)−C(1)−Ru(1)* = 135.9(7).

tively. The last signal ($\delta$ 74.8) is shifted to much higher field compared with that of neutral RcRc, suggesting stronger coordination of the Fv ligand to the metal sites. In the CP-MAS $^{13}C$ NMR spectrum of **1** ($\delta$ 97.7 ($C_5H_4$), 91.6 ($C_5H_4$), 88.9 (Cp), 76.5 (ipso-$C_5H_4$)), no significant spectral difference was observed, implying that the structure of **1** in the solid is the same as in solution.

To confirm the structure of **1**, a single-crystal X-ray analysis was carried out.[11] As can be seen in Figure 1, half of the molecule is crystallographically unique with the whole molecule located on an inversion center. The most interesting structural feature is the coordination of the C(1) to both the Ru(1) and Ru(1)* atoms. Thus, the C(1) atom is formally pentavalent, and this is the reason for the higher field shifts of the C(1) atom observed in the $^{13}C$ NMR. The Ru(1)−C(1) and Ru(1)*−C(1) distances are found to be 2.18(1) and 2.13(2) Å, respectively; the latter value is much shorter than the corresponding values of the pentafulvadiene complex $[CpRu(\mu_2\text{-}\eta^6{:}\eta^6\text{-}C_5H_4CHCHC_5H_4)RuCp]^{2+}$ (2.47, 2.57 Å)[12] and close to that in the fulvene complex $[Cp^*Ru(\eta^6\text{-}C_5(CH_3)_4CH_2)]^+$ (2.270(3) Å).[13a]

To fulfill the 18-electron configuration of the Ru atom (the formal oxidation state of Ru is $Ru^{II}$), the Ru atom is bonded to the C(2)−C(5) atoms of the $C_5H_4$ ring as a diene and the C(1) and C(1)* atoms as an exo double ligand with the formation of a three-center−two-electron bond. This coordination mode is similar to that reported in the pseudo-triple-decker complex $[Cp_2Ru_2(\mu\text{-}C_8H_8)]$.[14] The C(1)−C(1)* distance is 1.62(2) Å, which is longer than that of a normal C−C single bond, owing to the ligation to the two Ru atoms. The C(1)−C(1)* bond is inclined largely toward the two Ru atoms from the C(1)−C(5) plane to allow the formation of the three-center−two-electron bond. The inclination angle (52(1)°) is much larger than those in the analogous complexes ($\mu_2$-$\eta^6$:$\eta^6$-pentafulvadiene)ruthenium (ca. 29°),[12] $Fe(C_5H_4CH_2C_5H_4)(C_5H_4CH^+C_5H_4)Ru$ (ca. 35°),[13c,d] and $Cp^*M(\eta^6\text{-}C_5(CH_3)_4CH_2)^+$ (M = Ru, Os) (ca. 40−42°).[13a,b]

The Cp and $C_5H_4$ ring planes are planar, and the distances of the planes from Ru(1) are 1.817(1) and 1.814(1) Å, respectively, which are somewhat shorter than that in ruthenocene (1.84 Å)[15] and iodoruthenocenium cation (1.84 Å).[16] The tilt angle between the Cp and $C_5H_4$ ring planes is 12.4°, which is similar to that in the fulvene or fulvene-like complexes.[12,13] From all the facts, the cation in **1** can be formulated as $[(\eta^5\text{-Cp})Ru^{II}(anti\text{-}\mu_2\text{-}\eta^6{:}\eta^6\text{-}C_{10}H_8)Ru^{II}(\eta^5\text{-Cp})]^{2+}$, which is the first complex with a $\mu_2$-$\eta^6$:$\eta^6$-coordination mode.

A one-step 2e oxidation of RcRc was observed at $E_{1/2}$ = 0.15 V (vs FcH/FcH$^+$, $E_{pc}$ = +0.24, $E_{pa}$ = +0.07 V; see the Supporting Information). This redox behavior is quite different from that in ruthenocene. Moreover, the redox potential of RcRc is remarkably lower than that of ruthenocene ($E_{pc}$ = +0.52 V). These facts suggest that the redox process involves a structural rearrangement to a stable molecular species (vide supra). A similar redox process was observed in bis(ruthenocenyl)-ethylenes.[12] When the redox studies reported by Astruc are considered,[18] a possible redox mechanism for RcRc can be proposed as follows. The stable 36-electron complex RcRc is first oxidized by two successive one-electron oxidation processes for each ruthenocene moiety to give the unstable 34-electron biradical ion $[Ru^{III}CpFvCpRu^{III}]^{2+}$ **(A**; see Scheme 1), which is transformed to the unstable fulvalene complex **B** with the $Ru^{II}$ atoms. To fulfill the 18-electron configuration of the $Ru^{II}$ atom, further structural rearrangement takes place to afford the stable complex **1**.

The reaction of **1** with a stoichiometric amount of $Br_2$ gave the green complex **2**. From NMR and elemental analysis, the cation of **2** may be formulated as [Cp-

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[11] The X-ray diffraction measurements of **1**−**3** were performed on a MAC Science Rapid Diffraction Image Processor (DIP3000) with graphite-monochromatized Mo K$\alpha$ radiation and an 18 kW rotation-anode generator. Refections were collected using 30 continuous Weissenberg photographs with a $\phi$ range of 6°. The structure was solved with the Dirdif-Patty method in CRYSTAN-GM (software package for structure determination) and refined finally by the full-matrix least-squares procedure. Single crystals of **1**−**3** were prepared by recrystallization from $CH_3NO_2-Et_2O$ at 260 K. Crystal data for **1**: orange-yellow, $C_{20}H_{18}B_2F_8Ru_2$, $M_r$ = 634.108, monoclinic, space group $P2_1/a$, $a$ = 9.849(2) Å, $b$ = 12.542(4) Å, $c$ = 8.831(2) Å, $\beta$ = 113.47(2)°, $V$ = 1000.5(4) Å$^3$, $Z$ = 2, $\mu$ = 15.59 mm$^{-1}$, $R$ = 0.065, $(\Delta/\sigma)_{max}$ = 0.03. Crystal data for **2**: green needles, $C_{20}H_{18}B_2Br_2F_8Ru_2$, $M_r$ = 775.916, triclinic, space group $P\bar{1}$, $a$ = 9.046(2) Å, $b$ = 10.842(2) Å, $c$ = 11.950(2) Å, $\alpha$ = 95.59(1)°, $\beta$ = 104.431(9)°, $\gamma$ = 90.75(1)°, $V$ = 1128.8(3) Å$^3$, $Z$ = 2, $\mu$ = 84.09 mm$^{-1}$, $R$ = 0.067, $(\Delta/\sigma)_{max}$ = 0.07. Crystal data for **3**: yellow plane, $C_{38}H_{32}BF_4PRu_2$, $M_r$ = 808.592, monoclinic, space group $P2_1/n$, $a$ = 10.882(1) Å, $b$ = 17.999(1) Å, $c$ = 16.722(1) Å, $\beta$ = 97.472(3)°, $V$ = 3247.4(3) Å$^3$, $Z$ = 4, $\mu$ = 19.07 mm$^{-1}$, $R$ = 0.047, $(\Delta/\sigma)_{max}$ = 0.62.

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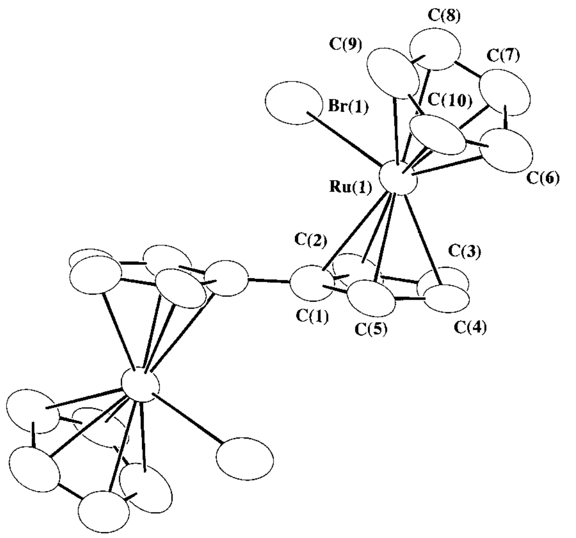


**Figure 2.** ORTEP drawing of the cation of [BrCpRu-FvRuCpBr]$(BF_4)_2$. Thermal ellipsoids are drawn at the 50% probability level. Bond distances (Å) are as follows: Ru(1)−Br(1) = 2.535(1), Ru(1)−C(1) = 2.27(1), Ru(1)−C(2) = 2.24(1), Ru(1)−C(3) = 2.29(1), Ru(1)−C(4) = 2.18(1), Ru(1)−C(5) = 2.22(1), Ru(1)−C(6) = 2.18(1), Ru(1)−C(7) = 2.25(1), Ru(1)−C(8) = 2.20(1), Ru(1)−C(9) = 2.21(2), Ru(1)−C(10) = 2.21(1), C(1)−C(1)* = 1.43(2).

$BrRu^{IV}FvRu^{IV}BrCp]^{2+}$. This assignment was verified by X-ray diffraction (see Figure 2).[11] From the ORTEP drawing, the cation of **2** can be formulated as $[(\eta^5\text{-Cp})BrRu^{IV}(anti\text{-}\mu_2\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)Ru^{IV}Br(\eta^5\text{-Cp})]^{2+}$, which contains two M atoms in oxidation state IV confirmed by X-ray diffraction. The unit has two independent molecules (unit Ru(1)Br(1), unit Ru(2)Br(2)). Because the basic molecular structures of the two molecules are essentially equal, only the cation containing the Ru(1)-Br(1) unit is discussed. As shown in Figure 2, half of the molecule is crystallographically unique with the cation located on an inversion center. The Ru(1)−Br(1) distance is 2.535(1) Å, which is close to that in the analogous molecule RuCp(CpO)Br (2.556(1) Å).[17] The distances between Ru(1) and the Cp and $C_5H_4$ ring planes are 1.850(9) and 1.876(2) Å, respectively, which are somewhat larger than that found in **1** and ruthenocene. The dihedral angle between the Cp and $C_5H_4$ ring planes is 36.6(1)°, being within the range of that reported in haloruthenocenium cations.[13,19]

Treatment of **1** with $PPh_3$ gave the 1′-substituted biruthenocene **3** as the major product. To confirm the structure of **3**, X-ray diffraction was carried out and the molecular structure is shown in Figure 3. From the NMR spectrum, elemental analysis, and X-ray diffraction, the cation can be formulated as $(\eta^5\text{-Cp})Ru^{II}(\mu_2\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)Ru^{II}(\eta^5\text{-}C_5H_4P^+Ph_3)$. Triphenylphosphine attacks exclusively at the Cp ring of **1**, giving the cation **3**. The structure of **3** is similar to that of the analogous complex $[RuCp(C_5H_3O\text{-}2\text{-}PPh_3)MeCN](PF_6)_2$.[20]

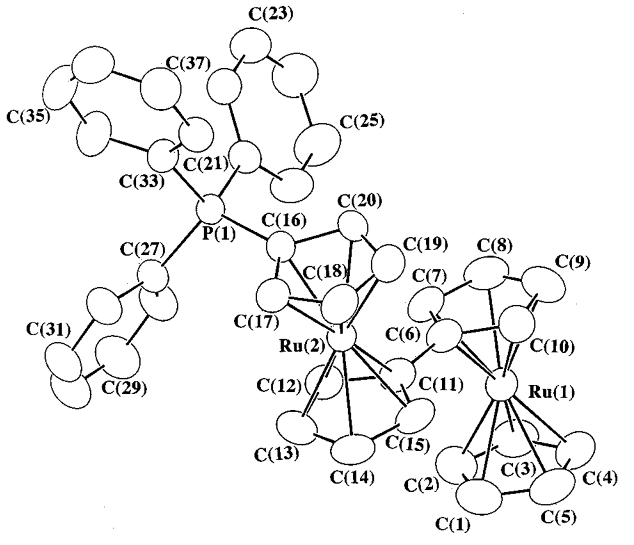
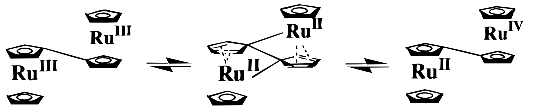


**Figure 3.** ORTEP drawing of the cation of $[CpRuFvRuC_5H_4\text{-}PPh_3]BF_4$. Thermal ellipsoids are drawn at the 50% probability level. Bond distances (Å) are as follows: Ru(1)−C(1) = 2.18(1), Ru(1)−C(2) = 2.18(1), Ru(1)−C(3) = 2.19(1), Ru(1)−C(4) = 2.20(1), Ru(1)−C(5) = 2.17(1), Ru(1)−C(6) = 2.18(1), Ru(1)−C(7) = 2.17(1), Ru(1)−C(8) = 2.18(1), Ru(1)−C(9) = 2.20(1), Ru(1)−C(10) = 2.17(1), Ru(2)−C(11) = 2.21(1), Ru(2)−C(12) = 2.18(1), Ru(2)−C(13) = 2.16(1), Ru(2)−C(14) = 2.17(1), Ru(2)−C(15) = 2.18(1), Ru(2)−C(16) = 2.15(1), Ru(2)−C(17) = 2.16(1), Ru(2)−C(18) = 2.20(1), Ru(2)−C(19) = 2.20(1), Ru(2)−C(20) = 2.19 (1), C(6)−C(11) = 1.46 (1), P(1)−C(16) = 1.769(3).

The C(16)−P(1) distance is 1.769(3) Å (cf. $[RuCp(C_5H_3O\text{-}2\text{-}PPh_3)MeCN](PF_6)_2$, 1.782(8) Å).

Complex **1** reacts with other nucleophiles such as $CH_3CN$, $C_2H_5CN$, $N(C_5H_5)$, $P(OPh)_3$, $N(CHCH)_2N$, and $O(CH_2CH_2)_2O$ in $CH_3NO_2$ to give the corresponding $Ru^{II}Ru^{IV}$ mixed-valence complexes.[10] These results suggest that there may be resonance between **1** and **1a** ($Ru^{III}Ru^{III}$) and **1b** ($Ru^{II}Ru^{V}$) species and that the product in the reaction with the reagents depends on the nucleophilicity of the reagents.



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In summary, the binuclear Ru complex **1** with a novel coordination mode for the Fv ligand, $[(\eta^5\text{-Cp})Ru^{II}(anti\text{-}\mu_2\text{-}\eta^6{:}\eta^6\text{-}C_{10}H_8)Ru^{II}(\eta^5\text{-Cp})]^{2+}$, was isolated. The reaction of **1** with $Br_2$ and $PPh_3$ in $CH_3NO_2$ gave cations formulated as $[BrCpRu^{IV}FvRu^{IV}CpBr]^{2+}$ (**2**) and $CpRu^{II}\text{-}Fv(C_5H_4P^+Ph_3)Ru^{II}$ (**3**), respectively.

**Supporting Information Available:** Tables of crystal data and structure refinement parameters, atomic coordinates, bond distances, and bond angles for **1**−**3** and a figure giving the cyclic voltammogram for RcRc. This material is available free of charge via the Internet at http://pubs.acs.org.

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