VII-F Activation of Carbon Dioxide and Creation of Reactive Hydroxy- and Oxo-metal Complexes through Activation of Water Molecules on Metals

An electrophilic attack of CO_2 to coordinatively unsaturated low valent metal complexes produces M-η^1-CO_2 complexes, which can be smoothly converted to M-CO ones. Metal complexes with a chelate ring that smoothly opens and closes depending on reaction conditions must be suitable for generation of M-η^1-CO_2 complexes by considering thermal lability of coordinatively unsaturated low valent metal complexes. A major problem of multi-electron reduction of CO_2 in homogeneous reactions is predominant cleavages of metal-CO bonds derived from CO_2 under reductive conditions, because accumulation of too many electrons in the central metals causes reductive cleavage of M-CO bonds. Electro- and photochemical reduction of CO_2 by using ligand localized redox reactions, therefore, may afford a new methodology for multi-electron reduction of CO_2.

The 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. $\Delta p = \Delta\psi - Z\Delta\mathrm{pH}$ ($Z = 2.303\ RT/F$) Proton gradient is equivalent to the neutralization energy because the neutralization reaction takes place if the separating membrane is removed. Biological system creates various valuable energies from the neutralization. Although acids or bases generated in industrial process are just wasted as thermal energy, neutralization energy is originated from the binding energy of acid and base, which is able to be converted directly to chemical energy. Along this line, we tried to convert the neutral energy to electronic energy by using ruthenium-aqua complexes.

VII-F-1 Stabilization of $[Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)]$ and Unprecedented Reversible Oxide Transfer Reactions from CO_3^{2-} to $[Ru(bpy)_2(CO)_2]^{2+}$ and from $[Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)]$ to CO_2

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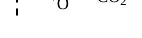
[*J. Organomet. Chem.* **561**, 61 (1998)]

Metal complexes with an η^1-CO_2 group, which is formed by overlap of the filled dz^2 orbital of d^8 metals and the empty CO_2 π^* orbital, are generally extremely labile to air, moisture and temperature. Unusual thermal stability of $[Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)]$ (**1**) as a metal-η^1-CO_2 complex was examined both in the solid state and in solutions. $LiCF_3SO_3$ assists solubilization of **1** in CH_3CN due to the interaction between Li^+ and the η^1-CO_2 group. Electron flow from Ru to the CO_2 ligand induced by Li^+ also largely stabilizes the Ru-CO_2 bond. Oxide transfer from $[Crown{\cdot}K]_2CO_3$ to $[Ru(bpy)_2(CO)_2](PF_6)_2$ smoothly took place in dry CH_3CN to afford **1** through the 1 : 1 adduct with the RuC(O)-OCO_2 moiety. On the other hand, Li^+ caused the oxide transfer from **1** to CO_2 giving $[Ru(bpy)_2(CO)_2]^{2+}$ and CO_3^{2-} due to insolubility of the Li_2CO_3 in organic solvents. Unprecedented reversible oxide transfer from **1** to CO_2 and from CO_3^{2-} to $[Ru(bpy)_2(CO)_2]^{2+}$ proceeds via their 1 : 1 adduct, which was confirmed by the NMR spectra.



VII-F-2 First Artificial Energy Conversion from Proton Gradient to Electricity

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[*Chem. Lett.* 1069 (1998)]

Metal-aqua, -hydroxy and -oxo complexes are expected to exist as equilibrium mixtures depending on proton concentrations in solutions (eq 1) when dimerization and

$$[M(H_2O)]^{2+} \rightleftarrows [M(OH)]^+ \rightleftarrows [M(O)] \qquad (1)$$

oligomerization of these complexes can be effectively depressed. Electron withdrawing ligands will decrease nucleophilicity of the terminal hydroxy and oxo groups, which would serve to depress the formation of μ-OH and μ-O bridged oligomers. We, therefore, introduce redox active quinone ligands to stabilize the aqua, hydroxy and oxo complexes to accommodate extra electrons generated deprotonation of the aqua and hydroxy ligands. As a result, the redox potentials of the complexes reversibly change depending on pH in solutions. The cyclic voltammogram (CV) of $[Ru(trpy)\text{-}(3,5\text{-di-tert-butylquinone})(H_2O)]^{2+}$ ($[Ru\text{-}H_2O]^{2+}$) in acetone showed two reversible redox couples at $E_{1/2} = -0.47$ V and $E_{1/2} = 0.38$ V ($E_{1/2} = (E_{pc} + E_{pa})/2$) assigned to the $[Ru\text{-}H_2O]^{0/+}$ and $[Ru\text{-}H_2O]^{+/2+}$ couples, respectively. When 0.7 equiv of OH^- was added to the solution, the rest potential of the solution (V_{rest}) shifted from 0.60 V to 0.30 V across the $E_{1/2}$ of the $[Ru\text{-}H_2O]^{+/2+}$ couple, and new redox couples appeared at $E_{1/2} = -0.80$ V and 0.00 V assignable to the $[Ru\text{-}OH]^{0/+}$ and $[Ru\text{-}OH]^{+/2+}$ couples (eq 2, 3).

$$[Ru\text{-}H_2O]^{2+} + OH^- \rightarrow [Ru\text{-}OH]^+ + H_2O \qquad (2)$$

$$[Ru\text{-}H_2O]^{2+} + [Ru\text{-}OH]^+ \rightarrow [Ru\text{-}H_2O]^+ + [Ru\text{-}OH]^{2+} \qquad (3)$$

Further addition of OH^- caused deprotonation of $[Ru\text{-}OH]^{2+}$ to produce [Ru-O] (eq 4), which equilibrates with the reactant (eq 5).

$$[Ru\text{-}OH]^{2+} + OH^- \rightarrow [Ru\text{-}O]^+ + H_2O \qquad (4)$$

$$[Ru\text{-}OH]^{2+} + [Ru\text{-}O]^+ \rightarrow [Ru\text{-}OH]^+ + [Ru\text{-}O]^{2+} \qquad (5)$$

The energy conversion was conducted with two compartment cells (I and II) separated by an anion exchange membrane filled with an acetone solution of $[Ru\text{-}H_2O]^{2+}$ (7.0 μmol/15 ml in each cell). Upon an addition of 1.6 equivalent of OH^- to cell(I), $[Ru\text{-}H_2O]^+$ and $[Ru\text{-}OH]^+$ formed and Vrest shifted from 0.60 V to –0.13 V (eqs 2-5). The connection of two cells induced current flow from the cell(II) to cell(I). At the end of the discharge (12 hr later), Vrest of two cells were 0.33 ±

0.02 V, and 0.50 C of electricity was obtained. Thus the proton gradient is catalytically converted to electricity by ruthenium aqua complex $[\mathrm{Ru(trpy)(3,5\text{-}di\text{-}tert\text{-}butylquinone)(H_2O)}]^{2+}$.

VII-F-3 Two-Electron Reduction of $[\{(bpy)_2Ru(dmbbbpy)\}_3Ru]^{8+}$ from $(BNA)_2$ via Photoinduced Electron Transfer [dmbbbpy = 2,2'-Bis-(*N*-Methylbenzimidazole-2-yl)-4,4'-bipyridine]

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[*Inorg. Chem.* **37**, 6176 (1998)]

Photoirradiation (λ > 500 nm) of $[\{(bpy)_2Ru(dmbbbpy)\}_3Ru]^{8+}$ ($\mathbf{1}^{8+}$) (dmbbbpy = 2,2'-Bis(*N*-methylbenzimidazole-2-yl)-4,4'-bipyridine and bpy = 2,2'-bipyridine) in the presence of dimeric *N*-benzyl-dihydronicotinamide, $(BNA)_2$ produced stable two-electron reduced species ($\mathbf{1}^{6+}$). Laser flash photolysis and emission spectroscopy were used to understand the reductive reaction pathways. The emission quenching k_q value (4.1×10^9 $M^{-1}s^{-1}$) obtained from Stern-Volmer plot is in excellent agreement with the electron transfer rate constant, k_{et} (4.7×10^9 $M^{-1}s^{-1}$) determined from the decay kinetics of transient $^3\mathbf{1}^{8+}$ triplet-triplet absorption at 650 nm indicating that photoreduction of $\mathbf{1}^{8+}$ proceeds via photoinduced electron transfer from $(BNA)_2$ to $^3\mathbf{1}^{8+}{}^*$. After bimolecular electron transfer process, $\mathbf{1}^{8+}$ was reduced to $\mathbf{1}^{7+}$ and electron donor $(BNA)_2$ was oxidized. Oxidation of $(BNA)_2$ leads to the formation of highly reactive species, BNA• which then reduces $\mathbf{1}^{7+}$ to $\mathbf{1}^{6+}$. The quantum yield for the formation of the photo-reduction product was 0.026.

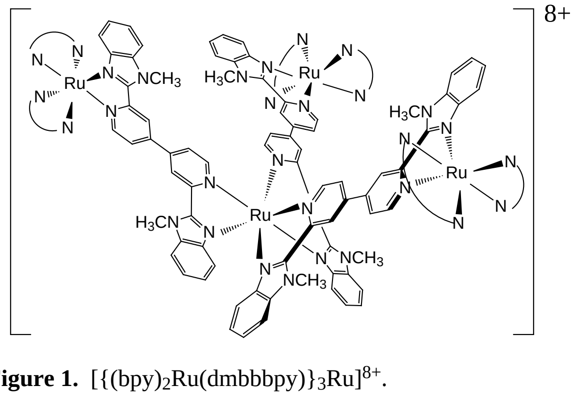

Figure 1. $[\{(bpy)_2Ru(dmbbbpy)\}_3Ru]^{8+}$.

VII-F-4 Selective Production of Acetone in Electrochemical Reduction of CO_2 Catalyzed by Ru-naphthyridine Complex

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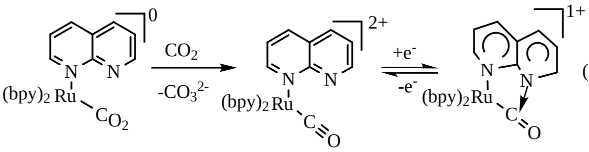
[*Angew. Chem., Int. Ed. Engl.* **111**, 373 (1999)]

Carbon dioxide is smoothly converted to CO on metals by oxide transfer from $M\text{-}CO_2$ 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

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

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 $[\mathrm{Ru(bpy)_2(napy)(CO)}](\mathrm{PF_6})_2$ (napy = 1,8-naphthyridine-κN) take place in napy localized orbitals, which induce nucleophilic attack of the free nitrogen of napy to the carbonyl carbon (eq2). 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 $[\mathrm{Ru(bpy)(napy\text{-}\kappa N)_2(CO)_2}](\mathrm{PF_6})_2$ in the presence of in CO_2-saturated DMSO when $(CH_3)_4NBF_4$ was used as an electrolyte (eq 3).



(2)

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

VII-F-5 Basicity of μ_3-X and η^1-Y Ligands (X, Y = S, Se) of Reduced, Oxidized and Super-Oxidized Forms of $[Fe_4X_4(YAd)_4]^{2-}$ (Ad = 1-Adamantane) in Aqueous Solutions

NAKAMOTO, Masami; FUKAISHI, Kenji; TAGATA, Tsuyoshi; KAMBAYASHI, Hide; TANAKA, Koji

[*Bull. Chem. Soc. Jpn.* **72**, 407 (1999)]

Synthetic 4Fe4S clusters are subject to hydrolysis under aqueous conditions. A series of $[\mathrm{Fe_4X_4(YAd)_4}]^{2-}$ (X, Y= S, Se; Ad= 1-adamantane) solubilized in aqueous poly[2-dimethylamino(hexanamide)] (PDAH) solutions were stable due to the enbedding effect in hydrophobic environment and inhibition of dissociation of the terminal ligand into the aqueous media. Cyclic voltammetry of the clusters in the solutions showed pH dependent redox potentials of not only $[\mathrm{Fe_4X_4}]^{+/2+}$ but also $[\mathrm{Fe_4X_4}]^{2+/3+}$ (X, Y = S and Se) couples, resulting from redox-linked protonation reactions of the three oxidation states of $[\mathrm{Fe_4X_4(YAd)_4}]^{n-}$ (n = 1–3), which enabled to determine the pK of each oxidation state. Computer simulation of the pH dependent redox potentials indicated the basicity of the μ_3-X cores (X = S and Se) of $[\mathrm{Fe_4X_4(YAd)_4}]^{n-}$ (n = 1, 2, 3) is stronger than the YAd (Y = S and Se) ligands. In the case of the mono-protonated $[\mathrm{Fe_4X_4(YAd)_4}]^{3-}(\mathrm{H}^+)$ and $[\mathrm{Fe_4X_4(YAd)_4}]^{2-}(\mathrm{H}^+)$, thre basicity of the η^1-Y ligand of $[\mathrm{Fe_4X_4(YAd)_4}]^{2-}(\mathrm{H}^+)$ becomes stronger than that of μ_3-X cores. On the other hand, the μ_3-X of $[\mathrm{Fe_4X_4(YAd)_4}]^{3-}$-$(\mathrm{H}^+)$ still show strong basicity compared with those of η^1-Y ligands.

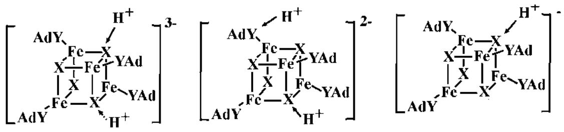


Figure 1. Protonation of $[Fe_4X_4(YAd)_4]^{n-}$ (X,Y = S, Se: *n* = 2, 1, 0) in aqueous PDAH solutions: dotted arrow is estimated by computer simulation.

VII-F-6 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.* in press.]

The reaction of $[Ru(CO)_2Cl(terpy)]PF_6$ and Na_2mnt in CH_3OH gave a yellow complex (**1**) with monodentate mnt. 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 thiocarboxylic acid and methoxy carbonyl groups rather than the expected $[Ru(CO)_2(SSC_2Ph_2\text{-}\kappa^1S)(terpy\text{-}\kappa^3N,N',N'')]$. 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.