VII-E Reductive Activation of Carbon Monoxide derived from Carbon Dioxide and Oxidative Activation of Hydroxy- and Oxo-Groups Derived from Water

An electrophilic attack of CO_2 to coordinatively unsaturated low valent metal complexes affords M-η^1-CO_2 complexes, which are easily converted to M-CO ones in both protic and aprotic media. Accordingly, organic synthesis through M-CO complexes derived from CO_2 is highly desired from the development of a new C1 resources. A major problem of the reduction of CO_2 using homogeneous catalysis is reductive cleavages of M-CO bonds under reductive conditions. Because of accumulation of too many electrons in the central metals. Ligand localized redox reactions rather than metal centered ones as electron sources would avoid unfavorable CO evolution in the reduction of CO_2. A flexible ligand which has an ability to change the bonding modes among monodentate, bidentate and bridging form to connect metals and carbonyl carbon of M-CO bonds would meet the requirements of smooth M-η^1-CO_2 formation and depression of reductive cleavage of M-CO bond under reduictive conditions.

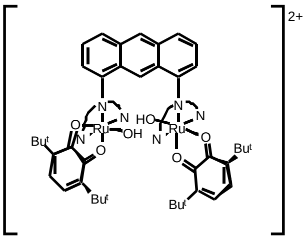
Acids or bases generated in industrial process are not utilized as resources and just wasted after neutralization. Proton gradient (Δp) between inside and outside of a cell is depicted as the sum of electric activity ($\Delta\psi$) and chemical activity (ΔpH) components. $\Delta \mathrm{p} = \Delta\psi - Z\Delta\mathrm{pH}$ ($Z = 2.303RT/F$) Proton gradient is equivalent to the neutralization energy because the neutralization reaction takes place to form water if the separating membrane is removed. Thus, neutralization energy results from the formation of water. Biological system effectively creates and consumes neutralization energy in various reactions. Acids and bases, therefore, have potential energy sources, which are provided by chemical bondings (chemical energy). Along this line, we tried to convert the neutral energy to electronic energy by using ruthenium-aqua complexes.

VII-E-1 Oxidation of Hydrocarbon by Mono- and Dinuclear Ruthenium Quinone Complexes via Hydrogen Atom Abstraction

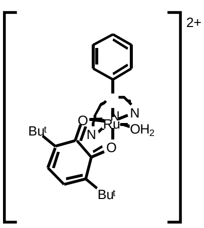
WADA, Tohru; TSUGE, Kiyoshi; TANAKA, Koji

[*Chem. Lett.* 910 (2000)]

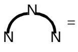
Deprotonation and two-electron oxidation of dinuclear $[\mathrm{Ru^{II}}_2(\mathrm{OH})_2(3,6\text{-}\mathrm{Bu^t}_2\mathrm{Q})_2(\mathrm{btpyan})]^{2+}$ ($\mathrm{Bu^t}_2\mathrm{Q}$ = 3,6-di(*tert*-butyl)-1,2-quinone, btpyan = 1,8-bis-(2,2':6',2"-terpyridyl)anthracene, $[\mathbf{1}]^{2+}$) was converted to bis(ruthenium-oxo) complex $[\mathrm{Ru^{II}}_2(\mathrm{O})_2(3,6\text{-}\ \mathrm{Bu^t}_2\mathrm{Q})_2(\mathrm{btpyan})]^{2+}$, which oxidized 1,3-cychrohexadiene, 1,2-dihydronaphtalene to corresponding aromatics in higher yields (90%, 94%) in the presence of $AgClO_4$ and $\mathrm{Bu^tOK}$. An analogous mononuclear $[\mathrm{Ru^{II}}(\mathrm{OH_2})(3,6\text{-}\mathrm{Bu^t}_2\mathrm{Q})(\mathrm{Ph\text{-}terpy})]^{2+}$ (Ph-terpy = 4'-phenyl-2,2':6',2"-terpyridine, $[\mathbf{2}]^{2+}$) was converted to the ruthenium-hydroxo complex $[\mathrm{Ru^{II}}(\mathrm{OH})(3,6\text{-}\mathrm{Bu^t}_2\mathrm{Q})(\mathrm{Ph\text{-}terpy})]^{2+}$ under similar condoitions, but displayed the low activity for the oxidation compared with the dinuclear complex $[\mathbf{1}]^{2+}$. On the other hand, 9,10-dihydroanthracene was converted to anthracene by $[\mathbf{2}]^{2+}$ in 42% yield, while it was not oxidized by $[\mathbf{1}]^2$ due to the steric hindrance.



$[\mathbf{1}]^{2+}$



$[\mathbf{2}]^{2+}$



= 2,2':6',2"-terpyridine

VII-E-2 Electrochemical Water-Oxidation to Dioxygen Catalyzed by Oxidized Form of Bis(ruthenium-hydroxo) Complex in H_2O

WADA, Tohru; TSUGE, Kiyoshi; TANAKA, Koji

[*Angew. Chem., Int. Ed. Engl.* **39**, 1479 (2000)]

Much attention has been paid to oxidation of water to dioxygen by homogeneous catalysts. Of particular interest are di- and tetranuclear complex derived from transition metals, since extended X-ray absorption fine structure studies indicated that the O_2-evolving center (OEC) in Photosystem II is composed of a tetranuclear Mn cluster with di-μ-oxo dimeric Mn units. The cyclic voltammetry of $[\mathrm{Ru(OH)(Q)Ru(OH)(Q)}]^{2+}$ showed two redox couples at $E_{1/2}$ = 0.43 V and 0.35 V in MeOH. After $[\mathrm{Ru(OH)(Q)Ru(OH)(Q)}]^{2+}$ was converted to $[\mathrm{Ru(O)(SQ)Ru(O)(SQ)}]^0$ by an addition of 2.0 equiv of *t*BuOK to the MeOH solution, the redox process of the resultant oxo complex displayed also two nearly reversible redox couples at $E_{1/2}$ = 0.40 V and 0.30 V (eq. 1).

$$
\begin{aligned}
&[\mathrm{Ru(Q)(O)Ru(Q)(O)}]^{2+}\\
&\qquad \underset{0.40\ \mathrm{V}}{\overset{e^-}{\rightleftharpoons}} [\mathrm{Ru(Q)(O)Ru(SQ)(O)}]^{+}\\
&\qquad \underset{0.30\ \mathrm{V}}{\overset{e^-}{\rightleftharpoons}} [\mathrm{Ru(SQ)(O)Ru(SQ)(O)}]^{0} \qquad (1)
\end{aligned}
$$

The complex on ITO electrode exhibited a broad redox couple centered at +0.40 V (*vs.* Ag/AgCl), and an irreversible anodic wave at +1.20 V, which is associated with two-electron oxidations of $[\mathrm{Ru(OH)(Q)Ru(OH)(Q)}]^{2+}$ and $[\mathrm{Ru(O)(Q)Ru(O)(Q)}]^{2+}$ affording $[\mathrm{Ru(OH)(Q)Ru(OH)(Q)}]^{4+}$ and $[\mathrm{Ru(O)(Q)Ru(O)(Q)}]^{4+}$, respectively. A strong anodic current at potential more positive than +1.5 V is apparently caused by the oxidation of water to dioxygen. Indeed, when controlled-potential electrolysis of the bis(ruthenium-hydroxo) complex modified on ITO electrode at 1.70 V (*vs.* Ag/AgCl) in water (pH 4.0), 1.1 ml of O_2 was evolved after 20.2 C passed in the electrolysis. The current efficiency for O_2 evolution was 95% and the turnover number was 500 based on the complex. The current density of the electrode was 0.12 mA/cm^2 in the initial stage. The current gradually decreased with decrement of pH in the aqueous phase and almost stopped at pH 1.2. The current density of the electrode for the oxidation of water recovered, when the pH of water was readjusted to 4.0 by an addition of aqueous KOH to the aqueous phase. The oxidation of water by the bis(ruthenium-hydroxo) complex modified ITO finally evolved 15.0 ml of O_2 (turnover 6730), before the evolution completely stopped in 40 h.

VII-E-3 Selective Production of Acetone in Electrochemical Reduction of CO_2 Catalyzed by Ru-naphthyridine Complex

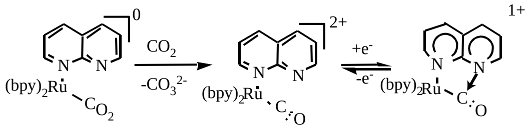
MIZUKAWA, Tetsunori; TSUGE, Kiyoshi; NAKAJIMA, Hiroshi; TANAKA, Koji

[*Angew. Chem., Int. Ed. Engl.* **111**, 373 (1999)]

Carbon dioxide is smoothly converted to CO on metals by oxide transfer from M–CO_2 to CO_2, while reductive cleavage of the resultant metal–CO bond (eq. 1) is the major problem in utilization of CO_2 as a C1 resource. Acylation of the metal–CO complexes

$$[\mathrm{M}\text{–}\eta^1\text{–}\mathrm{CO_2}]^0 \xrightarrow[-\mathrm{CO_3}^{2-}]{\mathrm{CO_2}} [\mathrm{M}\text{–}\mathrm{CO}]^{2+} \xrightarrow{2e^-} [\mathrm{M}]^0 + \mathrm{CO} \qquad (1)$$

derived from CO_2 under reductive conditions, therefore, would provide new methodologies for utilization of CO_2 as a staring material in organic synthesis. One and two-electron reductions of $[Ru(bpy)_2(napy)(CO)](PF_6)_2$ (napy = 1,8-naphthyridine-κ*N*) take place in napy localized orbitals, which induce nucleophilic attack of the free nitrogen of κ^1-napy to the carbonyl carbon (eq. 2). Electron transfer from the reduced form of napy to the CO group in the metallacycle enables reductive activation of the CO group without the metal–CO bond cleavage and gives rise to electrophilic attack of $(CH_3)_4N^+$ to the carbonyl carbon. As a result, $CH_3C(O)CH_3$ and $CO_3{}^{2-}$ were catalytically produced in the electrochemical reduction of [Ru(bpy)(napy–κ*N*)$_2$-$(CO)_2](PF_6)_2$ in the presence of in CO_2-saturated DMSO when $(CH_3)_4NBF_4$ was used as an electrolyte (eq. 3).



(2)

$$2\mathrm{CO_2} + 4e^- + 2(\mathrm{CH_3})_4\mathrm{N}^+ \rightarrow \mathrm{CH_3C(O)CH_3} + \mathrm{CO_3}^{2-} + 2(\mathrm{CH_3})_3\mathrm{N} \qquad (3)$$

VII-E-4 Energy Conversion from Proton Gradient to Electricity Based on Characteristic Redox Behavior of an Aqua Ruthenium Complex

TSUGE, Kiyoshi; KURIHARA, M.; TANAKA, Koji

[*Bull. Chem. Soc. Jpn.* **73**, 607 (2000)]

A ruthenium aqua complex with a quinone ligand $[Ru(trpy)(dbq)(H_2O)]^{2+}$ (trpy = 2,2':6,2"-terpyridine, dbq = 3,5-di-*t*-butyl-1,2-benzoquinone) $[Ru(q)(H_2O)]^{2+}$) was prepared. Its electrochemical properties and electronic absorption spectra were measured in the presence of a base in acetone. The detailed analysis of those measurements revealed that the addition of base caused not only the deprotonation but also the reduction of $[Ru(q)(H_2O)]^{2+}$. The redox reactions coupled with acid-base reactions were demonstrated from the large difference in redox properties of aqua and hydroxo complexes. Taking advantage of unique redox reactions induced by the acid-base equilibrium between aqua and hydroxo complexes, we have succeeded in construction of the first energy transducer which converts the proton gradient to electricity. A similar ruthenium aqua complex with a bipyridine ligand, [Ru(trpy)(bpy)-$(H_2O)]^{2+}$, also reversibly dissociates a proton of the aqua ligand. However, it has no ability to convert the proton gradient to electricity due to the lack of a suitable molecular orbital, which can accommodate electrons on the electron-rich hydroxo ligand.

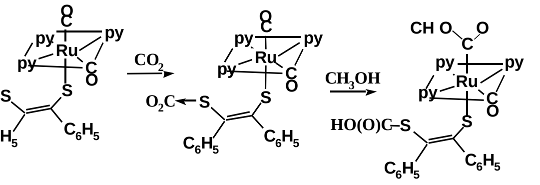
$$[\mathrm{M(Q)(H_2O)}]^{2+} + \mathrm{OH}^- \rightleftharpoons [\mathrm{M(S)(OH)}]^+ + \mathrm{H_2O} \quad (1)$$

VII-E-5 Double Addition of CO_2 and CH_3OH to Ruthenium Carbonyl Complex with Novel Mono-dentate Dithiolene

SUGIMOTO, Hideki; TSUGE, Kiyoshi; TANAKA, Koji

[*Chem. Lett.* 1007 (1999)]

The reaction of $[Ru(CO)_2Cl(terpy)]PF_6$ and Na_2mnt in CH_3OH gave a yellow complex (**1a**) with mono-dentate mnt [Ru(CO)$_2$(terpy-κ^3*N*,*N*',*N*")(mnt-κ*S*)] and with bidentate mnt [Ru(CO)$_2$(terpy-κ^2*N*,*N*')(mnt-κ^2*S*,*S*')]. On the other hand, the reaction between [Ru-$(CO)_2Cl(terpy)]^+$ and $Cs_2S_2C_2Ph_2$ in CH_3OH under aerobic conditions gave a complex (**2**) with thio-carboxylic acid and methoxy carbonyl groups rather than the expected [Ru(CO)$_2$(SSC$_2$Ph$_2$-κ^1*S*)(terpy-κ^3*N*,*N*',*N*")] (**1**). The most characteristic feature of **2** is that the carbonyl and the uncoordinate thiolate of **1** are changed to methoxy carbonyl and thio-carboxylato units, respectively. Although it is not clear that the carboxylato moiety of **2** exists as protonated or deprotonated form by X-ray analysis, the former is deduced from the elemental analysis and the charge balance of **2**. Unprecedented double addition of CO_2 and methanol to thiolate and carbonyl ligands located far from each other is apparently caused by the long-range π–π interaction between basic $Ph_2C_2SS^{2-}$ and acidic carbonyl units through d-orbitals of the rutheniurn atom.



VII-E-6 Structural and Spectroscopic Characterization of Ruthenium(II) Complexes with Methyl, Formyl and Acetyl Groups as Model Species in Multi-Step CO_2 Reduction

OOYAMA, Dai; TOMON, Takashi; TSUGE, Kiyoshi; TANAKA, Koji

The molecular structures of Ru(II) complexes with methyl, formyl and acetyl groups $[Ru(bpy)_2(CO)L]^+$ (L = CH_3, C(O)H and $C(O)CH_3$) were examined from the view point of active species in multi-step reduction of CO_2 on Ru. The methyl complex was prepared by the reaction of $[Ru(bpy)_2(OH_2)_2]^{2+}$ with trimethylsilyl acetylene and fully characterized by infrared, Raman, ^{13}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 $[Ru(bpy)_2(CO_3)]$ 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 $[Ru(bpy)_2(CO)L]^{n+}$ (L = CO_2, C(O)OH, CO and CH_2OH). On the other hand, the Ru–CH_3 and Ru–$C(O)CH_3$ bond distances showed unusual relationship against the stretching frequency in the raman spectra.

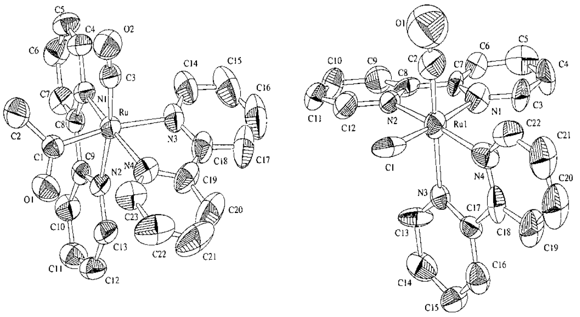


Figure 1. Molecular Structures of $[Ru(bpy)_2(CO)$-$(C(O)CH_3)]^+$ and $[Ru(bpy)_2(CO)(CH_3)]^+$.