

2B3b

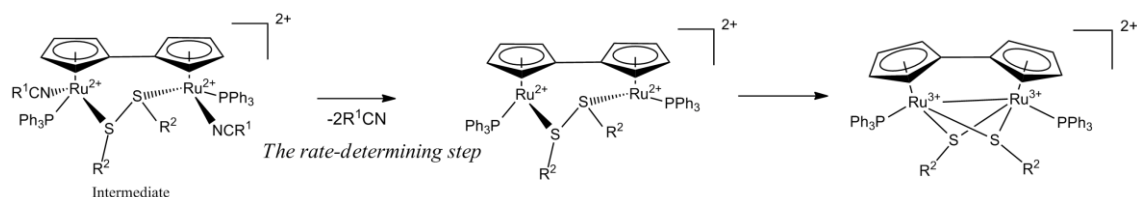
Reaction of Binuclear Ruthenium-Fulvalene Complexes Intramolecularly Bridged by Alkyldisulfides

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The oxidative addition reaction breaking disulfide bond is used for synthesis of bis(thiolato)-bridged complexes.¹ Although this type of reaction has been widely used in Ru complexes, a detail of the mechanism has been hardly reported. In the present study, we succeeded in isolating binuclear Ru-fulvalene complexes intramolecularly bridged by alkyldisulfide [(PPh₃)(R¹CN)Ru-(μ₂-η⁵:η⁵-C₁₀H₈)(μ₂-R²SSR²)Ru(R¹CN)(PPh₃)](BF₄)₂ (**1A**; R¹ = R² = Me, **2A**; R¹ = Me, R² = Et, **1B**; R¹ = Et, R² = Me, **2B**; R¹ = R² = Et) as intermediates of bis(thiolato)-bridging reaction. The intermediates reacted spontaneously in various solvents to produce [(PPh₃)Ru(μ₂-η⁵:η⁵-C₁₀H₈)(μ₂-SR)₂Ru(PPh₃)](BF₄)₂ (**3**; R = Me, **4**; R = Et), and the reaction rate constants obtained from ¹H NMR spectroscopy depended on a kind of solvent. Single crystal X-ray structural analysis revealed that the disulfide bond-lengths of intermediates extended compared with the corresponding non-coordinated disulfide bond-length. It is understood that the large lengthening of disulfide bond in intermediates enhances the reactivity of the disulfides. An excess amount of RCN added to the solution strongly blocked the reaction. It was estimated that the reaction was a stepwise, i.e., this occurred only after elimination of acetonitrile ligands. The reaction rate depended on a stabilization energy of eliminated RCN by solvation. The stabilization energies by solvation of each solvent were determined by DFT calculation. It was indicated that the reaction rate was faster in the case of larger stabilization energy. It is suggested that the rate-determining step of the reaction is where RCN ligands are eliminated, not where disulfide bond is broken. The reaction mechanism was shown in Scheme 1. It was found that bis(selenolato)-bridging reaction by oxidative addition of dimethyldiselenide also takes place in the similar reaction mechanism. [(PPh₃)(MeCN)Ru-(μ₂-η⁵:η⁵-C₁₀H₈)(μ₂-MeSeSeMe)Ru(MeCN)(PPh₃)](BF₄)₂ (**5A**) was isolated as the intermediate and the structure was determined by single crystal X-ray structural analysis. Although **5A** and **1A** have the same structures, the behaviors in solvent were different each other.



Scheme 1

[1] E. Becker, K. Mereiter, R. Schmid, K. Kirchner, *Organometallics*, **2004**, 23, 2876.