

## VII-E Reductive Activation of Carbon Dioxide and Oxidative Activation of Water Aimed at Energy Conversion

Free energy required in the reduction of CO<sub>2</sub> continuously decreases with an increase of the number of electrons participated in the reduction. Accordingly, multi-electron reduction of CO<sub>2</sub> is much favorable compared with two-electron reduction of CO<sub>2</sub>. An electrophilic attack of CO<sub>2</sub> to low valent coordinatively unsaturated metals complexes gives metal-η<sup>1</sup>-CO<sub>2</sub> complexes, which can be easily converted to M-CO ones. A major problem of reduction of CO<sub>2</sub> in homogeneous systems is reductive cleavages of M-CO bonds (CO evolution) under the reaction condition due to accumulation of too much electrons in the central metals. A catalytic system, in which electrons required in the reduction of CO<sub>2</sub> are provided by ligand localized redox reactions not but metal centered ones, therefore, may open a new methodology for the reduction of CO<sub>2</sub>. Based on the facts that naphthylidene works as not only monodentate, bidentate and bridging ligand between metals and carbonyl carbon but also electron source in the reduction of CO<sub>2</sub>, we have been preparing a variety of meta-naphthylidene complexes to aim at multi-electron reduction of CO<sub>2</sub>.

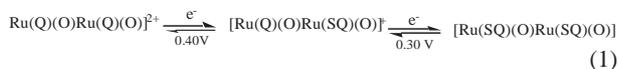
Much attention has been paid to high valent oxo-metal complexes from the view points of the fact that metal proteins participating in oxidation of various organic molecules contain one or multi oxo-metal centers. Among various synthetic route of metal-oxo complexes reported so far, metal aqua-complexes are reasonable precursors, since they undergo acid-base equilibrium among aqua-, hydroxo- and oxo-complexes. The distribution of those complexes can be controlled by selection of bases and pH. Polymerization of aqua-metal complexes upon deprotonation of aqua ligands would depress by introduction of appropriate ligands which can accept electrons generated in the hydroxy and oxo groups. Along the line, we have prepared a series of metal-aqua complexes with dioxolene and dithiolene ligands to decrease basicity of the hydroxy and oxo ligands.

### VII-E-1 Syntheses and Redox Properties of Bis(hydroxoruthenium) Complexes with Quinone and Bipyridine Ligands. Water-Oxidation Catalysis

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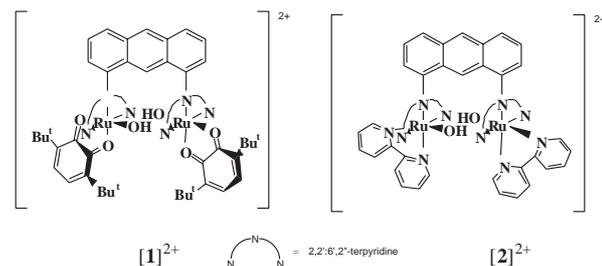
[*Inorg. Chem.* **40**, 329 (2001)]

A novel dimerizing ligand 1,8-bis(2,2':6',2''-terpyridyl)anthracene (btpyan) was prepared by three reactions from 1,8-diformylanthracene. Bis(ruthenium-hydroxo)complex with two 3,6-di(*tert*-butyl)-1,2-benzoquinone ligands (3,6-tBu<sub>2</sub>qui), [Ru<sup>II</sup><sub>2</sub>(OH)<sub>2</sub>(3,6-tBu<sub>2</sub>qui)<sub>2</sub>(btpyan)](SbF<sub>6</sub>)<sub>2</sub> (**[1]**)(SbF<sub>6</sub>)<sub>2</sub> and with two 2,2'-bipyridine ligands (bpy), [Ru<sup>II</sup><sub>2</sub>(OH)<sub>2</sub>(bpy)<sub>2</sub>(btpyan)](SbF<sub>6</sub>)<sub>2</sub> (**[2]**)(SbF<sub>6</sub>)<sub>2</sub> were synthesized by using btpyan ligand. **[1]**<sup>2+</sup> easily eliminated two protons by the addition of *t*-BuOK (2.0 equiv.) coupled with the reduction of quinone ligands in the MeOH solution, and converted to the [Ru<sup>II</sup><sub>2</sub>(O)<sub>2</sub>(3,6-tBu<sub>2</sub>sq)<sub>2</sub>(btpyan)]<sup>0</sup> (3,6-tBu<sub>2</sub>sq = 3,6-di(*tert*-butyl)-1,2-semiquinone), while **[2]**(SbF<sub>6</sub>)<sub>2</sub> was not changed by the addition of large excess of *t*-BuOK. Electrochemical and Spectroelectrochemical measurements revealed that the [Ru<sup>II</sup><sub>2</sub>(O)<sub>2</sub>(3,6-tBu<sub>2</sub>sq)<sub>2</sub>(btpyan)]<sup>0</sup> derived from **[1]**<sup>2+</sup> oxidized to [Ru<sup>III</sup><sub>2</sub>(O)<sub>2</sub>(3,6-t-Bu<sub>2</sub>qui)<sub>2</sub>(btpyan)]<sup>4+</sup> at +1.2 V via the [Ru<sup>II</sup><sub>2</sub>(O)<sub>2</sub>(3,6-tBu<sub>2</sub>qui)<sub>2</sub>(btpyan)]<sup>2+</sup> in the MeOH solution. **[1]**<sup>2+</sup> showed higher catalytic activity for the water-oxidation in a CF<sub>3</sub>CH<sub>2</sub>OH/ether solution containing water and in pH controlled-water (pH 4.0) by using modified ITO electrode, and the turnover number was 35000. The role



of the equilibrium of equation 1 in the O<sub>2</sub> evolution is evidenced by the fact that the analogous **[2]**(SbF<sub>6</sub>)<sub>2</sub> has

no ability to catalyze the oxidation of water under the same conditions.



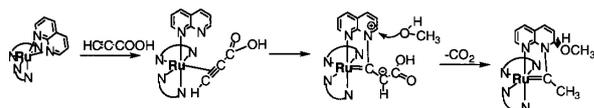
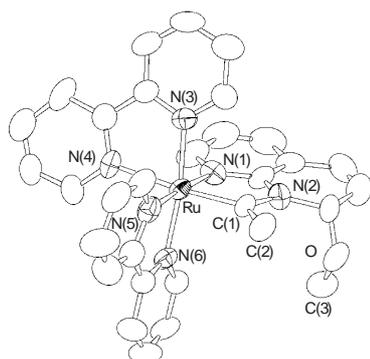
### VII-E-2 A Ru-Carbene Complex with a Metallacycle Involving a 1,8-naphthylidene Framework

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The reaction of [Ru(bpy)<sub>2</sub>(CO)(napy)](PF<sub>6</sub>)<sub>2</sub> with HCCC(O)OH in CH<sub>3</sub>OH/H<sub>2</sub>O (3:2 V/V) gave **[1]**(PF<sub>6</sub>)<sub>2</sub>. The molecular structure of **1**<sup>2+</sup> determined by X-ray diffraction analysis. The characteristic feature of **1**<sup>2+</sup> is the C-N bond formation between the CCH<sub>3</sub> group and one nitrogen of napy, and a unique five-membered metallacycle consisting of Ru-N-C-N-C(O) atoms. The metallacycle ring and the napy moiety form a coplane despite that aromaticity of the napy ligand substantially decreased due to the attachment of CH<sub>3</sub>OH to the carbon atom of 2-position of napy. The <sup>1</sup>H-NMR spectrum of the complex **1**<sup>2+</sup> in CD<sub>3</sub>CN/CD<sub>3</sub>OD (1:1 v/v) showed the equilibrium between the carbene species and the corresponding vinylidene species. The CH<sub>3</sub>O group of **1**<sup>2+</sup> was substituted by C<sub>2</sub>H<sub>5</sub>O in C<sub>2</sub>H<sub>5</sub>OH/CH<sub>3</sub>CN. In addition, treatments of **1**<sup>2+</sup> with the

equivalent amount of  $\text{OH}^-$  at room temperature in  $\text{CD}_2\text{Cl}_2$  gave the corresponding vinyl complex with a framework of the five membered metallacycle. The most likely path for the formation of  $\mathbf{1}^{2+}$  is depicted in Scheme. The reaction of  $\mathbf{1}^{2+}$  with propiolic acid would produce a vinylidene complex through  $\pi$  alkyne complex with monodentate napy. An intra-molecular attack of non-bonded nitrogen of napy to the  $\alpha$  carbon of the vinylidene group must increase in acidity of the vicinal carbon of the bonded nitrogen of napy, which will induce a nucleophilic attack of  $\text{CH}_3\text{OH}$  to the  $\text{C}_2$  carbon.



### VII-E-3 Characterization of $\text{Ru}(\text{bpy})_2(\text{CO})(\text{COO})$ Prepared by $\text{CO}_2$ Addition to $\text{Ru}(\text{bpy})_2(\text{CO})$ in Acetonitrile

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DMF solutions containing  $[\text{Ru}(\text{bpy})_3]^{2+}$ ,  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{X}]^{n+}$  ( $\text{X} = \text{Cl}, \text{H}, n = 1$  or  $\text{X} = \text{CO}, n = 2$ ), and triethanolamine (TEOA) as an electron donor have been used for photochemical  $\text{CO}_2$  reduction. These homogeneous systems produce  $\text{HCOO}^-$  and  $\text{CO}$  as the major and a minor products with a total quantum yield of approximately 15%. The  $\text{CO}_2$  reduction system involves a photochemical cycle for  $[\text{Ru}(\text{bpy})_3]^{2+}$  and a thermal cycle for  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{X}]^{n+}$ . The proposed mechanism involves reductive quenching of the  $[\text{Ru}(\text{bpy})_3]^{2+}$  excited state by TEOA to form  $[\text{Ru}(\text{bpy})_3]^+$  and reduction of  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{X}]^{n+}$  by two  $[\text{Ru}(\text{bpy})_3]^+$  molecules to produce  $[\text{Ru}(\text{bpy})_2(\text{CO})]^0$ . The latter reacts with  $\text{CO}_2$  to form  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{COO})]^0$  as a common intermediate for formate and  $\text{CO}$  production.  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{COO})]^0$  and  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{COOH})]^+$  have been previously prepared by addition of two and one equivalent of  $\text{OH}^-$ , respectively, to  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ . An alternative preparation of  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{COO})]^0$  from  $[\text{Ru}(\text{bpy})_2(\text{CO})]^0$  is the reaction of  $\text{CO}_2$  with a doubly reduced species generated from  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}]^+$  in acetonitrile, and the reaction is the key process of  $\text{CO}_2$  reduction in the photochemical system.

The CV of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  in acetonitrile indicates that the two-electron reduction wave at  $-1.0$  V vs. SCE is not affected by  $\text{CO}_2$ . Na-Hg reduction of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  produces a very intense blue solution of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^0$  which does not react with  $\text{CO}_2$ . The CV of  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}]^+$  indicates three reduction wave between  $-1.3$  V and  $-1.9$  V. The catalytic current observed under  $\text{CO}_2$  depends on the electrolytes. The first reduction seems to be the bpy-centered reduction. Within a few minute, two tiny peaks at 395 and 510 nm disappear, indicating that intra-molecular electron transfer is taking place to form  $[\text{Ru}(\text{bpy})_2(\text{CO})]$  with loss of a Cl ligand. The mono-reduced species does not react with  $\text{CO}_2$ .

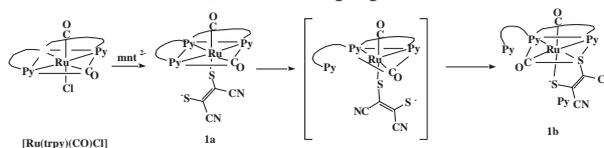


### VII-E-4 Ruthenium Terpyridine Complexes with mono- and bi-Dentate Dithiolene Ligands

SUGIMOTO, Hideki; TSUGE, Kiyoshi; TANAKA, Koji

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The reaction of  $[\text{Ru}(\text{CO})_2\text{Cl}(\text{trpy})]\text{PF}_6$  ( $\text{trpy} =$  terpyridine) with  $\text{Na}_2\text{mnt}$  ( $\text{mnt} = \text{S}_2\text{C}_2(\text{CN})_2$ ) initially produced  $[\text{Ru}(\text{CO})_2(\text{mnt}-\kappa\text{S})(\text{trpy}-\kappa^3\text{NN}'\text{N}'')]$  (**1a**), which rearranged to  $[\text{Ru}(\text{CO})_2(\text{mnt}-\kappa^2\text{S})(\text{trpy}-\kappa^2\text{NN}'\text{N}'')]$  (**1b**) in solutions. The rearrangement from **1a** to **1b** proceeds via the penta-coordinated complex with monodentate  $\text{mnt}$  and bidentate  $\text{trpy}$ . The reaction of  $[\text{Ru}(\text{CO})_2\text{Cl}(\text{trpy})]\text{PF}_6$  with 3,4-toluenedithiol ( $\text{H}_2\text{tdt}$ ) gave  $[\text{Ru}(\text{CO})_2(\text{tdt}-\kappa^2\text{S})(\text{trpy}-\kappa^2\text{NN}'\text{N}'')]$  (**2b**) but  $[\text{Ru}(\text{CO})_2(\text{tdt}-\kappa\text{S})(\text{trpy}-\kappa^3\text{NN}'\text{N}'')]$  (**2a**) was not identified in the reaction. Thus, ruthenium complexes with bidentate dithiolene and bidentate terpyridine seem to be more stable than those with monodentate dithiolene and tridentate terpyridine. Neither  $[\text{Ru}(\text{CO})_2(\text{pdt}-\kappa\text{S})(\text{trpy}-\kappa^3\text{NN}'\text{N}'')]$  (**3a**) nor  $[\text{Ru}(\text{CO})_2(\text{pdt}-\kappa^2\text{S})(\text{trpy}-\kappa^2\text{NN}'\text{N}'')]$  (**3b**) ( $\text{pdt} = \text{PhC}(\text{S})\text{C}(\text{S})\text{Ph}$ ) was obtained in the reaction of  $[\text{Ru}(\text{CO})_2\text{Cl}(\text{trpy})]\text{PF}_6$  with  $\text{Cs}^+$  salt of 4,5-diphenyldithiolate in  $\text{CH}_3\text{OH}$  under  $\text{N}_2$ . The same reaction conducted under aerobic conditions afforded  $[\text{Ru}(\text{CO})_2(\text{C}(\text{O})\text{OCH}_3)(\text{SC}(\text{Ph})\text{C}(\text{Ph})(\text{SC}(\text{O})\text{OH})(\text{trpy}-\kappa^2\text{NN}'\text{N}'')]$  (**3**) resulting from double addition of  $\text{CO}_2$  and  $\text{CH}_3\text{OH}$  to terminal sulfur of  $\text{pdt}$  and a carbonyl carbon of **3a**, respectively, followed by esterification of the resultant  $[\text{Ru}(\text{CO})(\text{C}(\text{O})\text{OCH}_3)(\text{SC}(\text{Ph})\text{C}(\text{Ph})(\text{SC}(\text{O})\text{OH})(\text{trpy}-\kappa^2\text{NN}'\text{N}'')]$  in  $\text{CH}_3\text{OH}$ . The addition of  $\text{CO}_2$  to sulfur of **3a** is ascribed to the strong basicity and weak chelating ability of  $\text{pdt}$  compared with those of  $\text{mnt}$  and  $\text{tdt}$ . A series of  $[\text{RuX}(\text{dithiolene})(\text{trpy})]^{n+}$  ( $\text{X} = \text{dmsO}, \text{Cl}, \text{OSO}_2\text{CF}_3; n = 0, 1$ ) were also prepared.



### VII-E-5 Syntheses of New Ruthenium Carbonyl Terpyridine *o*-Phenylene Complexes: Strong Interaction Between Carbonyl and *o*-Phenylene Ligands

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[*J. Organomet. Chem.* **622**, 280 (2001)]

Ruthenium carbonyl *o*-phenylene complexes, Ru(CO)(3,6-Bu<sub>2</sub>seq)(trpy)]PF<sub>6</sub> (**1**)]PF<sub>6</sub>) and [Ru(CO)(*o*-monothioat)(trpy)] (**2**), were prepared by the reaction of [Ru(CO)Cl<sub>2</sub>(trpy)] with the corresponding *o*-phenylenes in 2-methoxyethanol. X-ray crystallographic study of **1**]BF<sub>4</sub> indicated that the ruthenium center is coordinated by carbonyl, three nitrogens of trpy and two oxygens of 3,6-Bu<sub>2</sub>seq. ESR of **1**]PF<sub>6</sub> and **2** indicated that the electronic structures of ruthenium-*o*-phenylene unit of the complexes have Ru(II)-3,6-Bu<sub>2</sub>seq and Ru(II)-*o*-monothioat forms, respectively. Significant differences in the redox behavior and the spectroscopical properties between **1**]PF<sub>6</sub> and **2** and [RuCl(3,5-Bu<sub>2</sub>seq)(trpy)] were ascribed to the strong interaction between *o*-phenylene and carbonyl ligands through Ru(II).

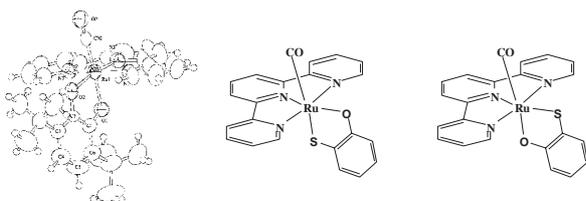


Figure 1. X-ray analysis of [Ru(CO)(*o*-monothioat)(trpy)]<sup>+</sup>.

### VII-E-6 Structural and Spectroscopic Characterization of Ruthenium(II) Complexes with Methyl, Formyl and Acetyl Groups as Model Species in Multi-Step CO<sub>2</sub> Reduction

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[*J. Organomet. Chem.* **619**, 299 (2001)]

The molecular structures of Ru(II) complexes with methyl, formyl and acetyl groups [Ru(bpy)<sub>2</sub>(CO)L]<sup>+</sup> (L = CH<sub>3</sub>, C(O)H and C(O)CH<sub>3</sub>) were examined from the view point of active species in multi-step reduction of CO<sub>2</sub> on Ru. The methyl complex was prepared by the reaction of [Ru(bpy)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>]<sup>2+</sup> with trimethylsilyl acetylene and fully characterized by infrared, Raman, <sup>13</sup>C NMR and single-crystal X-ray crystallography. Disorder of the Ru–CO and Ru–C(O)H bonds in the crystal structure of the formyl complex made it difficult to determine the bond parameters of the two groups accurately, but the molecular structure of the analogous acetyl complex, which was obtained by the reaction of [Ru(bpy)<sub>2</sub>(CO<sub>3</sub>)] with propiolic acid, was determined by X-ray analysis. The ruthenium–carbonyl (Ru–C–O) bond angles of the methyl and acetyl complex with 174(1) and 175.5(5)°, respectively, are in the ranges of

those of previously characterized [Ru(bpy)<sub>2</sub>(CO)L]<sup>n+</sup> (L = CO<sub>2</sub>, C(O)OH, CO and CH<sub>2</sub>OH). On the other hand, the Ru–CH<sub>3</sub> and Ru–C(O)CH<sub>3</sub> bond distances showed unusual relationship against the stretching frequency in the raman spectra.

