

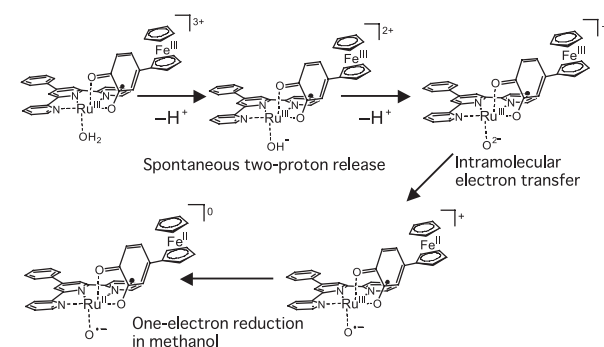
VIII-H Development of Metal-Conjugated Multi-Electron Redox Systems in Metal-Dioxolene Complexes and Activation of Water Ligand

Dioxolenes act as a versatile electron-acceptor and/or -donor through the reversible two-electron redox reaction among three oxidation forms, catechol (Cat), semiquinone (SQ), and quinone (Q). The *o*-dioxolene ligands offer a wide range of the metal complexes showing a unique metal-conjugated intramolecular electron transfer, that is valence tautomerization. Development of the metal-conjugated multi-electron redox systems is one of the most essential in order to design electrocatalysts and electronic molecular devices. The ruthenium-dioxolene complexes exhibit the reversible two-electron redox behavior and each oxidation form has been recognized as the metal-conjugated resonance hybrids, on account of the accessible redox potentials between the metal center and the dioxolene ligands. A new three-electron redox system could be constructed in ruthenium complexes containing a ferrocene-attached dioxolene, leading to metal-conjugated resonance hybrids among the three redox sites, metal, dioxolene, and ferrocene. The ruthenium-dioxolene framework successfully activates its water ligand *via* the intramolecular electron transfer to produce $\text{Ru}^{\text{II}}\text{-O}^{\bullet-}$ species, accompanied by compelling proton release from $\text{Ru}^{\text{III}}\text{-OH}_2$ using an additive strong base. In this study, we prepared a similar $\text{Ru}\text{-OH}_2$ complex bearing the ferrocene-attached dioxolene. In the three-electron redox system, the water molecule is activated through spontaneous two-proton release and the intramolecular electron transfer to the ruthenium-dioxolene-ferrocene framework.

VIII-H-1 Synthesis of a $\text{Ru}\text{-OH}_2$ Complex Bearing a Ferrocene-Attached Catecholato Ligand and Its Spontaneous Proton Release

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A ruthenium-acetato-terpyridine complex containing 4-ferrocenyl-1,2-benzoquinone, $[\text{Ru}^{\text{II}}(\text{OAc})(\text{SQ-Fc})(\text{ph-terpy})]$ (**1**) was synthesized. Complex **1** showed the reversible three-electron redox behavior, derived from $(\text{1}^-/\text{1})$, $(\text{1}^+/\text{1})$, $(\text{1}^+/1^{2+})$ redox couples. The one-electron oxidation form, $[\text{Ru}^{\text{III}}(\text{OAc})(\text{SQ-Fc})(\text{ph-terpy})]\text{CF}_3\text{SO}_3$ (**1**⁺) was isolated as a blue precipitate from a dichloromethane solution of **1** on addition of 1 equivalent of AgCF_3SO_3 in the yield of 78%. Our attempt to prepare the two-electron oxidation form, $[\text{Ru}^{\text{III}}(\text{OAc})(\text{SQ-Fc}^+)(\text{ph-terpy})](\text{CF}_3\text{SO}_3)_2$ (**1**²⁺) has been unsuccessful, because **1**²⁺ is labile under the synthetic conditions. The hydrolytic exchange of **1**⁺ from the acetate to an aquo ligand was carried out using HBF_4 in an acetone-water solution. The isolated hydrolysis form, **2** was characterized by ESI-mass and elemental analyses. On the basis of the elemental analysis, **2** consists of 90% of a $\text{Ru}\text{-OH}$ form, $[\text{Ru}^{\text{III}}(\text{OH})(\text{SQ-Fc}^+)(\text{ph-terpy})](\text{BF}_4)_2$ and 10% of a $\text{Ru}\text{-O}$ form, $[\text{Ru}^{\text{III}}(\text{O})(\text{SQ-Fc}^+)(\text{ph-terpy})](\text{BF}_4)$. The mass signals due to the acetate complex completely disappeared in the ESI-mass spectrum of an acetone solution of **2**. The main signal at 719 *m/z* and the isotope pattern are ascribable to a $[\text{Ru}^{\text{III}}(\text{O})(\text{SQ-Fc}^+)(\text{ph-terpy})]^+$. These results suggest that the $\text{Ru}\text{-OH}_2$ and $\text{Ru}\text{-OH}$ forms are changed into the $\text{Ru}\text{-O}$ form through spontaneous two-proton release as an only stable state in the solution, because of the strong electron attraction of $\text{Ru}^{\text{III}}\text{-SQ-Fc}^+$ framework (Scheme 1). The $\text{Ru}\text{-O}$ complex, $[\text{Ru}^{\text{III}}(\text{O})(\text{SQ-Fc}^+)(\text{ph-terpy})]^+$ underwent one-electron reduction in a methanol solution to generate $[\text{Ru}^{\text{II}}(\text{O}^{\bullet-})(\text{SQ-Fc})(\text{ph-terpy})]$, according to the electronic spectral change (Scheme 1).



Scheme 1.