

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Electrochemical/Photochemical CO₂ Reduction Catalyzed by Transition Metal Complexes

Hitoshi Ishida

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/intechopen.75199>

Abstract

Conversion of CO₂ into useful chemicals is attractive as a solution of the fossil fuel shortage and the global warming problems. Reduction of CO₂ into carbon monoxide (CO) and formic acid (HCOOH) is also important for obtaining the materials in organic syntheses. There are a lot of studies on the catalysts for electrochemical/photochemical CO₂ reduction. Especially, transition metal complexes have actively researched as the molecular catalysts for CO₂ reduction. In this chapter, the electrochemical/photochemical CO₂ reduction catalyzed by *cis*-[Ru(bpy)₂(CO)₂]²⁺ (bpy: 2,2'-bipyridine) and *trans*(Cl)-[Ru(bpy)(CO)₂Cl₂] is described as a representative example.

Keywords: CO₂ reduction, artificial photosynthesis, electrochemistry, photochemistry, ruthenium

1. Introduction

Utilization of CO₂ becomes more and more important with increasing CO₂ emission which causes the global warming and the ocean acidification problems [1, 2]. The huge CO₂ emission also relates on depletion of fossil fuels. The conversion of CO₂ into useful fuels and chemicals is very urgent to solve the abovementioned problems. The use of biomass instead of fossil fuels is actively researched and partly undertaken [3]. In many chemical laboratories, fixation of CO₂ into organic compounds by organometallic catalysts is vigorously studied [4].

Reduction of CO₂ with electrons is an attractive chemical conversion to obtain the useful products for fuels and chemical materials. It is so simple that it can be applied to photocatalyses which supply electrons from electron donors such as water. The equilibrium potentials (E⁰ V vs. SHE

at pH 7) for CO₂ reduction are listed in **Figure 1** [5, 6]; they are thermodynamic values and tend to positively shift with increasing the numbers of electrons participated. One-electron reduction of CO₂ requires very high energy. Furthermore, the product, CO₂ anion radical (CO₂^{•-}), is difficult to give useful organic chemicals because it is a very strong reducing reagent to reduce other molecules and recover CO₂. Thus, the CO₂ reductions with multielectrons are desired; however, their reactions are generally difficult even in the electrochemical reduction. A reason is that the intermediates would release from the surface of the electrode as the products before accepting further electrons. To achieve CO₂ reduction with more than two electrons, the catalysts which allow to lower the activation energies are required. In other words, the catalysts can undergo the CO₂ reduction at the potentials closed to the equilibrium ones. The two-electron reduction of CO₂ produces carbon monoxide (CO) and formic acid (HCOOH). The equilibrium potentials are more negative than the proton reduction to afford H₂. Therefore, the catalysts which can selectively reduce CO₂ rather than H⁺ are also desired. Both CO and HCOOH are useful chemicals: CO can be converted into liquid hydrocarbons by using the Fischer-Tropsch reaction [7], and HCOOH which can be readily converted to H₂ is a safe storage material for H₂ [8].

A lot of metal complexes have been researched for the CO₂ reduction catalyses [9–16]. Until now, the metal complexes of Mn [17–19], Fe [20, 21], Co [22–24], Ni [24–28], Cu [29], Mo [30], Ru [31–64], Rh [65, 66], Pd [67, 68], W [30], Re [69–76], Os [77, 78], Ir [65, 66, 79, 80] have been reported as the catalysts for CO₂ reduction. **Figure 2A** shows the elements of the metal complexes acting as the electrochemical CO₂ reduction catalysts. The metal complexes indicated in red include the catalysts for photochemical reduction. **Figure 2B** shows the examples of the metal complexes as the CO₂ reduction catalysts. These catalysts based on metal complexes are sometimes called as “molecular catalysts” because they can be designed on the molecular levels by selecting the metal elements and the ligands. The representative and efficient catalysts for CO₂ reduction are nickel(II) cyclam (cyclam: 1,4,8,11-tetraazacyclotetradecane),

				$E^{0'}$	
CO_2	+	e^-	\longrightarrow	$\text{CO}_2^{\cdot-}$	-1.90 V
CO_2	+	$2 \text{ H}^+ + 2 \text{ e}^-$	\longrightarrow	HCOOH	-0.61 V
CO_2	+	$2 \text{ H}^+ + 2 \text{ e}^-$	\longrightarrow	$\text{CO} + \text{H}_2\text{O}$	-0.52 V
CO_2	+	$4 \text{ H}^+ + 4 \text{ e}^-$	\longrightarrow	$\text{HCHO} + \text{H}_2\text{O}$	-0.48 V
CO_2	+	$6 \text{ H}^+ + 6 \text{ e}^-$	\longrightarrow	$\text{CH}_3\text{OH} + \text{H}_2\text{O}$	-0.38 V
CO_2	+	$8 \text{ H}^+ + 8 \text{ e}^-$	\longrightarrow	$\text{CH}_4 + 2\text{H}_2\text{O}$	-0.24 V
<hr/>					
2 H^+	+	2 e^-	\longrightarrow	H_2	-0.41 V

Figure 1. Equilibrium potentials for CO₂ reduction (*E*^{0'} V vs. SHE (pH 7)).

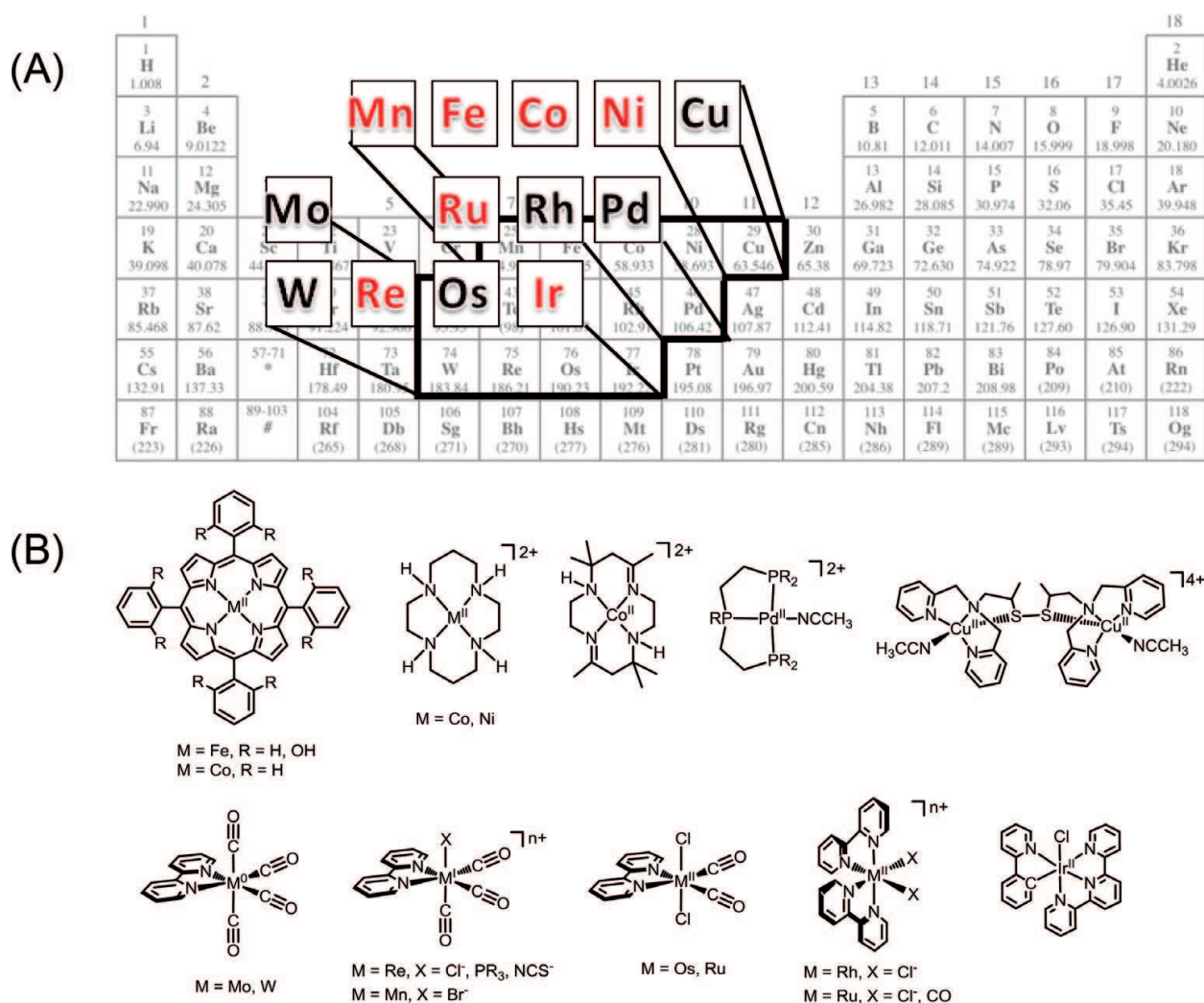


Figure 2. Metal complexes reported as CO₂ reduction catalysts: (A) the metal elements in the complexes (the elements in the metal complexes for photocatalyses are indicated in red) and (B) the molecular structures.

ruthenium(II) polypyridyl carbonyl complexes and rhenium(I) bipyridyl tricarbonyl complexes. Recently, the complexes with nonprecious metals such as manganese(II) and iron(II) attract much attention. They are abundant and readily available, while they are less durable and efficient as the disadvantageous points.

In this chapter, the electrochemical CO₂ reduction catalyzed by the ruthenium complexes as the examples is described. The reduction products are CO and formic acid, while the nickel and rhenium complexes selectively yield CO. Discussion for the catalytic mechanisms is introduced particularly for the factors determining the product selectivity. In the next section, the photocatalytic CO₂ reduction assisting by the photosensitizers is described. The reaction procedures, the principles for selecting the photosensitizers and the electron donors, and the photocatalytic mechanisms are summarized. Furthermore, application of the homogeneous catalytic systems to heterogeneous catalyses, which is practically advantageous in the viewpoints of separation of the catalysts from the reactants and the products, is described. In the final section, the artificial photosynthetic systems, which would be realized by utilizing the molecular catalysts, are prospected.

2. Electrochemical CO₂ reduction

The representative molecular catalysts based on ruthenium complexes are *cis*-[Ru(bpy)₂(CO)₂]²⁺ (bpy: 2,2'-bipyridine), *trans*(Cl)-[Ru(bpy)(CO)₂Cl₂] and the derivatives (**Figure 3**). They have the bipyridyl ligand which would act as an electron reservoir. The efficient catalysts have the carbonyl ligand, which would draw electrons. It tends to lower the reduction potentials of the metal complexes as well as to lower the overpotentials for the CO₂ reduction.

2.1. Electrochemical analysis

Electrochemical analyses (e.g., cyclic voltammetric measurements) are recommended to know the electrochemical properties of the molecular catalysts. The analyses do not only teach us the reduction potentials of the metal complexes but also show whether the complexes can react with CO₂ or not. **Figure 4** shows the cyclic voltammograms (CVs) of *cis*-[Ru(bpy)₂(CO)₂]²⁺ in CH₃CN or CH₃CN/H₂O (9:1). The Ag-Ag⁺ (CH₃CN) reference electrode (0.10 M Tetrabutylammonium perchlorate (TBAP) / 0.01 M AgNO₃ in CH₃CN) is used; the potential (0.00 V vs. Ag/AgNO₃ (CH₃CN)) corresponds to -0.09 V vs. Fc/Fc⁺ in CH₃CN. The CV of *cis*-[Ru(bpy)₂(CO)₂]²⁺ in CH₃CN under Ar shows an irreversible reduction wave at -1.3 V vs. Ag-Ag⁺ (CH₃CN) as shown in **Figure 4** (black line). The irreversible reduction suggests that the one-electron reduction accompanies with a chemical reaction followed by further one-electron reduction. Such a reaction mechanism is called as electrochemical-chemical-electrochemical (ECE) one. The CV under CO₂ is a little different from that under Ar, suggesting that the reduced species react with CO₂ (**Figure 4**, blue line). In CH₃CN/H₂O (9:1), the CV exhibits a strong cathodic current under CO₂ (**Figure 4**, red line), which corresponds to the catalytic reduction of CO₂ in the presence of a proton source such as water. The catalytic reduction currents can be analyzed to estimate the efficiency of the catalyst [20, 81]; however, it should be noted that the cathodic currents do not always exhibit the catalytic CO₂ reduction [82]. The electrolyses of the metal complexes under CO₂ should be carried out to confirm the catalytic efficiency.

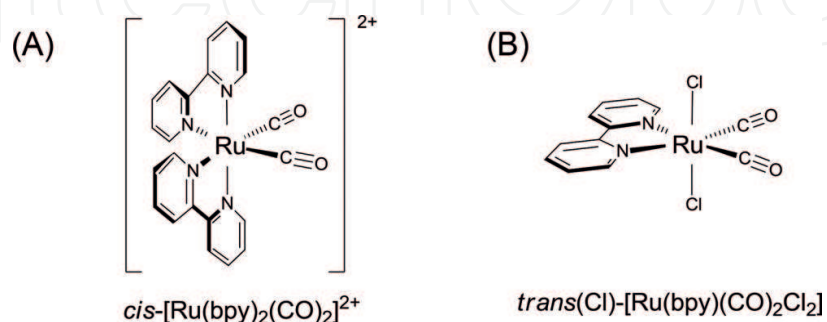


Figure 3. Ruthenium-bipyridyl complexes as electrochemical CO₂ reduction catalysts: (A) *cis*-[Ru(bpy)₂(CO)₂]²⁺ and (B) *trans*(Cl)-[Ru(bpy)(CO)₂Cl₂].

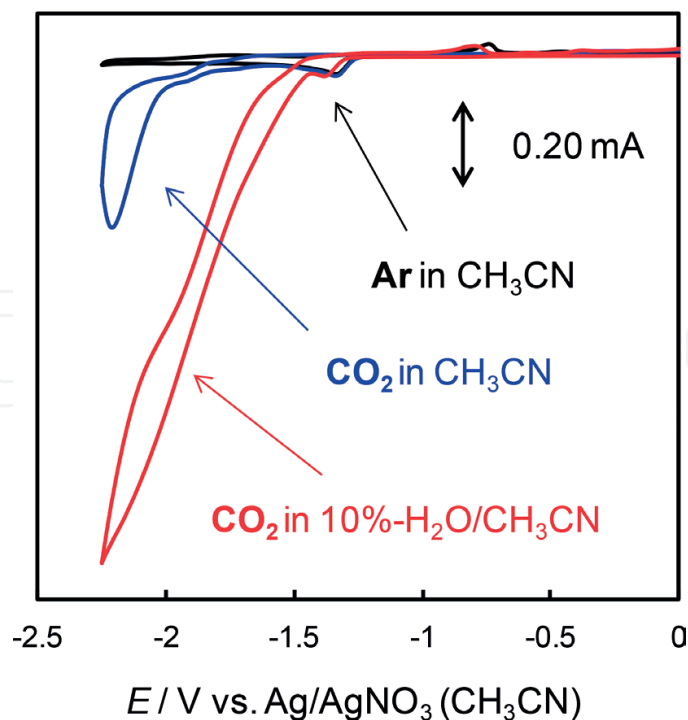


Figure 4. Cyclic voltammograms of *cis*-[Ru(bpy)₂(CO)₂](PF₆)₂: In Ar (black) or CO₂-saturated CH₃CN (blue) or in CO₂-saturated CH₃CN/H₂O (9:1) (red) containing NBu₄ClO₄ (0.10 M).

2.2. Electrolysis

A typical electrolysis cell is shown in **Figure 5**. The cell for reduction (the side of the working electrode) is separated from the cell for oxidation (the counter electrode) with a membrane such as Nafion. A glassy carbon or a Pt plate is used for the electrodes. The metal complex is dissolved in the reaction solution and acts as the homogenous catalyst. CO₂ is bubbled

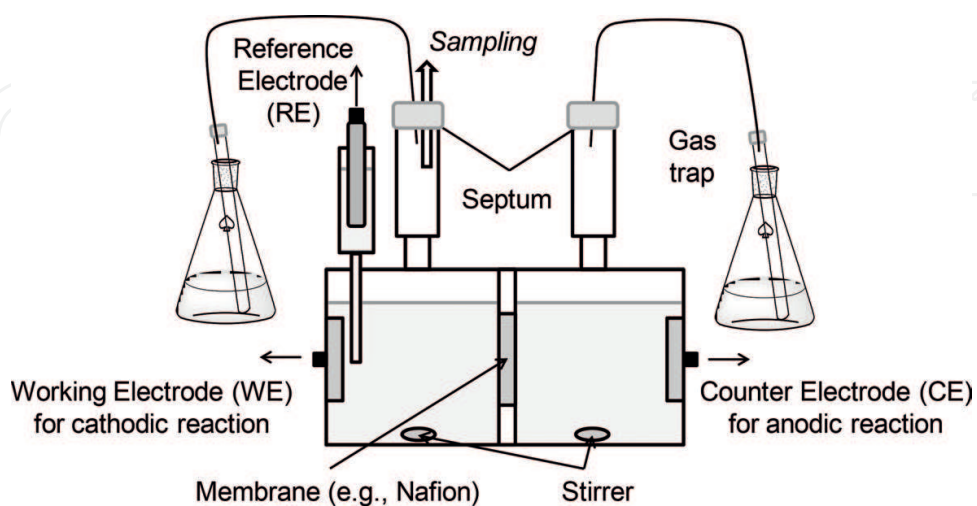


Figure 5. Electrolysis cell for electrochemical CO₂ reduction.

with a needle through the septum before electrolysis. Electrochemical CO_2 is carried out in batch mode. Reduction of CO_2 occurs on the working electrode at the electrochemical cell. Sampling of the gaseous and liquid phases is performed by a syringe through the septum. The gaseous products (CO and H_2) are analyzed by gas chromatography. The liquid product, HCOOH , is analyzed by electrophoresis, ion chromatography or gas chromatography. The electrolysis is carried out by the controlled potential method, where the potential is determined from the electrochemical analysis (e.g., CVs). The chronopotentiometry, in which the current is constant during the electrolysis, is important for the industrial use. However, the results in the constant potential lead to elucidate the catalyses because the electrolysis potential relates on the catalytic species. Thus, almost all the scientific researches adopt the controlled potential electrolyses.

2.3. Electrocatalytic CO_2 reduction by $\text{cis-}[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$

The ruthenium complexes are used as the homogeneous catalysts by dissolving in the reaction solution. The electrolysis of the CO_2 -saturated $\text{H}_2\text{O}/\text{DMF}$ (1:1) solution of $\text{cis-}[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ was carried out at -1.50 V vs. SCE with an Hg pool as the working electrode (**Figure 6**) [62]. The catalyst could selectively reduce CO_2 to afford CO and HCOOH , while H_2 , the reduction product of water, scarcely evolved. As the reaction proceeded, the speed for CO production got slow, but HCOOH production became fast. It was interpreted as the result of the decreasing the proton concentration ($[\text{H}^+]$) in the reaction solution by consumption of the proton during the reduction. Actually, the reactions in the buffered solution with $\text{H}_3\text{PO}_4\text{-NaOH}$ exhibited that the production speeds of the CO_2 reduction were unchanged during the reactions. It was the decisive result that HCOOH selectively produced when phenol with the high pK_a (ca. 9.95) was used as the proton source. These results suggest that there is an acid-base equilibrium between two intermediates in which one is for CO production and another for HCOOH .

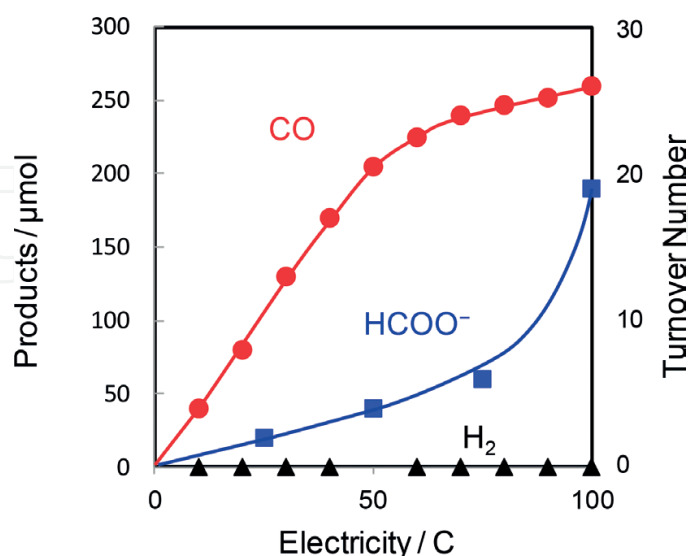


Figure 6. Plots of the amounts of products vs. the electricity in the electrolysis (-1.50 V vs. SCE) of CO_2 -saturated $\text{H}_2\text{O}/\text{DMF}$ (1:1 v/v) solution containing $\text{cis-}[\text{Ru}(\text{bpy})_2(\text{CO})_2](\text{PF}_6)_2$ (5.0×10^{-4} M) and LiCl (0.10 M) as the supporting electrolyte at room temperature.

Thus, the mechanism involving the equilibrium among the carbonyl complex $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$, the carboxylic acid complex $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{C}(\text{O})\text{OH})]^+$ and the CO₂ adduct complex $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{CO}_2)]$ was proposed for the catalytic CO₂ reduction (**Figure 7**, left cycle) [58, 62]. All the complexes were isolated, and the crystal structures were characterized [83]. In the mechanism, $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ is reduced to yield the coordinated unsaturated species $[\text{Ru}(\text{bpy})_2(\text{CO})]$ with evolving CO. The five coordinated complex reacts with CO₂ to afford the η^1 -CO₂ adduct complex, $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{CO}_2)]$, in which CO₂ coordinates to the metal center at the carbon atom. The electronic structure of the CO₂ bound complex still remains unknown. In the original report [62], it is drawn as $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{COO}^-)]^+$ in which as electron localizes on the CO₂ ligand. In **Figure 7**, it is drawn as $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{CO}_2)]^0$ which is the resonance structure of $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{COO}^-)]^+$. The CO₂ adduct complex is protonated to give the carboxylic acid complex $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{C}(\text{O})\text{OH})]^+$ and further protonated to recover the carbonyl complex $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$. The carboxylic acid complex could be reduced to yield HCOOH, and the carbonyl complex to produce CO. The proposed idea reasonably elucidates the experimental results that the catalytic CO₂ reduction gives CO and HCOOH under protic and less protic conditions, respectively. This idea is also supported by the result that the ruthenium complex derivatives give the CO/HCOO⁻ selectivity depending on the different equilibrium constants [58]. The carbonyl complex reacts with dimethylamine to afford the carbamoyl complex $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{C}(\text{O})\text{N}(\text{CH}_3)_2)]^+$, and the electrochemical CO₂ reduction in the presence of dimethylamine produces *N,N*-dimethylformamide (DMF) [84]. It is also an evidence which the carbonyl complex would exist in the catalysis.

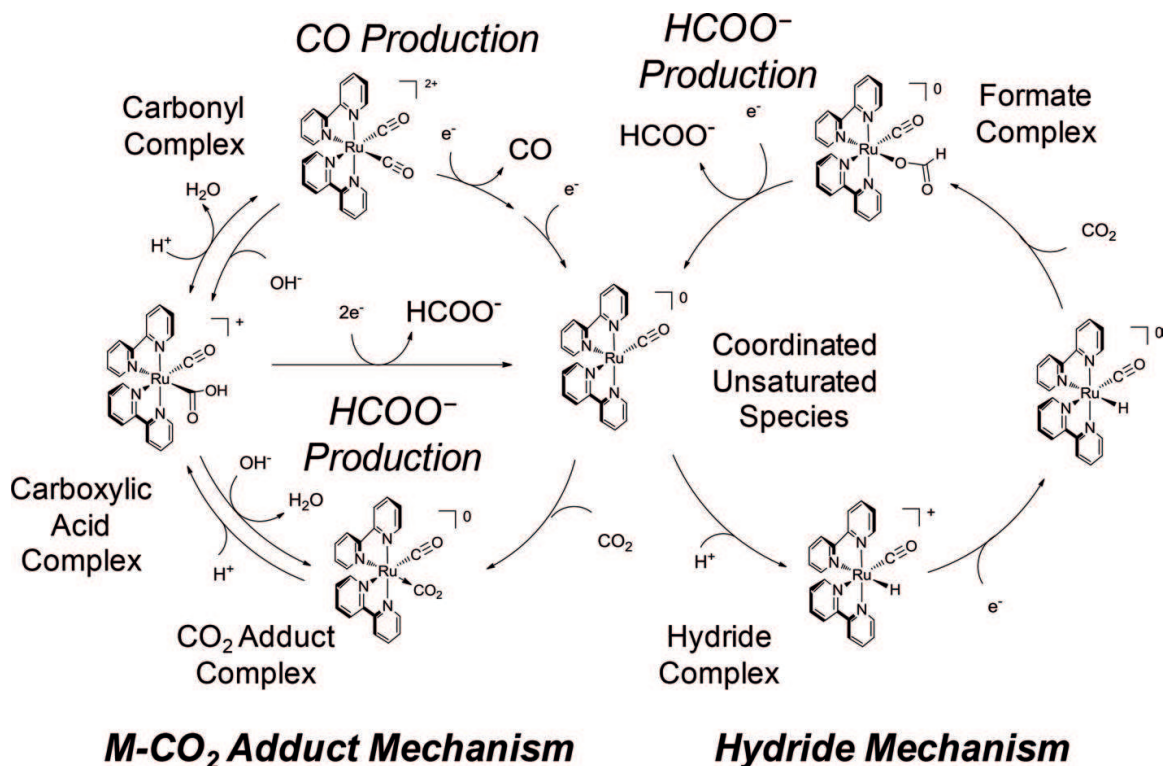


Figure 7. Two proposed mechanisms for CO₂ reduction catalyzed by *cis*-[Ru(bpy)₂(CO)X]ⁿ⁺ (X = CO (n = 2); H (n = 1)): Metal-CO₂ adduct mechanism and hydride mechanism.

On the other hand, the ruthenium hydride complex $[\text{Ru}(\text{bpy})_2(\text{CO})\text{H}]^+$ is known to react with CO_2 to yield the formate complex $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{OC}(\text{O})\text{H})]^+$ [85]. In the conversion, CO_2 is inserted into the Ru-H bond. The formate complex can release formate ion (HCOO^-) and is considered to be an intermediate for HCOO^- production. Based on the results, the hydride mechanism is proposed (Figure 7, right cycle). In the mechanism, the coordinated unsaturated species $[\text{Ru}(\text{bpy})_2(\text{CO})]$ does not react with CO_2 but a proton to yield the hydride complex. The hydride mechanism reasonably explains the CO_2 reduction to produce HCOO^- . However, it has a couple of problems [16]. One is that the mechanism is difficult to elucidate the CO production. Production of HCOO^- may occur through the hydride mechanism, while CO may produce through the M- CO_2 adduct mechanism. In this case, the product selectivity (CO/HCOO^-) should be controlled by the reactivity difference between CO and H^+ with the coordinated unsaturated complex. Under the protic conditions, the selectivity of HCOO^- production should be enhanced; however, the selectivity of the catalyses gives the opposite tendency. Thus, the pH in the solution or the pKa value of the proton source dependence on the electrochemical CO_2 reduction cannot be explained. Another is that the ruthenium catalyst does not evolve H_2 so much in the CO_2 reduction. It suggests that the catalyst intermediate strongly binds with CO_2 rather than H^+ .

Nevertheless, the hydride mechanism is supported by many researchers. It is because there are many research works on the CO_2 insertion into Metal-H bonds to afford the corresponding metal formate complexes. On the other hand, the research works on the carboxylic acid complex are fewer, and no mechanical pathways of HCOO^- production from the carboxylic acid complex are not understood on the molecular levels.

2.4. Electrocatalytic CO_2 reduction by *trans*(Cl)- $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]$

Trans(Cl)- $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]$ is known to be an efficient catalyst for electrochemical CO_2 reduction [58]. The catalytic activity and the product selectivity are similar as these of *cis*- $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$. Reduction of *trans*(Cl)- $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]$ induces to release Cl^- ion to afford the coordinated unsaturated complex. This complex is considered to an intermediate which can bind with CO_2 ; however, it induces polymerization in the absence of CO_2 as shown in Figure 8 [86, 87]. The polymer with Ru(0)-Ru(0) bonds is also an efficient electrocatalyst for CO_2 reduction [50, 54]. The complex is electrochemically reduced to polymerize on the cathode electrode. The electrode modified with the polymer is moved to another electric cell, and it works in the presence of CO_2 as the active electrode for electrochemical CO_2 reduction. Researches to make

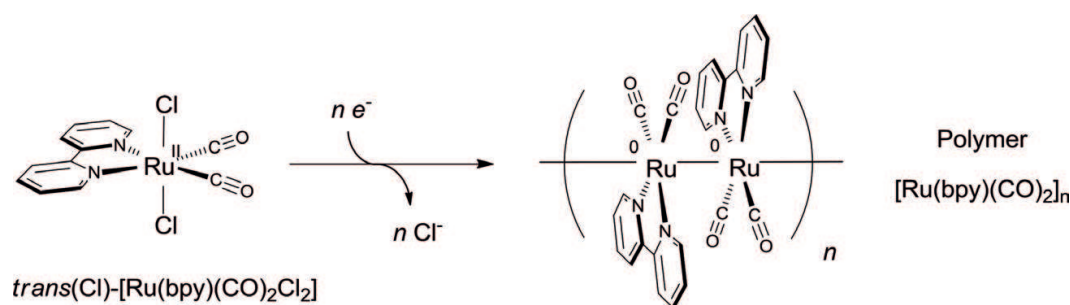


Figure 8. Electroreductive polymerization of *trans*(Cl)- $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]$.

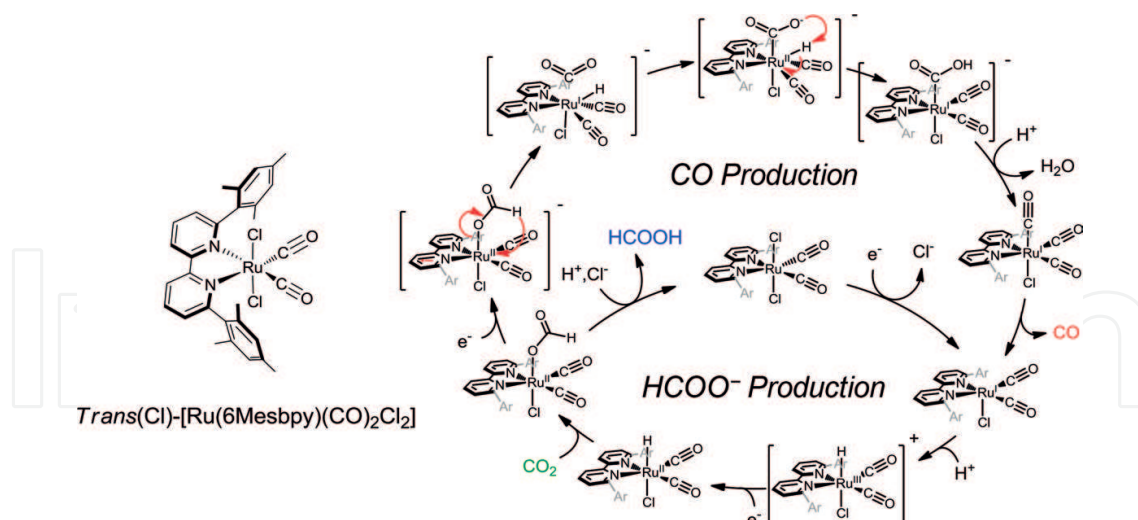


Figure 9. A proposed mechanism of electrochemical CO₂ reduction catalyzed by *trans(Cl)-[Ru(6Mesbpy)(CO)₂Cl₂]*.

the modified electrode stable have been actively done: introduction of pyrrole groups to the bipyridyl ligand also yields pyrrole polymers to stabilize the ruthenium polymer.

The catalytic reaction mechanisms are also unknown but are considered similar as these of *cis*-[Ru(bpy)₂(CO)₂]²⁺. Machan et al. reported the electrochemical CO₂ reduction catalyzed by *trans(Cl)-[Ru(6Mesbpy)(CO)₂Cl₂]*, which has two bulky groups at 6,6'-positions in 2,2'-bipyridine [35]. The complex does not polymerize because of the steric hindrance. They discussed the reaction mechanisms based on the hydride mechanism (**Figure 9**). The precursor complex is at the center of the scheme. It is reduced with releasing Cl⁻ ion to yield the coordinated unsaturated species, which does not bind with CO₂ but H⁺ to afford the hydride complex. The hydride complex reacts with CO₂ to yield the formate complex, which is reduced to produce HCOO⁻ with recovering the original complex. However, the catalyst mainly produces CO not HCOO⁻. In the mechanism, the formate complex converts to the carboxylic acid complex and then the carbonyl complex by dehydration. The conversion of the formate complex to the carbonyl complex via the carboxylic acid complex is not known, and therefore further researches are expected.

Homogeneous catalysts are advantageous from the viewpoints of elucidating the catalytic reaction mechanisms compared to heterogeneous ones because the homogenous catalysts can be examined by using many spectroscopic techniques. Nevertheless, the mechanisms of the electrochemical CO₂ reduction catalyzed by the ruthenium complexes still remain unknown. There may be potentially many intermediates and pathways in the catalyses, and they depend on the reaction conditions and the subtle difference among the catalyst structures [16, 37].

3. Photochemical CO₂ reduction

In the preceding section, the electrocatalytic activities of the ruthenium complexes are introduced. The electrocatalyst can be utilized in photocatalytic systems by combining with a photosensitizer (PS). **Figure 10** shows a schematic drawing of the photocatalytic system, in which the excited PS (PS*) receives an electron from an electron donor to afford the one-electron

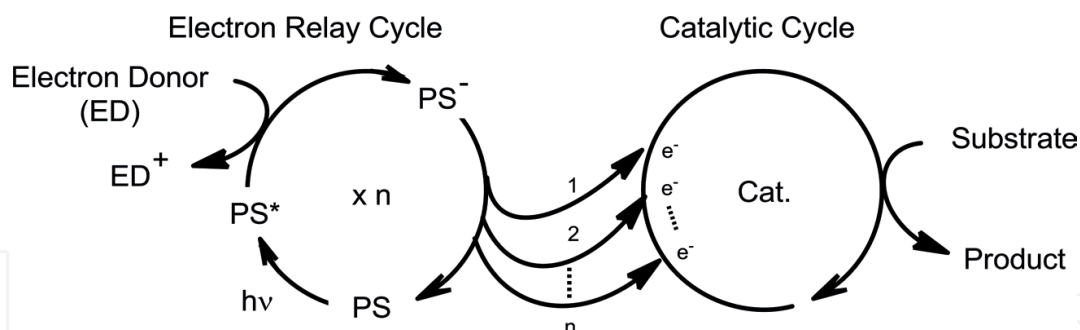


Figure 10. A schematic drawing of photocatalytic reduction by combining a photosensitizer (PS) with an electrocatalyst (Cat.).

reduced PS (PS^-). The PS^- is the more powerful reagent than PS^* , and it can inject an electron to the electrocatalyst. The catalyst can work similarly as the electroreduction occurs. In this section, the photocatalytic CO_2 reduction by the ruthenium complexes is expounded.

3.1. Photosensitizer and sacrificial electron donors

The most common photosensitizer used in photocatalytic CO_2 reduction is $[\text{Ru}(\text{bpy})_3]^{2+}$ and the derivatives. **Figure 11** shows the absorption and emission spectra of $[\text{Ru}(\text{bpy})_3]^{2+}$ in acetonitrile. The complex exhibits an absorption band at 400–500 nm, which is assignable to metal-to-ligand charge transfer (MLCT). When excited at the band, the emission at the longer wavelengths is observed. The emission is not fluorescence but room-temperature phosphorescence, which is sensitive to O_2 . Therefore, the emission spectrum should be carefully measured under deaerated conditions [88]. The lifetime of the excited state of $[\text{Ru}(\text{bpy})_3]^{2+}$ is 1.10 μs in acetonitrile [89, 90]. The quantum yield has been recently reevaluated as 0.095 in acetonitrile [91]. The oxidation potential (corresponding to the reducing ability) of the excited state (PS^*) is -0.81 V vs. SCE (CH_3CN), while this of the one-electron reduced species (PS^-) is -1.33 V. As the electrochemical

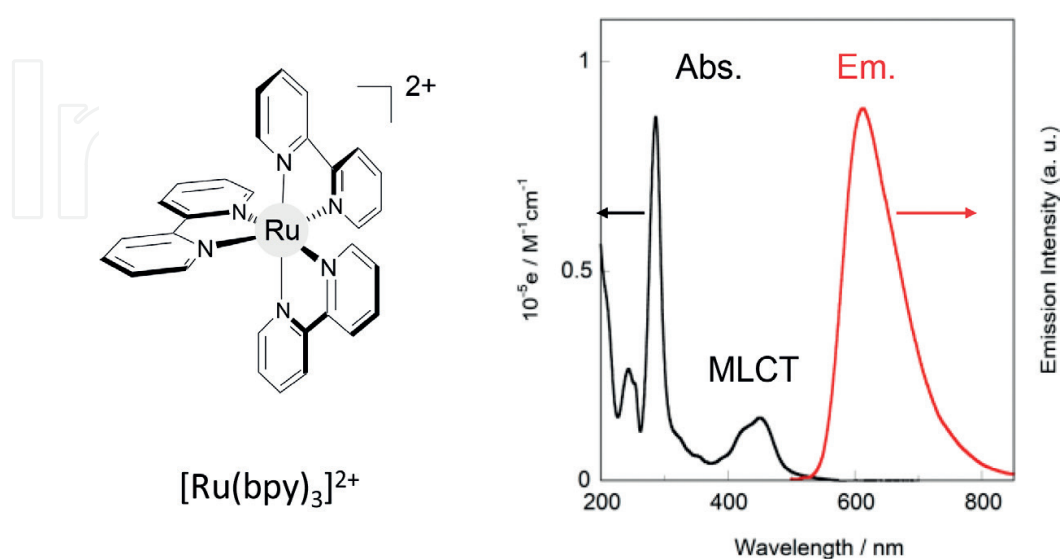


Figure 11. Absorption and emission (phosphorescence) spectra of $[\text{Ru}(\text{bpy})_3]^{2+}$ in deaerated CH_3CN at room temperature.

CO₂ reduction catalyzed by the ruthenium complexes proceeds under electrolysis at -1.30 V vs. SCE, it requires the reducing ability of PS^{•−}. In general, the CO₂ reduction requires higher energy than H₂ production by reduction of H₂O, and therefore, the photocatalytic CO₂ reduction does not utilize the excited state but the one-electron reduced species.

To generate the one-electron reduced species PS^{•−}, the electron donors can reductively quench the excited state of the photosensitizer. As the reduction potential of the excited state of [Ru(bpy)₃]²⁺ is $+0.77$ V vs. SCE (CH₃CN), the electron donors which can be oxidized at less positive potentials than $+0.77$ V. **Figure 12** shows the examples of the electron donors which are actually used in photocatalytic CO₂ reduction [16, 92]. Ascorbate ion (AscH^{•−}) can be used in aqueous solution, but amines (triethylamine (TEA) and triethanolamine (TEOA)) cannot work in the presence of water because they are protonated to afford the ammonium ions which cannot give an electron. 1-Benzyl-1,4-dihydronicotineamide (BNAH) is a model compound of NADH in nature. NADH is a two-electron donor and is oxidized to yield NAD⁺. However, the model compound BNAH cannot give two electrons in the oxidation by the excited state of [Ru(bpy)₃]²⁺ but provides one electron to afford the dimer BNA₂. 1,3-Dimethyl-2-phenyl-2,3-dihydro-1*H*-benzo[d]imidazole (BIH) and the derivatives (e.g., BI(OH)H), which have much stronger reducing power than BNAH, have been recently utilized in photocatalytic CO₂ reduction. BIH provides two electrons to yield the oxidation product BI⁺.

These electron donors are called the sacrificial reagents because the one-electron oxidized species occur chemical changes or decompose so as to prevent back electron transfer. They are useful in order to investigate the reductive half reaction. However, from the viewpoint of the energy balance, the reduction-oxidation (redox) systems in which water is oxidized and CO₂ is reduced are desired.

3.2. Photocatalytic CO₂ reduction

Our group have investigated the photochemical CO₂ reduction by the system consisting of *trans*(Cl)-[Ru(bpy)(CO)₂Cl₂], [Ru(bpy)₃]²⁺ and BNAH as the catalyst, the photosensitizer, and the electron donor, respectively (**Figure 13**). The catalysis had been carried out in *N,N*-dimethylformamide (DMF)/water [57, 59]. However, it was indicated that hydration of DMF affording formate became a serious problem in quantifying formate [93]. We proposed the use of *N,N*-dimethylacetamide (DMA), of which the dehydration does not produce formate but acetate, instead of DMF [39]. Although the photocatalysis strongly depends on the solvent system, the reaction proceeds in DMA/water similarly as in DMF/water.

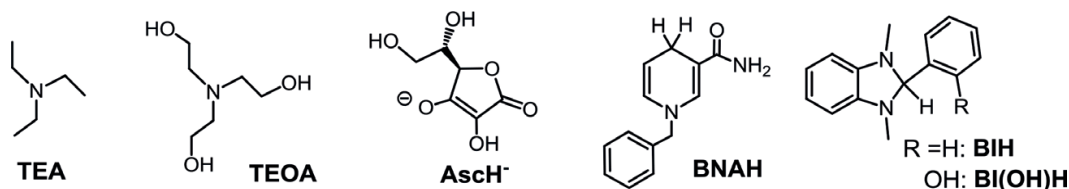


Figure 12. Examples of the electron donors (D) used in photochemical CO₂ reduction.

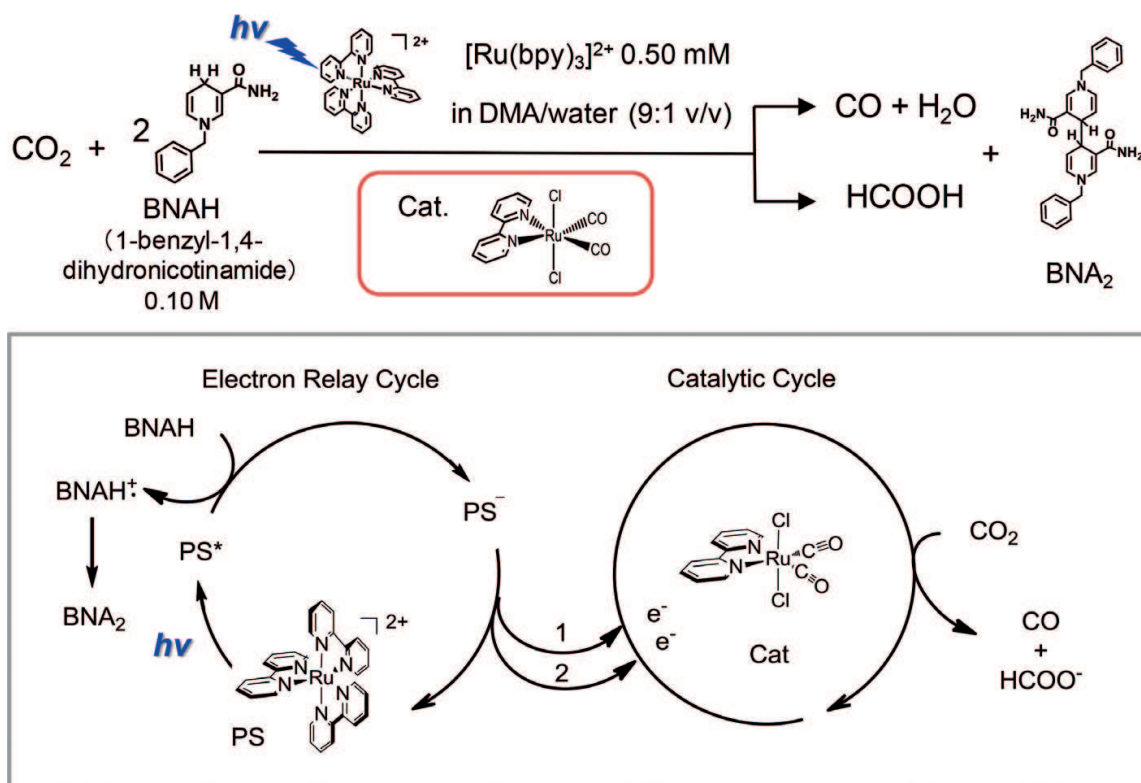


Figure 13. Photochemical CO_2 reduction catalyzed by $\text{trans}(\text{Cl})\text{-}[\text{Ru}(\text{bpy})_2(\text{CO})_2\text{Cl}]$ with $[\text{Ru}(\text{bpy})_3]^{2+}$ (a photosensitizer (PS)) and BNAH (an electron donor).

The catalytic reaction proceeds by receiving electrons from the photochemically driven electron relay system. For two-electron reduction of CO_2 to CO or HCOOH , the electron relay cycle has to go round two times when the catalytic cycle turns one time. The electron source is not an electrode, but the reaction had been supposed to proceed according to the same mechanism as in electrochemical reduction. However, it has been recently indicated that in some cases, the reaction mechanisms of the photochemical CO_2 reduction are likely different from the electrochemical one [16]. For example, unusual catalyst concentration dependence on the product selectivity (CO/HCOO^-) in the photocatalysis has been observed: at high catalyst concentration the selectivity of HCOO^- increases [37]. To elucidate the peculiar catalyst concentration effect, the mechanisms as shown in the right cycle in **Figure 14** are proposed. At the high concentration of the catalyst, the reduced catalyst forms a dimer, which is proposed to selectively afford HCOO^- . The dimer of the complex is similar as the intermediate of polymerization, but it is not detected in the photocatalytic system because the absorption spectrum cannot be conformed due to the overlapped absorption of $[\text{Ru}(\text{bpy})_3]^{2+}$. Alternatively, the photocatalytic CO_2 reduction by $\text{trans}(\text{Cl})\text{-}[\text{Ru}(\text{6Mesbpy})(\text{CO})_2\text{Cl}]$ which does not dimerize because of the steric hindrance of the ligand has been examined. The ruthenium complex selectively produces CO in the photochemical CO_2 reduction, and it demonstrates that the dimerization of the catalyst relates on the HCOO^- production. It is suggested that the catalyst concentration dependence is not observed in a DMA/ethanol solution. It indicates that HCOO^- also produces in the cycle consisting of mono-nuclear ruthenium complexes as proposed for the electrocatalytic CO_2 reduction (**Figure 14**, left cycle) [31].

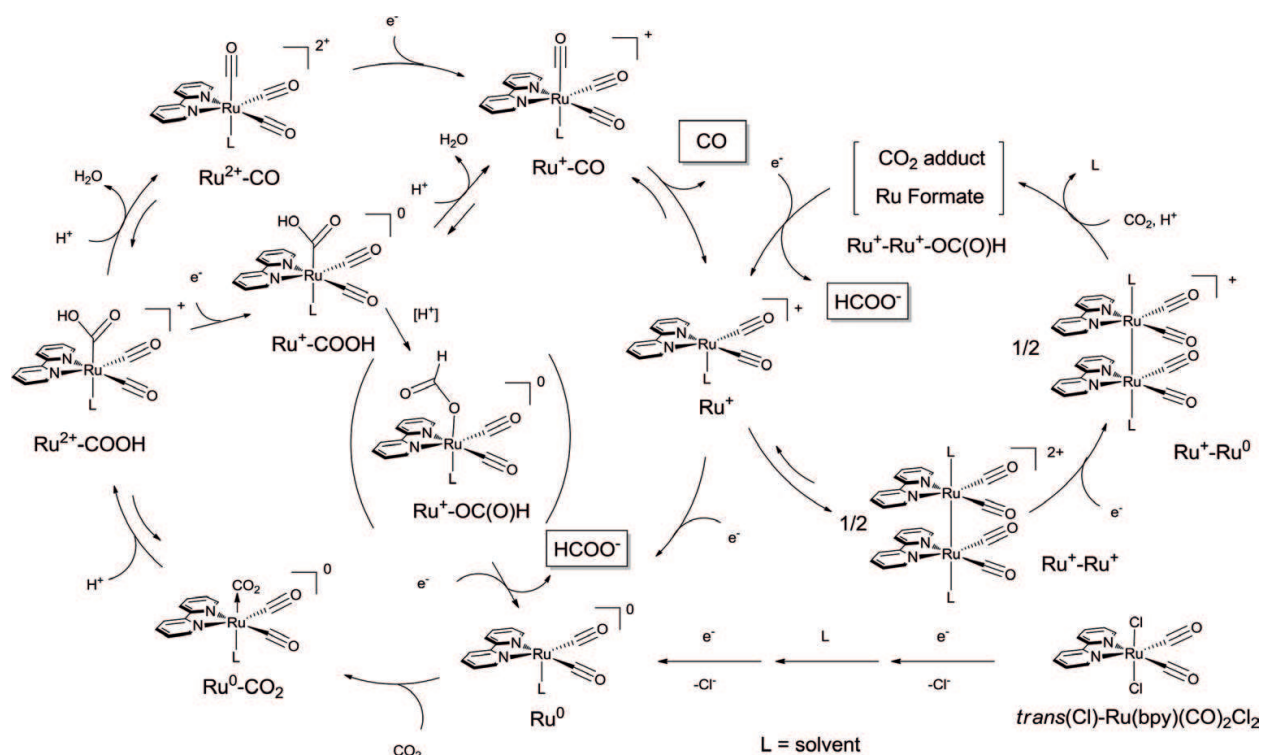


Figure 14. A proposed reaction mechanism for photocatalytic CO₂ reduction by *trans*(Cl)-[Ru(bpy)(CO)₂Cl₂].

The photochemical CO₂ reduction catalyzed by *trans*(Cl)-[Ru(2,2'-bipyridine)(CO)₂Cl₂] bearing two methyl groups at 4,4'- or 5,5'-positions in the ligand has been recently reported [64]. As the catalytic activities of these complexes at low catalyst concentrations are almost the same, the intrinsic activities are considered to be identical. However, the catalytic activities of these complexes are different at high catalyst concentration, where the rate-determining step is not in the catalytic cycle but in the electron relay cycle: the ruthenium complex with dimethyl groups at 5,5'-positions in the 2,2'-bipyridyl ligand is higher than that at 4,4'-positions. The efficiency of the back-electron transfer from the reduced catalyst to the photosensitizer is lower, or the cage escape yield for the sensitizer-catalyst complex is higher in the 5,5'-dimethyl complex than in the 4,4'-complex.

These phenomena have not been observed in electrochemical CO₂ reduction. It is probably because that the homogenous photocatalytic CO₂ reduction contains the diffusion process of the electron relay between the photosensitizer and the catalyst. The speed of the electron supply also sometimes affects the reaction mechanisms [16, 37].

3.3. Application to heterogeneous catalysts

Heterogeneous catalysts are industrially important because they are useful for separating the starting materials and the products from the catalyst and can be recovered and reused. The molecular catalysts can be utilized to develop the heterogeneous catalysts. For photocatalysts of CO₂ reduction, combining the molecular catalysts with semiconductor [32, 94, 95], metal-organic frameworks (MOFs) [96, 97] or periodic mesoporous organosilicas (PMOs) [98–101]

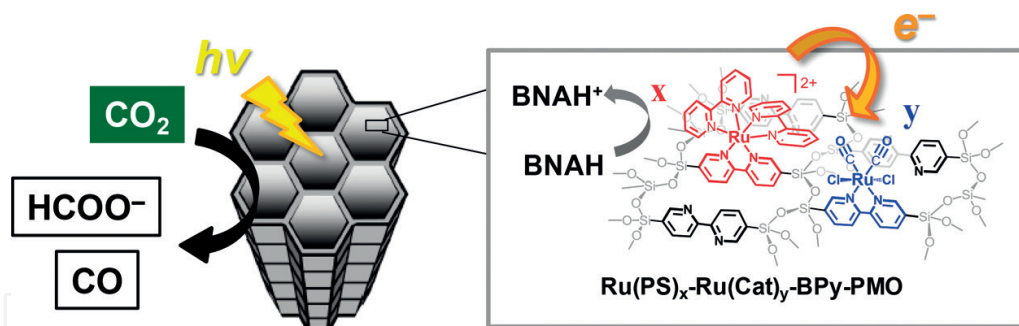


Figure 15. Photocatalytic CO_2 reduction by periodic mesoporous organosilica (PMO) containing two different ruthenium complexes as photosensitizing and catalytic sites.

are actively researched. We have also developed a novel PMO consisting of 2,2'-bipyridyl framework by introducing two different ruthenium complexes as a photosensitizing site (Ru(PS)) and a catalytic site (Ru(Cat)) as shown in **Figure 15** [99]. Photochemical CO_2 reduction by the PMO catalyst has catalytically produced CO and formate. The product selectivity (CO/formate) becomes large with increasing the ratio of Ru(PS) to Ru(Cat) (x/y). The photocatalysts can be recycled at least three times without losing the catalytic activity, demonstrating that the Ru(PS) and Ru(Cat) units are strongly immobilized on the BPy-PMO framework.

4. Future prospects

The molecular catalysts are applicable to various photocatalytic systems. Ultimately, our goal is to construct an artificial photosynthetic system. An example is shown in **Figure 16**. In the system, the electrons are not supplied from the sacrificial electron donor but from water which is the same as in natural photosynthetic system. As the CO_2 reduction requires a high potential, two photosensitizing systems would be combined as the Z-scheme mechanism in the natural photosynthesis. In order to realize the artificial photosynthesis, we have to overcome some problems. One is to perform these reactions (water oxidation, photo-induced electron transfer and CO_2 reduction, etc.) under the similar conditions or in the separated circumstances. Another is to match the velocities among the reactions; even if the efficient catalyst for CO_2 reduction was obtained, the speeds for the water oxidation and the electron supply have to match with that of CO_2 reduction.

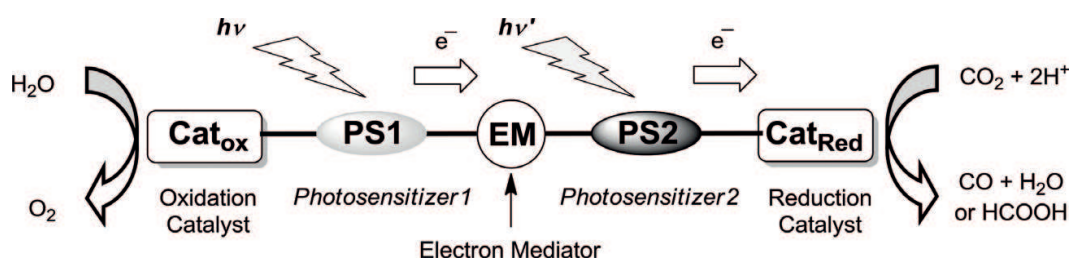


Figure 16. A schematic drawing for an artificial photosynthetic system.

There would be many other problems to construct the artificial photosynthesis. However, the real system which can efficiently work has already existed in nature. We will realize it with a lot of ideas to overcome many problems one by one.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research (C) from the Ministry of Education, Culture, Sports, Science and Technology (17K05815). This work was also supported by the PRESTO Program of JST, and a Grant-in-Aid for Scientific Research on Innovative Areas, "Artificial Photosynthesis (AnApple)" (No. 15H00882), from the Japan Society for the Promotion of Science (JSPS).

Author details

Hitoshi Ishida

Address all correspondence to: ishida@sci.kitasato-u.ac.jp

Department of Chemistry, Graduate School of Science, Kitasato University, Japan

References

- [1] Olah GA, Prakash GKS, Goepfert A. Anthropogenic chemical carbon cycle for a sustainable future. *Journal of the American Chemical Society*. 2011;**133**:12881-12898. DOI: 10.1021/ja202642y
- [2] Arakawa H, Aresta M, Armor JN, Barteau MA, Beckman EJ, Bell AT, Bercaw JE, Creutz C, Dinjus E, Dixon DA, Domen K, DuBois DL, Eckert J, Fujita E, Gibson DH, Goddard WA, Goodman DW, Keller J, Kubas GJ, Kung HH, Lyons JE, Manzer LE, Marks TJ, Morokuma K, Nicholas KM, Periana R, Que L, Rostrup-Nielson J, Sachtler WMH, Schmidt LD, Sen A, Somorjai GA, Stair PC, Stults BR, Tumas W. Catalysis research of relevance to carbon management: Progress, challenges, and opportunities. *Chemical Reviews*. 2001;**101**:953-996. DOI: 10.1021/cr000018s
- [3] Mikkelsen M, Jorgensen M, Krebs FC. The teraton challenge. A review of fixation and transformation of carbon dioxide. *Energy & Environmental Science*. 2010;**3**:43-81. DOI: 10.1039/b912904a
- [4] Sakakura T, Choi J-C, Yasuda H. Transformation of carbon dioxide. *Chemical Reviews*. 2007;**107**:2365-2387. DOI: 10.1021/cr068357u
- [5] Schwarz HA, Dodson RW. Reduction potentials of CO₂⁻ and the alcohol radicals. *The Journal of Physical Chemistry*. 1989;**93**:409-414. DOI: 10.1021/j100338a079

- [6] Yamazaki Y, Takeda H, Ishitani O. Photocatalytic reduction of CO₂ using metal complexes. *Journal of Photochemistry and Photobiology C Photochemistry Reviews*. 2015;**25**:106-137. DOI: <https://doi.org/10.1016/j.jphotochemrev.2015.09.001>
- [7] Hildebrandt D, Glasser D, Hausberger B, Patel B, Glasser BJ. Producing transportation fuels with less work. *Science*. 2009;**323**:1680-1681. DOI: 10.1126/science.1168455
- [8] Singh AK, Singh S, Kumar A. Hydrogen energy future with formic acid: A renewable chemical hydrogen storage system. *Catalysis Science & Technology*. 2016;**6**:12-40. DOI: 10.1039/c5cy01276g
- [9] DuBois DL. Development of molecular electrocatalysts for energy storage. *Inorganic Chemistry*. 2014;**53**:3935-3960. DOI: 10.1021/ic4026969
- [10] Appel AM, Bercaw JE, Bocarsly AB, Dobbek H, DuBois DL, Dupuis M, Ferry JG, Fujita E, Hille R, Kenis PJA, Kerfeld CA, Morris RH, Peden CHF, Portis AR, Ragsdale SW, Rauchfuss TB, Reek JNH, Seefeldt LC, Thauer RK, Waldrop GL. Frontiers, opportunities, and challenges in biochemical and chemical catalysis of CO₂ fixation. *Chemical Reviews*. 2013;**113**:6621-6658. DOI: 10.1021/cr300463y
- [11] Schneider J, Jia H, Muckerman JT, Fujita E. Thermodynamics and kinetics of CO₂, CO, and H⁺ binding to the metal centre of CO₂ reduction catalysts. *Chemical Society Reviews*. 2012;**41**:2036-2051. DOI: 10.1039/c1cs15278e
- [12] Windle CD, Perutz RN. Advances in molecular photocatalytic and electrocatalytic CO₂ reduction. *Coordination Chemistry Reviews*. 2012;**256**:2562-2570. DOI: 10.1016/j.ccr.2012.03.010
- [13] Yui T, Tamaki Y, Sekizawa K, Ishitani O. Photocatalytic reduction of CO₂: From molecules to semiconductors. *Topics in Current Chemistry*. 2011;**303**:151-184. DOI: 10.1007/128_2011_139
- [14] Takeda H, Ishitani O. Development of efficient photocatalytic systems for CO₂ reduction using mononuclear and multinuclear metal complexes based on mechanistic studies. *Coordination Chemistry Reviews*. 2010;**254**:346-354. DOI: 10.1016/j.ccr.2009.09.030
- [15] Savéant J-M. Molecular catalysis of electrochemical reactions. Mechanistic aspects. *Chemical Reviews*. 2008;**108**:2348-2378. DOI: 10.1021/cr068079z
- [16] Kuramochi Y, Ishitani O, Ishida H. Reaction mechanisms of catalytic photochemical CO₂ reduction using Re(I) and Ru(II) complexes. *Coordination Chemistry Reviews*. 2018. DOI: 10.1016/j.ccr.2017.11.023
- [17] Sampson MD, Nguyen AD, Grice KA, Moore CE, Rheingold AL, Kubiak CP. Manganese catalysts with bulky bipyridine ligands for the electrocatalytic reduction of carbon dioxide: Eliminating dimerization and altering catalysis. *Journal of the American Chemical Society*. 2014;**136**:5460-5471. DOI: 10.1021/ja501252f
- [18] Takeda H, Koizumi H, Okamoto K, Ishitani O. Photocatalytic CO₂ reduction using a Mn complex as a catalyst. *Chemical Communications*. 2014;**50**:1491-1493. DOI: 10.1039/c3cc48122k

- [19] Bourrez M, Molton F, Chardon-Noblat S, Deronzier A. [Mn(bipyridyl)(CO)₃Br]: An abundant metal carbonyl complex as efficient electrocatalyst for CO₂ reduction. *Angewandte Chemie, International Edition*. 2011;**50**:9903-9906. DOI: 10.1002/anie.201103616
- [20] Costentin C, Drouet S, Robert M, Savéant J-M. A local proton source enhances CO₂ electroreduction to CO by a molecular Fe catalyst. *Science*. 2012;**338**:90-94. DOI: 10.1126/science.1224581
- [21] Hammouche M, Lexa D, Momenteau M, Saveant JM. Chemical catalysis of electrochemical reactions. Homogeneous catalysis of the electrochemical reduction of carbon dioxide by iron(0) porphyrins. Role of the addition of magnesium cations. *Journal of the American Chemical Society*. 1991;**113**:8455-8466. DOI: 10.1021/ja00022a038
- [22] Matsuoka S, Yamamoto K, Ogata T, Kusaba M, Nakashima N, Fujita E, Yanagida S. Efficient and selective electron mediation of cobalt complexes with cyclam and related macrocycles in the p-terphenyl-catalyzed photoreduction of carbon dioxide. *Journal of the American Chemical Society*. 1993;**115**:601-609. DOI: 10.1021/ja00055a032
- [23] Ziessel R, Hawecker J, Lehn J-M. Photogeneration of carbon monoxide and of hydrogen via simultaneous photochemical reduction of carbon dioxide and water by visible-light irradiation of organic solutions containing Tris(2,2'-bipyridine)ruthenium(II) and cobalt(II) species as homogeneous catalysts. *Helvetica Chimica Acta*. 1986;**69**:1065-1084. DOI: 10.1002/hlca.19860690514
- [24] Tinnemans AHA, Koster TPM, Thewissen DHMW, Mackor A. Tetraaza-macrocyclic cobalt(II) and nickel(II) complexes as electron-transfer agents in the photo(electro)chemical and electrochemical reduction of carbon dioxide. *Recueil des Travaux Chimiques des Pays-Bas*. 1984;**103**:288-295. DOI: 10.1002/recl.19841031004
- [25] Rudolph M, Dautz S, Jäger E-G. Macrocyclic [N₄²⁺] coordinated nickel complexes as catalysts for the formation of oxalate by electrochemical reduction of carbon dioxide. *Journal of the American Chemical Society*. 2000;**122**:10821-10830. DOI: 10.1021/ja001254n
- [26] Grant JL, Goswami K, Spreer LO, Otvos JW, Calvin M. Photochemical reduction of carbon dioxide to carbon monoxide in water using a nickel(II) tetra-azamacrocycle complex as catalyst. *Journal of the Chemical Society, Dalton Transactions*. 1987:2105-2109. DOI: 10.1039/dt9870002105
- [27] Beley M, Collin JP, Ruppert R, Sauvage JP. Electrocatalytic reduction of carbon dioxide by nickel cyclam²⁺ in water: Study of the factors affecting the efficiency and the selectivity of the process. *Journal of the American Chemical Society*. 1986;**108**:7461-7467. DOI: 10.1021/ja00284a003
- [28] Beley M, Collin J-P, Ruppert R, Sauvage J-P. Nickel(II)-cyclam: An extremely selective electrocatalyst for reduction of CO₂ in water. *Journal of the Chemical Society, Chemical Communications*. 1984:1315-1316. DOI: 10.1039/c39840001315
- [29] Angamuthu R, Byers P, Lutz M, Spek AL, Bouwman E. Electrocatalytic CO₂ conversion to oxalate by a copper complex. *Science*. 2010;**327**:313-315. DOI: 10.1126/science.1177981

- [30] Clark ML, Grice KA, Moore CE, Rheingold AL, Kubiak CP. Electrocatalytic CO₂ reduction by M(bpy-R)(CO)₄ (M = Mo, W; R = H, tBu) complexes. Electrochemical, spectroscopic, and computational studies and comparison with group 7 catalysts. *Chemical Science*. 2014;**5**:1894-1900. DOI: 10.1039/c3sc53470g
- [31] Ishida H, Sakaba A. Temperature dependence of photocatalytic CO₂ reduction by trans(Cl)-Ru(bpy)(CO)₂Cl₂: Activation energy difference between CO and formate production. *Faraday Discussions*. 2017;**198**:263-277. DOI: 10.1039/c6fd00242k
- [32] Kuriki R, Matsunaga H, Nakashima T, Wada K, Yamakata A, Ishitani O, Maeda K. Nature-inspired, highly durable CO₂ reduction system consisting of a binuclear ruthenium(II) complex and an organic semiconductor using visible light. *Journal of the American Chemical Society*. 2016;**138**:5159-5170. DOI: 10.1021/jacs.6b01997
- [33] Kuriki R, Ishitani O, Maeda K. Unique solvent effects on visible-light CO₂ reduction over ruthenium(II)-complex/carbon nitride hybrid photocatalysts. *ACS Applied Materials & Interfaces*. 2016;**8**:6011-6018. DOI: 10.1021/acsami.5b11836
- [34] Yoshitomi F, Sekizawa K, Maeda K, Ishitani O. Selective formic acid production via CO₂ reduction with visible light using a hybrid of a perovskite tantalum oxynitride and a binuclear ruthenium(II) complex. *ACS Applied Materials & Interfaces*. 2015;**7**:13092-13097. DOI: 10.1021/acsami.5b03509
- [35] Machan CW, Sampson MD, Kubiak CP. A molecular ruthenium electrocatalyst for the reduction of carbon dioxide to CO and Formate. *Journal of the American Chemical Society*. 2015;**137**:8564-8571. DOI: 10.1021/jacs.5b03913
- [36] Kuriki R, Sekizawa K, Ishitani O, Maeda K. Visible-light-driven CO₂ reduction with carbon nitride: Enhancing the activity of ruthenium catalysts. *Angewandte Chemie, International Edition*. 2015;**54**:2406-2409. DOI: 10.1002/anie.201411170
- [37] Kuramochi Y, Itabashi J, Fukaya K, Enomoto A, Yoshida M, Ishida H. Unexpected effect of catalyst concentration on photochemical CO₂ reduction by trans(Cl)-Ru(bpy)(CO)₂Cl₂: New mechanistic insight into the CO/HCOO⁻ selectivity. *Chemical Science*. 2015;**6**:3063-3074. DOI: 10.1039/c5sc00199d
- [38] Kuramochi Y, Fukaya K, Yoshida M, Ishida H. Trans(Cl)-[Ru(5,5'-diamide-2,2'-bipyridine)(CO)₂Cl₂]: Synthesis, structure, and photocatalytic CO₂ reduction activity. *Chemistry—A European Journal*. 2015;**21**:10049-10060. DOI: 10.1002/chem.201500782
- [39] Kuramochi Y, Kamiya M, Ishida H. Photocatalytic CO₂ reduction in N,N-dimethylacetamide/water as an alternative solvent system. *Inorganic Chemistry*. 2014;**53**:3326-3332. DOI: 10.1021/ic500050q
- [40] Maeda K, Kuriki R, Zhang M, Wang X, Ishitani O. The effect of the pore-wall structure of carbon nitride on photocatalytic CO₂ reduction under visible light. *Journal of Materials Chemistry A*. 2014;**2**:15146-15151. DOI: 10.1039/c4ta03128h
- [41] Maeda K, Sekizawa K, Ishitani O. A polymeric-semiconductor-metal-complex hybrid photocatalyst for visible-light CO₂ reduction. *Chemical Communications*. 2013;**49**:10127-10129. DOI: 10.1039/c3cc45532g

- [42] Tamaki Y, Morimoto T, Koike K, Ishitani O. Photocatalytic CO₂ reduction with high turnover frequency and selectivity of formic acid formation using Ru(II) multinuclear complexes. *Proceedings of the National Academy of Sciences of the United States of America*. 2012;**109**:15673-15678. DOI: 10.1073/pnas.1118336109
- [43] Yamanaka K-I, Sato S, Iwaki M, Kajino T, Morikawa T. Photoinduced electron transfer from nitrogen-doped tantalum oxide to adsorbed ruthenium complex. *Journal of Physical Chemistry C*. 2011;**115**:18348-18353. DOI: 10.1021/jp205223k
- [44] Suzuki TM, Tanaka H, Morikawa T, Iwaki M, Sato S, Saeki S, Inoue M, Kajino T, Motohiro T. Direct assembly synthesis of metal complex-semiconductor hybrid photocatalysts anchored by phosphonate for highly efficient CO₂ reduction. *Chemical Communications*. 2011;**47**:8673-8675. DOI: 10.1039/c1cc12491a
- [45] Sato S, Arai T, Morikawa T, Uemura K, Suzuki TM, Tanaka H, Kajino T. Selective CO₂ conversion to Formate conjugated with H₂O oxidation utilizing semiconductor/complex hybrid photocatalysts. *Journal of the American Chemical Society*. 2011;**133**:15240-15243. DOI: 10.1021/ja204881d
- [46] Arai T, Tajima S, Sato S, Uemura K, Morikawa T, Kajino T. Selective CO₂ conversion to formate in water using a CZTS photocathode modified with a ruthenium complex polymer. *Chemical Communications*. 2011;**47**:12664-12666. DOI: 10.1039/c1cc16160a
- [47] Sato S, Morikawa T, Saeki S, Kajino T, Motohiro T. Visible-light-induced selective CO₂ reduction utilizing a ruthenium complex electrocatalyst linked to a p-type nitrogen-doped Ta₂O₅ semiconductor. *Angewandte Chemie International Edition in English*. 2010;**49**:5101-5105. S5101/5101-S5101/5111. DOI: 10.1002/anie.201000613
- [48] Arai T, Sato S, Uemura K, Morikawa T, Kajino T, Motohiro T. Photoelectrochemical reduction of CO₂ in water under visible-light irradiation by a p-type InP photocathode modified with an electropolymerized ruthenium complex. *Chemical Communications*. 2010;**46**:6944-6946. DOI: 10.1039/c0cc02061c
- [49] Creutz C, Chou MH. Rapid transfer of hydride ion from a ruthenium complex to C1 species in water. *Journal of the American Chemical Society*. 2007;**129**:10108-10109. DOI: 10.1021/ja074158w
- [50] Chardon-Noblat S, Deronzier A, Ziessel R, Zsoldos D. Electroreduction of CO₂ catalyzed by polymeric [Ru(bpy)(CO)₂]_n films in aqueous media: Parameters influencing the reaction selectivity. *Journal of Electroanalytical Chemistry*. 1998;**444**:253-260. DOI: 10.1016/s0022-0728(97)00584-6
- [51] Chardon-Noblat S, Deronzier A, Ziessel R, Zsoldos D. Selective synthesis and electrochemical behavior of trans(Cl)- and cis(Cl)-[Ru(bpy)(CO)₂Cl₂] complexes (bpy = 2,2'-Bipyridine). Comparative studies of their electrocatalytic activity toward the reduction of carbon dioxide. *Inorganic Chemistry*. 1997;**36**:5384-5389. DOI: 10.1021/ic9701975
- [52] Nagao H, Mizukawa T, Tanaka K. Carbon-carbon bond formation in the electrochemical reduction of carbon dioxide catalyzed by a ruthenium complex. *Inorganic Chemistry*. 1994;**33**:3415-3420. DOI: 10.1021/ic00093a033

- [53] Collomb-Dunand-Sauthier M-N, Deronzier A, Ziessel R. Electrocatalytic reduction of carbon dioxide with mono(bipyridine)carbonylruthenium complexes in solution or as polymeric thin films. *Inorganic Chemistry*. 1994;**33**:2961-2967. DOI: 10.1021/ic00091a040
- [54] Collomb-Dunand-Sauthier MN, Deronzier A, Ziessel R. Electrocatalytic reduction of CO₂ in water on a polymeric [{Ru⁰(bpy)(CO)₂}_n] (bpy = 2,2'-bipyridine) complex immobilized on carbon electrodes. *Journal of the Chemical Society, Chemical Communications*. 1994:189-191. DOI: 10.1039/c39940000189
- [55] Chardon-Noblat S, Collomb-Dunand-Sauthier MN, Deronzier A, Ziessel R, Zsoldos D. Formation of polymeric [{Ru⁰(bpy)(CO)₂}_n] films by electrochemical reduction of [Ru(bpy)₂(CO)₂](PF₆)₂: Its implication in CO₂ electrocatalytic reduction. *Inorganic Chemistry*. 1994;**33**:4410-4412. DOI: 10.1021/ic00097a034
- [56] Lehn JM, Ziessel R. Photochemical reduction of carbon dioxide to formate catalyzed by (2,2'-bipyridine)- or (1,10-phenanthroline)ruthenium(II) complexes. *Journal of Organometallic Chemistry*. 1990;**382**:157-173. DOI: 10.1016/0022-328x(90)85224-m
- [57] Ishida H, Terada T, Tanaka K, Tanaka T. Photochemical carbon dioxide reduction catalyzed by bis(2,2'-bipyridine)dicarbonylruthenium(2+) using triethanolamine and 1-benzyl-1,4-dihydronicotinamide as an electron donor. *Inorganic Chemistry*. 1990;**29**:905-911. DOI: 10.1021/ic00330a004
- [58] Ishida H, Fujiki K, Ohba T, Ohkubo K, Tanaka K, Terada T, Tanaka T. Ligand effects of ruthenium 2,2'-bipyridine and 1,10-phenanthroline complexes on the electrochemical reduction of carbon dioxide. *Journal of the Chemical Society, Dalton Transactions*. 1990:2155-2160. DOI: 10.1039/DT9900002155
- [59] Ishida H, Tanaka K, Tanaka T. Photochemical carbon dioxide reduction by an NADH model compound in the presence of ruthenium complexes [Ru(bpy)₃]²⁺ and [Ru(bpy)₂(CO)₂]²⁺ (bpy = 2,2'-bipyridine) in water/DMF. *Chemistry Letters*. 1988;**17**:339-342. DOI: 10.1246/cl.1988.339
- [60] Ishida H, Tanaka K, Tanaka T. Photoreduction of carbon dioxide in the [Ru(bpy)₂(CO)₂]²⁺ (bpy = 2,2'-bipyridine)/[Ru(bpy)₃]²⁺ or [Ru(phen)₃]²⁺ (phen = phenanthroline)/triethanolamine/N,N-dimethylformamide system. *Chemistry Letters*. 1987;**16**:1035-1038. DOI: 10.1246/cl.1987.1035
- [61] Ishida H, Tanaka H, Tanaka K, Tanaka T. Selective formation of formate in the electrochemical carbon dioxide reduction catalyzed by [Ru(bpy)₂(CO)₂]²⁺ (bpy = 2,2'-bipyridine). *Journal of the Chemical Society, Chemical Communications*. 1987:131-132. DOI: 10.1039/c39870000131
- [62] Ishida H, Tanaka K, Tanaka T. Electrochemical CO₂ reduction catalyzed by ruthenium complexes [Ru(bpy)₂(CO)₂]²⁺ and [Ru(bpy)₂(CO)Cl]⁺. Effect of pH on the formation of CO and HCOO. *Organometallics*. 1987;**6**:181-186. DOI: 10.1021/om00144a033
- [63] Ishida H, Tanaka K, Tanaka T. The electrochemical reduction of carbon dioxide catalyzed by ruthenium carbonyl complexes. *Chemistry Letters*. 1985;**14**:405-406. DOI: 10.1246/cl.1985.405

- [64] Kuramochi Y, Itabashi J, Toyama M, Ishida H. Photochemical CO₂ reduction catalyzed by trans(Cl)-Ru(2,2'-bipyridine)(CO)₂Cl₂ bearing two methyl groups at 4,4'-, 5,5'- or 6,6'-positions in the ligand. *ChemPhotoChem*. 2018;**2**:314-322. DOI: 10.1002/cptc.201700201
- [65] Rasmussen SC, Richter MM, Yi E, Place H, Brewer KJ. Synthesis and characterization of a series of novel rhodium and iridium complexes containing polypyridyl bridging ligands: Potential uses in the development of multimetal catalysts for carbon dioxide reduction. *Inorganic Chemistry*. 1990;**29**:3926-3932. DOI: 10.1021/ic00345a005
- [66] Bolinger CM, Story N, Sullivan BP, Meyer TJ. Electrocatalytic reduction of carbon dioxide by 2,2'-bipyridine complexes of rhodium and iridium. *Inorganic Chemistry*. 1988;**27**:4582-4587. DOI: 10.1021/ic00298a016
- [67] Bernatis PR, Miedaner A, Haltiwanger RC, DuBois DL. Exclusion of six-coordinate intermediates in the electrochemical reduction of CO₂ catalyzed by [Pd(triphosphine)(CH₃CN)] (BF₄)₂ complexes. *Organometallics*. 1994;**13**:4835-4843. DOI: 10.1021/om00024a029
- [68] DuBois DL, Miedaner A. Mediated electrochemical reduction of CO₂. Preparation and comparison of an isoelectronic series of complexes. *Journal of the American Chemical Society*. 1987;**109**:113-117. DOI: 10.1021/ja00235a019
- [69] Riplinger C, Sampson MD, Ritzmann AM, Kubiak CP, Carter EA. Mechanistic contrasts between manganese and rhenium bipyridine electrocatalysts for the reduction of carbon dioxide. *Journal of the American Chemical Society*. 2014;**136**:16285-16298. DOI: 10.1021/ja508192y
- [70] Kou Y, Nabetani Y, Masui D, Shimada T, Takagi S, Tachibana H, Inoue H. Direct detection of key reaction intermediates in photochemical CO₂ reduction sensitized by a rhenium bipyridine complex. *Journal of the American Chemical Society*. 2014;**136**:6021-6030. DOI: 10.1021/ja500403e
- [71] Morimoto T, Nishiura C, Tanaka M, Rohacova J, Nakagawa Y, Funada Y, Koike K, Yamamoto Y, Shishido S, Kojima T, Saeki T, Ozeki T, Ishitani O. Ring-shaped Re(I) multinuclear complexes with unique photofunctional properties. *Journal of the American Chemical Society*. 2013;**135**:13266-13269. DOI: 10.1021/ja406144h
- [72] Tamaki Y, Koike K, Morimoto T, Yamazaki Y, Ishitani O. Red-light-driven Photocatalytic reduction of CO₂ using Os(II)-re(I) supramolecular complexes. *Inorganic Chemistry*. 2013;**52**:11902-11909. DOI: 10.1021/ic4015543
- [73] Agarwal J, Fujita E, Schaefer HF, Muckerman JT. Mechanisms for CO production from CO₂ using reduced rhenium tricarbonyl catalysts. *Journal of the American Chemical Society*. 2012;**134**:5180-5186. DOI: 10.1021/ja2105834
- [74] Takeda H, Koike K, Inoue H, Ishitani O. Development of an efficient photocatalytic system for CO₂ reduction using rhenium(I) complexes based on mechanistic studies. *Journal of the American Chemical Society*. 2008;**130**:2023-2031. DOI: 10.1021/ja077752e
- [75] Gholamkhash B, Mametsuka H, Koike K, Tanabe T, Furue M, Ishitani O. Architecture of supramolecular metal complexes for photocatalytic CO₂ reduction: Ruthenium-rhenium

- bi- and tetranuclear complexes. *Inorganic Chemistry*. 2005;**44**:2326-2336. DOI: 10.1021/ic048779r
- [76] Hawecker J, Lehn JM, Ziessel R. Photochemical and electrochemical reduction of carbon dioxide to carbon monoxide mediated by (2,2'-bipyridine)tricarbonylchlororhenium(I) and related complexes as homogeneous catalysts. *Helvetica Chimica Acta*. 1986;**69**:1990-2012. DOI: 10.1002/hlca.19860690824
- [77] Chauvin J, Lafalet F, Chardon-Noblat S, Deronzier A, Jakonen M, Haukka M. Towards new molecular photocatalysts for CO₂ reduction: Photo-induced electron transfer versus CO dissociation within [Os(NN)(CO)₂Cl₂] complexes. *Chemistry – A European Journal*. 2011;**17**:4313-4322. DOI: 10.1002/chem.201003098
- [78] Bruce MRM, Megehee E, Sullivan BP, Thorp HH, O'Toole TR, Downard A, Pugh JR, Meyer TJ. Electrocatalytic reduction of carbon dioxide based on 2,2'-bipyridyl complexes of osmium. *Inorganic Chemistry*. 1992;**31**:4864-4873. DOI: 10.1021/ic00049a027
- [79] Sato S, Morikawa T, Kajino T, Ishitani O. A highly efficient mononuclear iridium complex photocatalyst for CO₂ reduction under visible light. *Angewandte Chemie International Edition In English*. 2013;**52**:988-992. DOI: 10.1002/anie.201206137
- [80] Kang P, Cheng C, Chen Z, Schauer CK, Meyer TJ, Brookhart M. Selective electrocatalytic reduction of CO₂ to formate by water-stable iridium dihydride pincer complexes. *Journal of the American Chemical Society*. 2012;**134**:5500-5503. DOI: 10.1021/ja300543s
- [81] Costentin C, Passard G, Savéant J-M. Benchmarking of homogeneous electrocatalysts: Overpotential, turnover frequency, limiting turnover number. *Journal of the American Chemical Society*. 2015;**137**:5461-5467. DOI: 10.1021/jacs.5b00914
- [82] Mukhopadhyay TK, MacLean NL, Gan L, Ashley DC, Groy TL, Baik M-H, Jones AK, Trovitch RJ. Carbon dioxide promoted H⁺ reduction using a bis(imino)pyridine manganese electrocatalyst. *Inorganic Chemistry*. 2015;**54**:4475-4482. DOI: 10.1021/acs.inorgchem.5b00315
- [83] Tanaka H, Tzeng BC, Nagao H, Peng SM, Tanaka K. Comparative study on crystal structures of ruthenium bipyridine carbonyl complexes [Ru(bpy)₂(CO)₂](PF₆)₂, [Ru(bpy)₂(CO)(C(O)OCH₃)]B(C₆H₅)₄·CH₃CN, and [Ru(bpy)₂(CO)(η¹-CO₂)]·3H₂O (bpy = 2,2'-bipyridyl). *Inorganic Chemistry*. 1993;**32**:1508-1512. DOI: 10.1021/ic00060a029
- [84] Hitoshi I, Hiroaki T, Koji T, Toshio T. Electrochemical reaction of CO₂ with Me₂NH to afford N,N-dimethylformamide, catalyzed by [Ru(bpy)₂(CO)₂]²⁺ (bpy = 2,2'-bipyridine). *Chemistry Letters*. 1987;**16**:597-600. DOI: 10.1246/cl.1987.597
- [85] Pugh JR, Bruce MRM, Sullivan BP, Meyer TJ. Formation of a metal-hydride bond and the insertion of carbon dioxide. Key steps in the electrocatalytic reduction of carbon dioxide to formate anion. *Inorganic Chemistry*. 1991;**30**:86-91. DOI: 10.1021/ic00001a016
- [86] Chardon-Noblat S, Deronzier A, Zsoldos D, Ziessel R, Haukka M, Pakkanen T, Venalainen T. Mode of formation of polymer [{Ru(bipy)(CO)₂}]_n (bipy = 2,2'-bipyridine) films. *Journal of the Chemical Society, Dalton Transactions*. 1996:2581-2583

- [87] Masciocchi N, Sironi A, Chardon-Noblat S, Deronzier A. X-ray powder diffraction study of organometallic polymers: [Ru(L)(CO)₂]_n (L = 2,2'-bipyridine or 1,10-phenanthroline). *Organometallics*. 2002;**21**:4009-4012. DOI: 10.1021/om020298x
- [88] Ishida H, Bünzli J-C, Beeby A. Guidelines for measurement of luminescence spectra and quantum yields of inorganic and organometallic compounds in solution and solid state (IUPAC technical report). *Pure and Applied Chemistry*. 2016;**88**:701. DOI: 10.1515/pac-2014-0706
- [89] Kalyanasundaram K. Photophysics, photochemistry and solar energy conversion with tris(bipyridyl)ruthenium(II) and its analogues. *Coordination Chemistry Reviews*. 1982;**46**:159-244. DOI: 10.1016/0010-8545(82)85003-0
- [90] Juris A, Balzani V, Barigelli F, Campagna S, Belser P, von Zelewsky A. Ru(II) polypyridine complexes: Photophysics, photochemistry, electrochemistry, and chemiluminescence. *Coordination Chemistry Reviews*. 1988;**84**:85-277. DOI: 10.1016/0010-8545(88)80032-8
- [91] Suzuki K, Kobayashi A, Kaneko S, Takehira K, Yoshihara T, Ishida H, Shiina Y, Oishi S, Tobita S. Reevaluation of absolute luminescence quantum yields of standard solutions using a spectrometer with an integrating sphere and a back-thinned CCD detector. *Physical Chemistry Chemical Physics*. 2009;**11**:9850-9860. DOI: 10.1039/b912178a
- [92] Tamaki Y, Ishitani O. Supramolecular photocatalysts for the reduction of CO₂. *ACS Catalysis*. 2017;**7**:3394-3409. DOI: 10.1021/acscatal.7b00440
- [93] Paul A, Connolly D, Schulz M, Pryce MT, Vos JG. Effect of water during the quantitation of formate in photocatalytic studies on CO₂ reduction in dimethylformamide. *Inorganic Chemistry*. 2012;**51**:1977-1979. DOI: 10.1021/ic202121s
- [94] Sekizawa K, Maeda K, Domen K, Koike K, Ishitani O. Artificial Z-scheme constructed with a supramolecular metal complex and semiconductor for the photocatalytic reduction of CO₂. *Journal of the American Chemical Society*. 2013;**135**:4596-4599. DOI: 10.1021/ja311541a
- [95] Nakada A, Nakashima T, Sekizawa K, Maeda K, Ishitani O. Visible-light-driven CO₂ reduction on a hybrid photocatalyst consisting of a Ru(II) binuclear complex and a Ag-loaded TaON in aqueous solutions. *Chemical Science*. 2016;**7**:4364-4371. DOI: 10.1039/c6sc00586a
- [96] Kajiwaru T, Fujii M, Tsujimoto M, Kobayashi K, Higuchi M, Tanaka K, Kitagawa S. Photochemical reduction of low concentrations of CO₂ in a porous coordination polymer with a ruthenium(II)-CO complex. *Angewandte Chemie, International Edition*. 2016;**55**:2697-2700. DOI: 10.1002/anie.201508941
- [97] Sun D, Gao Y, Fu J, Zeng X, Chen Z, Li Z. Construction of a supported Ru complex on bifunctional MOF-253 for photocatalytic CO₂ reduction under visible light. *Chemical Communications*. 2015;**51**:2645-2648. DOI: 10.1039/c4cc09797a
- [98] Wang X, Thiel I, Fedorov A, Coperet C, Mougél V, Fontecave M. Site-isolated manganese carbonyl on bipyridine-functionalities of periodic mesoporous organosilicas: Efficient CO₂ photoreduction and detection of key reaction intermediates. *Chemical Science*. 2017;**8**:8204-8213. DOI: 10.1039/c7sc03512h

- [99] Kuramochi Y, Sekine M, Kitamura K, Maegawa Y, Goto Y, Shirai S, Inagaki S, Ishida H. Photocatalytic CO₂ reduction by periodic mesoporous organosilica (PMO) containing two different ruthenium complexes as photosensitizing and catalytic sites. *Chemistry – A European Journal*. 2017;**23**:10301-10309. DOI: 10.1002/chem.201701466
- [100] Ueda Y, Takeda H, Yui T, Koike K, Goto Y, Inagaki S, Ishitani O. A visible-light harvesting system for CO₂ reduction using a RuII-ReI photocatalyst adsorbed in mesoporous organosilica. *ChemSusChem*. 2015;**8**:439-442. DOI: 10.1002/cssc.201403194
- [101] Takeda H, Ohashi M, Tani T, Ishitani O, Inagaki S. Enhanced photocatalysis of rhenium(I) complex by light-harvesting periodic mesoporous organosilica. *Inorganic Chemistry*. 2010;**49**:4554-4559. DOI: 10.1021/ic1000914

IntechOpen