

Synthesis, structures and electrochemical properties of ruthenium (II) complexes bearing bidentate 1,8-naphthyridine and terpyridine analogous (N,N,C)-tridentate ligands

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Abstract

1,8-Naphthyridine (napy) and terpyridine-analogous (N,N,C) tridentate ligands coordinated ruthenium (II) complexes, $[\text{RuL}(\text{napy-}\kappa^2\text{N,N}')(\text{dmsO})](\text{PF}_6)_2$ (**1**: $\text{L}=\text{L}^1=\text{N}''\text{-methyl-4'-methylthio-2,2':6',4''-terpyridinium}$, **2**: $\text{L}=\text{L}^2=\text{N}''\text{-methyl-4'-methylthio-2,2':6',3''-terpyridinium}$) were prepared and their chemical and electrochemical properties were characterized. The structure of complex **1** was determined by X-ray crystallographic study, showing that it has a distorted octahedral coordination style. The cyclic voltammogram of **1** in DMF exhibited two reversible ligand-localized redox couples. On the other hand, the CV of **2** shows two irreversible cathodic peaks, due to the Ru–C bond of **2** containing the carbenic character. The IR spectra of **1** in CO_2 -saturated CH_3CN showed the formation of Ru-($\eta^1\text{-CO}_2$) and Ru–CO complexes under the controlled potential electrolysis of the solution at -1.44 V (vs. Fc/Fc^+). The electrochemical reduction of CO_2 catalyzed by **1** at -1.54 V (vs. Fc/Fc^+) in DMF-0.1 M Me_4NBF_4 produced CO with a small amount of HCO_2H .

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Keywords: Ruthenium; IR spectroscopy; CO_2 reduction; Electrochemistry; N,N,C ligands

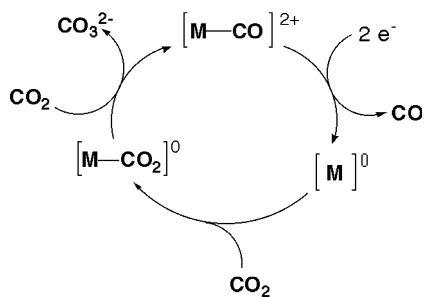
1. Introduction

Ruthenium complexes bearing polypyridyl ligand (2,2'-bipyridine (bpy), 2,2':6',2''-terpyridine (terpy), etc.) have attracted increasing attention as a catalyst for the photo- and electrochemical reactions [1]. Some of polypyridyl(carbonyl)ruthenium complexes work as homogeneous catalysts in the electrochemical reduction of carbon dioxide [2], where ligand localized redox reactions work as electron receivers in the reactions. Introduction of the metal–carbon σ -bond in the Ru-polypyridyl moiety would induce substantial changes

of the electron density of the metal center and the redox potential of the complexes compared with those of Ru-polypyridyl ones [3–10]. Along the line, we have examined the redox behavior of ruthenium complexes bearing terpy-analogous (N,N,C)-tridentate ligands containing a quaternized framework [10]. To our knowledge, there have not been investigated the electrochemical reduction of CO_2 by using the complexes containing these (N,N,C) or (N,C,N) tridentate ligands. Scheme 1 shows the proposed reduction mechanism of the electrochemical reduction of carbon dioxide catalyzed by a ruthenium carbonyl complex bearing polypyridyl ligands in aprotic solvents. When the Ru–CO complex receives two electrons, the Ru–CO bond becomes labile and penta-coordinated-electron rich intermediate is produced. In the presence of carbon dioxide, which is a kind of Lewis

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Scheme 1.

acid, the empty coordination site is occupied by CO_2 to give an $\text{Ru}-(\eta^1\text{-CO}_2)$ intermediate, followed by the disproportionation with another CO_2 molecule to reproduce the Ru-CO complex with production of CO_3^{2-} . If $\text{Ru}-(\eta^1\text{-CO}_2)$ and Ru-CO complexes (or their one- or two electron reduced products) that are intermediates of the electrochemical CO_2 reduction can be observed under the electrochemical reduction atmosphere, they can become strong evidences for the above-mentioned reaction mechanism correctness. However, there have been few examples for observations of the coordination process of CO_2 to the metal center and the transformation process of CO_2 to CO by spectroscopic methods [11], in particular, to our knowledge, no report for ruthenium complexes. In this study, we have prepared ruthenium complexes bearing 1,8-naphthyridine (napy) and a quaternized (N,N,C)-tridentate ligand to elucidate the catalytic activity toward the reduction of carbon dioxide. Napy gives rise to the exchange of coordination mode between monodentate and bidentate easily, thus the complex containing chelated napy could smoothly provide the coordination site for CO_2 when the complex is reduced. We have succeeded the observation of the $\text{Ru}-(\eta^1\text{-CO}_2)$ and Ru-CO complexes as intermediates of electrochemical CO_2 reduction by infrared spectroscopic studies under controlled potential electrolysis conditions in CO_2 -saturated MeCN, and have demonstrated the electrochemical reduction of CO_2 by using the ruthenium complex as a catalyst precursor.

2. Experimental

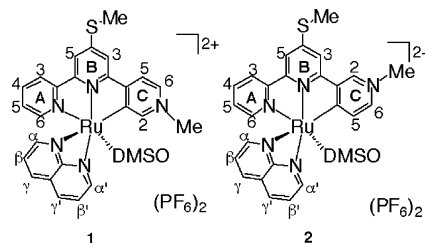
2.1. General, measurement, and materials

^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^1\text{H}-^1\text{H}$ COSY NMR spectra were recorded on a JEOL GX-500 spectrometer. IR spectra were recorded on a Shimadzu-FTIR 8100 spectrophotometer. Electronic spectra were collected on a Shimadzu UV-3100PC UV-Vis-NIR scanning spectrometer. ESI-MS spectra were obtained on a Shimadzu LCMS-2010 spectrometer. Electrochemical measurements were performed with ALS/chi Electrochemical Analyzer 660A. A conventional three-electrode configuration was used,

with a glassy carbon working (BAS PFCE carbon electrode) and a platinum wire auxiliary electrode (BAS special order) and an Ag/Ag^+ reference (BAS RE-5). Cyclic voltammograms were recorded at a scan rate of 100 mV s^{-1} . Electrochemical reduction of CO_2 was performed in CO_2 -saturated DMF containing a ruthenium complex ($1.0 \times 10^{-3} \text{ mol L}^{-1}$), Me_4NBF_4 (0.1 mol L^{-1}) as a supporting electrolyte, and $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ ($1.0 \times 10^{-2} \text{ mol L}^{-1}$) as an electron carrier under controlled potential electrolysis at -1.45 to -1.60 V (vs. Fc/Fc^+). The electrolysis cell consisted of a glassy carbon working electrode, a magnesium ribbon auxiliary electrode, and an Ag/AgNO_3 0.1 M reference electrode. The electrolysis was performed with a Hokuto Denko HA-501 potentiostat, and the electricity consumed was measured with a Hokuto Denko HF-201 Coulomb meter. Carbon dioxide evolved in the gaseous phase was analyzed by a Shimadzu GC-8A gas chromatograph equipped with a 2 m column filled with Molecular Sieve 13X at 40°C using He as the carrier gas. The amount of HCO_2H produced in the reduction was measured by a Shimadzu IP-3A isotachopheric analyzer. Elemental analyses were carried out by the Molecular Scale Nano-Science Center of IMS. $(\text{L}^1\text{H})(\text{PF}_6)$ [10a], $(\text{L}^2\text{H})(\text{PF}_6)$ [10a], and $\text{RuCl}_2(\text{napy-}\kappa^2\text{N,N}')(\text{dms})_2$ [10b] were prepared according to the literature method. Solution IR spectra under electrolysis conditions were obtained by using a KBr cell equipped with a spacer made of Novix Films (purchased from Iwaki Co. Ltd.), an Au mesh for a working electrode, a Pt wire for an auxiliary electrode, and a luggin capillary to separate a reference electrode from the working electrode. The thickness of the cell was 0.3 mm , and the total cell volume was 0.1 cm^3 . A CH_3CN or CD_3CN solution containing a metal complex ($1 \times 10^{-2} \text{ mol L}^{-1}$) and Me_4NBF_4 ($5 \times 10^{-2} \text{ mol L}^{-1}$) in the IR cell was exposed to an IR ray only on measuring to prevent the evaporation of CO_2 from the solution. The numbering of aromatic protons of **1** and **2** is shown in Scheme 2.

2.2. preparation of $[\text{RuL}^1(\text{napy-}\kappa^2\text{N,N}')(\text{dms})](\text{PF}_6)_2$ (**1**)

To a $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$ solution (20 mL) of $\text{RuCl}_2(\text{napy-}\kappa^2\text{N,N}')(\text{dms})_2$ (100 mg, 0.218 mmol) was added a $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$ solution (5 mL) of AgPF_6



Scheme 2.

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