Mechanistic Investigation of CO_2 Activation on Ruthenium(II) Bipyridine Complexes

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1992

To my parents

Contents

Abstracts

Utilization of CO_2 under mild conditions is interesting in the viewpoints of predictable energy shortage in near future and the increase in the concentration of CO_2 in the atmosphere. Photo- and electrochemical CO_2 reductions using homogeneous catalysts have been intensively studied, and several reaction mechanisms have been proposed so far. None of them, however, is generally accepted due to the lack of the evidence concerning the structural changes in the conversion from CO_2 to CO on metal atoms. Such the fundamental problem, therefore, may be provided the elucidation of the bonding characters between CO_2 and metal complexes of the reaction intermediates, and the relative nucleophilicities of CO_2 and proton toward metal centers in protic media. The purpose of the present work is to give some insight into the reaction mechanism of the electro- and photochemical CO_2 reduction catalyzed by metal complexes.

To clarify the acidity of CO ligated on metal complexes may give fundamental information on the conversion of CO_2 to CO. It is reported that not only CO but also NO ligated on some metals reversibly react with OH^- to form $M\text{-}XO_2$ and M-X(O)OH complexes (X=C, N) in H_2O. The acidity of those ligands, however, has not been directly compared with each other under the same conditions, so far. In the Chapter II, $[Ru(NO_2)(CO)(bpy)_2]PF_6$ (bpy=2,2'-bipyridine) was prepared by a reaction of $[RuCl(CO)(bpy)_2]PF_6$ with $NaNO_2$ in order to elucidate the acidic and basic characters of CO and NO_2^- ligands on Ru. X-Ray structural analysis of $[Ru(NO_2)(CO)(bpy)_2]PF_6$ reveals that CO and NO_2 ligands on Ru(II) are in a cis-position. The Ru-N (bpy ligands) bond distances (trans to CO and NO_2^-) are 2.10 (1) and 2.11 (1) Å, respectively, and the remaining two Ru-N bond distances (trans to bpy ligands) are 2.07 (1) and 2.08 (1) Å. Thus, any distinct differences between CO and NO_2^- ligands were not observed from the Ru-N bond distances. Treatment of $[Ru(NO_2)(CO)(bpy)_2]^+$ with HCl resulted in the formation of $[RuCl(CO)(bpy)_2]^+$, and a reaction product of $[Ru(NO_2)(CO)(bpy)_2]^+$ with H_2SO_4 showed $\nu(C{\equiv}O)$ and $\nu(N{\equiv}O)$ at 1968 and 1911 cm^{-1}, respectively. On the other hand, $[Ru(NO_2)(CO)(bpy)_2]^+$ reversibly reacts with Bu_4NOH to afford $[Ru(C(O)OH)(NO_2)(bpy)_2]$ in CH_3CN. These results indicate that the acidity of a carbonyl ligand is weaker than a nitrosyl one.

Among a variety of CO_2 metal complexes, η^1(C)-CO_2 metal complexes are generally believed to be plausible intermediates in the electrochemical CO_2 reduction affording CO. In the Chapter III, the molecular structures of $[Ru(CO)_2(bpy)_2](PF_6)_2$, $[Ru(C(O)OCH_3)(CO)(bpy)_2]BPh_4{\cdot}CH_3CN$ as a model of $[Ru(C(O)OH)(CO)(bpy)_2]^+$, and $[Ru(\eta^1(C)\text{-}CO_2)(CO)(bpy)_2]{\cdot}3H_2O$ were described. The latter two were prepared by the reactions of $[Ru(CO)_2(bpy)_2]^{2+}$ with CH_3ONa and two equiv of OH^-. On the basis of the fact that the Ru-$C(O)OCH_3$ bond distance of $[Ru(C(O)OCH_3)(CO)(bpy)_2]^+$ is shorter than the Ru-CO_2 one of $[Ru(\eta^1(C)\text{-}CO_2)(CO)(bpy)_2]$, a multi-bond character of the Ru-CO_2 bond is not larger than that of the Ru-$C(O)OCH_3$ bond. One extra electron pair involved

in $[Ru(\eta^1(C)\text{-}CO_2)(CO)(bpy)_2]$ resulting from dissociation of the terminal proton of $[Ru(C(O)OH)(CO)(bpy)_2]^+$ may, therefore, localize mainly in the CO_2 ligand. The increase in the electron density of the CO_2 moiety is effectively compensated by the extended three-dimensional network of hydrogen bondings between the CO_2 ligand and three water molecules of $[Ru(\eta^1(C)\text{-}CO_2)(CO)(bpy)_2]\cdot 3H_2O$.

Smooth conversion of $[Ru(\eta^1(C)\text{-}CO_2)(CO)(bpy)_2]$ to $[Ru(C(O)OH)(CO)(bpy)_2]^+$ is the one of the key reactions in the catalytic cycle of the CO_2 reduction by $[Ru(CO)_2(bpy)_2]^{2+}$. In the Chapter IV, the reactivity of $[Ru(\eta^1(C)\text{-}CO_2)(CO)(bpy)_2]$ was examined to elucidate the basicity of the CO_2 moiety. All the oxygen atoms of $[Ru(\eta^1(C)\text{-}CO_2)(CO)(bpy)_2]$ undergo an exchange reaction by $H_2{}^{18}O$. The reactions of $[Ru(\eta^1(C)\text{-}CO_2)(CO)(bpy)_2]$ with CH_3I and ICH_2CH_2I gave $[Ru(C(O)OCH_3)(CO)(bpy)_2]^+$ and $[RuI(CO)(bpy)_2]^+$ in quantitative yields. A C-H bond of organic molecules with active hydrogen such as malonic acid derivatives was also cleaved by the CO_2 moiety of $[Ru(\eta^1(C)\text{-}CO_2)(CO)(bpy)_2]$.

There still remains a matter of controversy about the initial step of the CO_2 reduction catalyzed by metal complexes, which of proton or CO_2 initially attacks on low valent metal centers. In the Chapter V, interaction between CO_2 and reduced quinones is examined in CH_3CN, CH_3CN/H_2O, and CH_3OH to evaluate the nucleophilicity of CO_2 in protic media. Carboxylation predominantly took place on the oxygen atoms of 2,3,5,6-tetramethyl-1,4-benzoquinone dianion in CO_2-saturated CH_3OH and CH_3CN/H_2O (9:1 v/v). This result implies the formation of M-CO_2 bond rather than that of M-H one in catalytic cycles in photo- and electrochemical CO_2 reduction catalyzed by transition metal complexes.

Abbreviations

bpy	2,2'-bipyridine
SCE	saturated calomel electrode
TCNE	tetracyanoethylene
CV	cyclic voltammogram
TMQ	2,3,5,6-tetramethyl-1,4-benzoquinone
TCQ	2,3,5,6-tetrachloro-1,4-benzoquinone
TBQ	2,3,5,6-tetrabromo-1,4-benzoquinone
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
dmpe	1,2-bis(dimethylphosphino)ethane

Chapter I

General Introduction

The rapid increase in the concentration of CO_2 in the atmosphere due to consumption of fossil fuels may cause the serious problem for human beings in near future. Disposal of CO_2 exhausted from power plants into the deep seas has been proposed to cope with this problem.[1] Thus, CO_2 is considered as useless materials at present. On the other hand, if CO_2 can be activated and converted to organic molecules under mild conditions, CO_2 will be recognized as C_1 resources as well as CO in the chemical industry. Activation of CO_2 under mild conditions, therefore, may open a new era in the chemistry of CO_2.

The bond dissociation energy of CO_2, D (C-O) = 5.453 eV (127 kcal), is much larger than COS, N_2O, and CS_2 that have a linear three-atom structure with the isoelectronic structure as CO_2, and only a few percent CO_2 molecules are cleaved to CO and oxygen even at 2000 °C.[2] Thus, CO_2 as the ultimate oxidation product of organic compound is a very stable molecule thermodinamically. CO_2 is lacking in donor ability, because of its large ionization potential of 13.79 eV. On the other hand, the electron affinity of CO_2, 3.6-3.8 eV, is close to that of NO and $CH\equiv CH$. On the basis of the analysis of ^{13}C ESR of CO_2^- in a formate matrix, 80% of the electron of the frontier orbital is localized in the C atom of CO_2^- [2] with the O-C-O angle of 134°.[4] This means that the C atom of CO_2 readily can be changed to a strong nucleophile once CO_2 undergoes one-electron reduction. Therefore, electrochemical, photochemical, and chemical reductions are suitable procedures for the activation of CO_2. It is, however, required at potentials more negative than -2.1 V *vs.* SCE to reduce CO_2 to CO_2^- at moderate rates by an electrode directly.[3]

In case that adsorption and coordination of CO_2 on the surface of solids and metal complexes are possible, an electron transfer to CO_2 is expected to take place at potentials much more positive than the reduction potential of free CO_2. Under such notion, electrochemical and photochemical reductions of CO_2 catalyzed by transition metal complexes have been widely studied, and various homogeneous[5] and heterogeneous[6] catalysts which are capable of affording CO, HCOOH, HCHO, CH_3OH, and/or CH_4 have been reported. No reaction intermediate which can activate CO_2, however, has been isolated in those reactions so far and the reaction schemes have been proposed without any evidence. In addition, comparison of acidity between H^+ and CO_2, the former of which is also requisite for CO_2 reduction, has not been investigated in spite of a controversy about the initial stage of the reduction; either proton or CO_2 attacks on low valent coordinatively unsaturated metal centers. In the former, metal-hydride (M-H) bonds are initially formed, followed by insertion of CO_2 to the resulting M-H bonds to generate formato complexes (M-OC(O)H)[5f]. On the other hand, protonation of M-CO_2 formed in the latter[12] would produce metal carboxylates (M-

C(O)OH), although another path from M-H to M-C(O)OH has been proposed without any evidence.[5s]

Synthesis of CO_2 complexes has intensively been attempted to aim activation of CO_2 on metal atoms.[7] The first one is the Rh complex, $[Rh_2Cl_2(CO_2)(PPh_3)_5]$, reported by Val'pin et al. in 1969.[7a] Although many CO_2 complexes have been prepared after the Rh complex, X-ray structure analysis, which is necessary to comprehend character of ligated CO_2, is achieved for only a few CO_2 complexes. The study of the CO_2 complexes has been limited to the reactivity in stoichiometric reactions[8-11] and no catalytic fixation or reduction of CO_2 has been succeeded so far.

Along this line, I paid attention to $[Ru(CO)_2(bpy)_2]^{2+}$ having an ability to catalyze electrochemical[12] and photochemical[13] CO_2 reduction. It has been reported that $[Ru(CO)_2(bpy)_2]^{2+}$ exists as equilibrium mixtures with $[Ru(C(O)OH)(CO)(bpy)_2]^+$ and its deprotonated species $[Ru(CO_2)(CO)(bpy)_2]$ (eqs 1 and 2) with the equilibrium constants, K_1 and K_2 of 1.32×10^5 and 2.27×10^4 $mol^{-1}\cdot dm^3$, respectively, in H_2O, and the conversion

$$[Ru(CO)_2(bpy)_2]^{2+} + OH^- \overset{K_1}{\rightleftharpoons} [Ru(C(O)OH)(CO)(bpy)_2]^+ \qquad (1)$$

$$[Ru(C(O)OH)(CO)(bpy)_2]^+ + OH^- \overset{K_2}{\rightleftharpoons} [Ru(CO_2)(CO)(bpy)_2] + H_2O \qquad (2)$$

between $[Ru(CO_2)(CO)(bpy)_2]$ and $[Ru(C(O)OH)(CO)(bpy)_2]^+$ takes place in a diffusion controlled reaction.[14] Those complexes function as active species in not only CO_2 reduction but also a water gas shift reaction.[14] Furthermore, two electron reduction of $[Ru(CO)_2(bpy)_2]^{2+}$ in dry CH_3CN under a CO_2 atmosphere produces $[Ru(CO_2)(CO)(bpy)_2]$[15] with evolution of CO (eq 3).[13] It is, therefore, proposed that $[Ru(CO_2)(CO)(bpy)_2]$ formed in eq 2 is a kind of an η^1(C)-CO_2 complex.

$$[Ru(CO)_2(bpy)_2]^{2+} + CO_2 + 2e^- \longrightarrow [Ru(CO_2)(CO)(bpy)_2] + CO \qquad (3)$$

In order to give some insight into the structural changes in the conversion of CO_2 to CO on metal complexes and the relative nucleophilicities of CO_2 and protons in protic media, this thesis discusses the acidic and basic character of CO and NO_2^- ligated on bis(bpy)ruthenium complexes, X-ray structure analysis of $[Ru(CO_2)(CO)(bpy)_2]$, $[Ru(C(O)OCH_3)(CO)(bpy)_2]^+$ as a model compound of $[Ru(C(O)OH)(CO)(bpy)_2]^+$, and $[Ru(CO)_2(bpy)_2]^{2+}$, the reactivity of $[Ru(CO_2)(CO)(bpy)_2]$, and comparison of acidity of H^+ and CO_2 in protic media.

Chapter II

Comparison of Acidity between CO and NO Coordinated to *cis*-Bis(2,2'-bipyridine)ruthenium Complex

Introduction

CO_2 and NO_2^- ligated on ruthenium(II) complexes can be smoothly converted into CO and nitrosyl ligands by acid-base equilibria. For example, *cis*-$[Ru(CO)_2(bpy)_2]^{2+}$ reversibly reacts with OH^- in a neutral aqueous solution to afford *cis*-$[Ru(C(O)OH)(CO)(bpy)_2]^+$, which dissociates the hydroxycarbonyl proton to form $[Ru(CO_2)(CO)(bpy)_2]$ in alkaline solution. Carbonyl, hydroxycarbonyl and CO_2 complexes exist as an equilibrium mixture in weak alkaline conditions, as described in Chapter I (eqs 1 and 2).[14] Similarly, *cis*- [16a] and *trans*-$[RuCl(bpy)_2(NO)]^{2+}$ [16b] are converted into *cis*- and *trans*-$[RuCl(NO_2)(bpy)_2]$ *via* $[RuCl(bpy)_2(NO_2H)]^+$ by a reversible nucleophilic attack of OH^- to nitrosyl ligand, followed by a dissociation of a terminal

$$[RuCl(bpy)_2(NO)]^{2+} + OH^- \rightleftharpoons [RuCl(bpy)_2(N(O)OH)]^+ \qquad (4)$$

$$[RuCl(bpy)_2(N(O)OH)]^+ + OH^- \rightleftharpoons [RuCl(NO_2)(bpy)_2] + H_2O \quad (5)$$

proton of hydroxynitrosyl moiety (eqs 4 and 5).[16] In electrochemical CO_2 reduction, the carbonyl complex of ruthenium has been considered as a precursor for CO generation.[12,13] Accordingly, comparison of the acidity between CO and NO ligated on a metal seems to be very interesting in connection with CO_2 reduction. I have prepared $[Ru(NO_2)(CO)(bpy)_2]^+$ in order to compare acidity of CO with NO among $[Ru(NO_2)(CO)(bpy)_2]^+$, $[Ru(CO)_2(bpy)_2]^{2+}$, and $[RuCl(NO_2)(bpy)_2]$. This chapter describes the crystal structure of *cis*-$[Ru(NO_2)(CO)(bpy)_2]PF_6$ and the reactivity of the complex toward OH^- and H^+.

Experimental Section

Preparation of $[Ru(NO_2)(CO)(bpy)_2]PF_6$. A CH_3OH/H_2O solution (30:1 v/v, 30 cm^3) containing $[RuCl(CO)(bpy)_2]PF_6$[14] (165 mg, 0.27 mmol) and $NaNO_2$ (49 mg, 0.71 mmol) was refluxed under an N_2 atmosphere for 24 h. On cooling the solution to -20 °C, orange $[Ru(NO_2)(CO)(bpy)_2]PF_6$ was crystallized in a 70% yield. Anal. Calcd for $C_{21}H_{16}F_6N_5O_3PRu$: C, 39.88; H, 2.55; N, 11.07. Found: C, 39.94; H, 2.69; N, 11.09. IR spectrum (KBr): $\nu(C{\equiv}O)$ 1983 cm^{-1}, $\nu_{as}(NO_2)$ 1372 cm^{-1}, $\nu_s(NO_2)$ 1316 cm^{-1}. Quite similarly, $[Ru(^{15}NO_2)(CO)(bpy)_2]PF_6$ was prepared by using $[RuCl(CO)(bpy)_2]PF_6$ and $Na^{15}NO_2$ (90% enriched, Isotech) in CH_3OH/H_2O. IR spectrum of $[Ru(^{15}NO_2)(CO)(bpy)_2]PF_6$: $\nu(C{\equiv}O)$ 1983 cm^{-1}, $\nu_{as}(^{15}NO_2)$ 1345 cm^{-1}, $\nu_s(^{15}NO_2)$ 1293 cm^{-1}.

This work is published in *Inorg. Chem.* **1992**, *31*, 1972.

X-Ray Crystallographic Studies. The reflections of X-ray analysis were collected by θ-2θ technique ($0 < 2\theta < 60°$) on an Enraf-Nonius CAD4-GX21 automated four-circle diffractometer with Mo Kα radiation (0.7107 Å). The 1792 independent reflections with $|F_o| > 3\sigma|F_o|$ were used for the structure refinement. All the calculations were carried out on a HITAC-M680H computer, using a UNICS III program. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions and included in the structure factor calculations. The data for crystal structure analysis are shown in Table I. The final coordinates and average temperature factors of the atoms without hydrogen atoms of $[Ru(NO_2)(CO)(bpy)_2]PF_6$ are shown in Table II.

Table I. Data for Crystal Structure Analysis of $[Ru(NO_2)(CO)(bpy)_2]PF_6$

formula	$C_{21}H_{16}F_6N_5O_3PRu$
fw	632.46
a, Å	11.112 (4)
b, Å	12.318 (4)
c, Å	17.501 (4)
Z; *V*, Å^3	4; 2395.5
space group	$P2_12_12_1$
D_{calcd}, g/cm^3	1.75
θ range, deg.	<30
no. of data used($\|F_o\|>3\sigma\|F_o\|$)	1792
no. of variables	417
final R/R_W, $^{a)}$%	6.44/6.82

a) $R = (\Sigma||F_o|-|F_c||)/\Sigma|F_o|$.
$R_W = [\Sigma W(|F_o|-|F_c|)^2]/\Sigma W|F_o|^2$.

Table II. Positional parameters and *B*(eq) Values for $[Ru(NO_2)(CO)(bpy)_2]^+$.

atom	x	y	z	*B*, Å^2
Ru1	0.0324(1)	0.2438(1)	0.3637(0)	3.5
N1	-0.0812(8)	0.0975(7)	0.3627(5)	3.7
N2	0.1385(7)	0.3847(7)	0.3752(6)	4.0
N3	0.0417(8)	0.2598(7)	0.4817(5)	4.1
N4	0.0088(8)	0.2524(7)	0.2464(5)	4.1
N5	0.1198(9)	0.3445(6)	0.3564(5)	3.9
O1	0.2472(11)	0.1024(10)	0.3668(8)	10.8
O2	-0.0536(16)	0.0289(11)	0.3963(11)	16.1
O3	-0.1481(14)	0.1010(12)	0.3322(11)	15.4
C1	0.1887(11)	0.4409(11)	0.3151(8)	4.9
C2	0.2613(13)	0.5264(9)	0.3305(8)	5.6
C3	0.2838(13)	0.5645(9)	0.4058(8)	5.4
C4	0.2325(12)	0.5056(11)	0.4643(9)	5.2
C5	0.1590(10)	0.4157(8)	0.4465(6)	2.9
C6	0.1012(10)	0.3515(8)	0.5067(6)	3.5
C7	0.1010(13)	0.3778(10)	0.5843(6)	4.8
C8	0.0410(13)	0.3142(10)	0.6333(7)	5.7
C9	-0.0174(11)	0.2211(9)	0.6077(7)	4.7
C10	-0.0152(12)	0.1975(9)	0.5321(7)	4.7
C11	0.0784(13)	0.2053(11)	0.1916(7)	5.4
C12	0.0490(15)	0.2067(12)	0.1173(7)	6.4
C13	-0.0470(14)	0.2640(11)	0.0919(7)	6.5
C14	-0.1194(13)	0.3127(10)	0.1459(8)	6.0
C15	-0.0885(11)	0.3072(9)	0.2246(6)	4.1
C16	-0.1618(11)	0.3620(8)	0.2839(6)	3.9
C17	-0.2614(12)	0.4262(10)	0.2679(8)	5.1
C18	-0.3214(13)	0.4750(10)	0.3289(9)	5.6
C19	-0.2779(12)	0.4612(10)	0.4019(9)	5.8
C20	-0.1753(13)	0.3956(10)	0.4121(8)	5.0
C21	0.1730(10)	0.1476(8)	0.3720(7)	3.9

Results and Discussion

The structure of $[Ru(NO_2)(CO)(bpy)_2]PF_6$ is presented in Figure 1. CO and NO_2^- on Ru(II) coordinate in cis-position. The structural parameters of two bpy ligands are not so different from those of the cis-type of bis-(bpy)ruthenium complexes reported so far.[17] The two oxygen atoms of the nitro group were disordered presumably due to a rotation around the Ru-N1 bond (2.20 (1) Å), and the O2-N1-O3 angle of the nitro ligand (126 (2)°) is also approximately same as that of nitro complexes reported elsewhere.[18] The Ru-C and C-O bond lengths are 1.97 (1) and 1.02 (2) Å, respectively. The Ru-C-O angle, 170 (1)°, shows slight distortion. The Ru-N3 distance (trans to bpy), 2.08 (1) Å, is very close to that for Ru-N4 (trans to bpy), 2.07 (1) Å. In addition, the Ru-N5 (trans to CO) distance, 2.10 (1) Å, is also close to the Ru-N2 (trans to NO_2) distance, 2.11 (1) Å. A distinct difference in electron-donor and/or acceptor character of the carbonyl and nitro ligands of $[Ru(NO_2)(CO)(bpy)_2]^+$ was not observed from the comparison of bond lengths between Ru and bpy ligands. Since the resulting complex has CO and NO_2^- ligands, NO ligated on a metal seems to be more acidic than CO ligand.

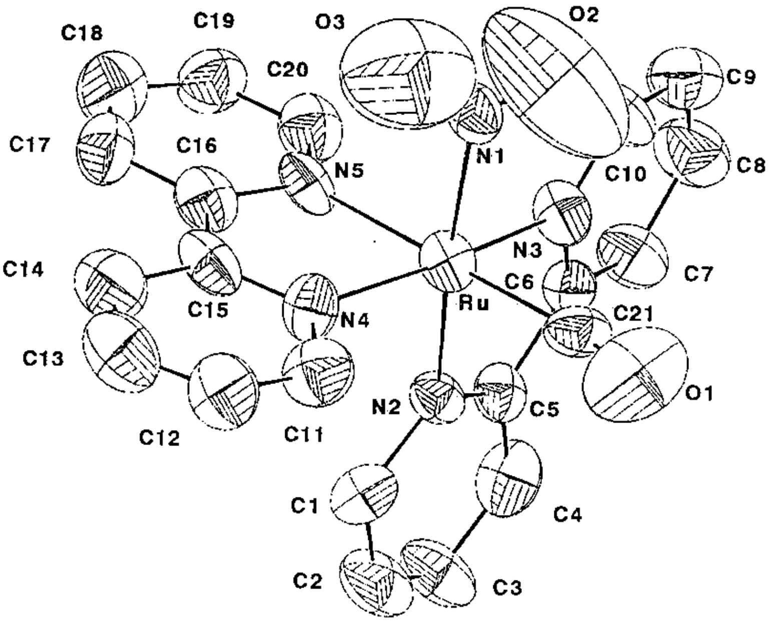

Figure 1. Molecular structure of $[Ru(NO_2)(CO)(bpy)_2]^+$.

Although two oxygen atoms of the nitro group of $[Ru(NO_2)(CO)(bpy)_2]PF_6$ are disordered in the solid state, dissociation of NO_2^- from $[Ru(NO_2)(CO)(bpy)_2]^+$ may be neglected in a solution, since no ligand exchange between NO_2^- and $^{15}NO_2^-$ took place at all in the reaction of $[Ru(NO_2)(CO)(bpy)_2]PF_6$ with 2 equiv of $Na^{15}NO_2$ in MeOH for 2 days.[19] The electronic absorption spectrum of $[Ru(NO_2)(CO)(bpy)_2]PF_6$ showed no change between acidic (pH 1.0) and alkaline (pH 12.0) aqueous solutions. On the basis of smooth reactions of eqs 1 and 5 in H_2O, both CO and NO_2^- of $[Ru(NO_2)(CO)(bpy)_2]^+$ are considered to be less reactive than the CO of $[Ru(CO)_2(bpy)_2]^{2+}$ and NO_2^- of $[RuCl(NO_2)(bpy)_2]$. It is well known that basicity of OH^- is effectively enhanced in organic solvents compared with that in H_2O.[20] In fact, an addition of a methanolic solution of Bu_4NOH (0.26 mol/dm^3) to a CH_3CN solution of $[Ru(NO_2)(CO)(bpy)_2]PF_6$ (0.055 mmol/dm^3) results in an increase in electronic absorption bands at 290 and 490 nm with an isosbestic point at 310 nm up to a certain concentration of OH^- (0.35 mmol/dm^3) (Figure 2), and neutralization of the resulting solution by aqueous $HClO_4$ (0.20 mol/dm^3) regenerated the electronic absorption spectrum of $[Ru(NO_2)(CO)(bpy)_2]^+$. However, an addition of a large excess of Bu_4NOH into a CH_3CN solution of $[Ru(NO_2)(CO)(bpy)_2]PF_6$ (0.102 mmol/dm^3) caused a decrease in the absorbance at the 490 nm band and an appearance of a new band at 585 nm, which remained even after neutralization by aqueous $HClO_4$. In accordance with these observations, a crude product obtained from the reaction of $[Ru(NO_2)(CO)(bpy)_2]PF_6$ with 2 equiv of KOH in CH_3OH showed strong IR bands at 1650, 1378, and 1331 cm^{-1} assigned to $\nu(C=O)$ of a hydroxycarbonyl moiety,[21] $\nu_{as}(NO_2)$, and $\nu_s(NO_2)$, respectively, with a weak $\nu(C\equiv O)$ band at 1983 cm^{-1} due to a contamination of $[Ru(NO_2)(CO)(bpy)_2]PF_6$, and neutralization of the product by aqueous HCl in MeOH regenerated $[Ru(NO_2)(CO)$-

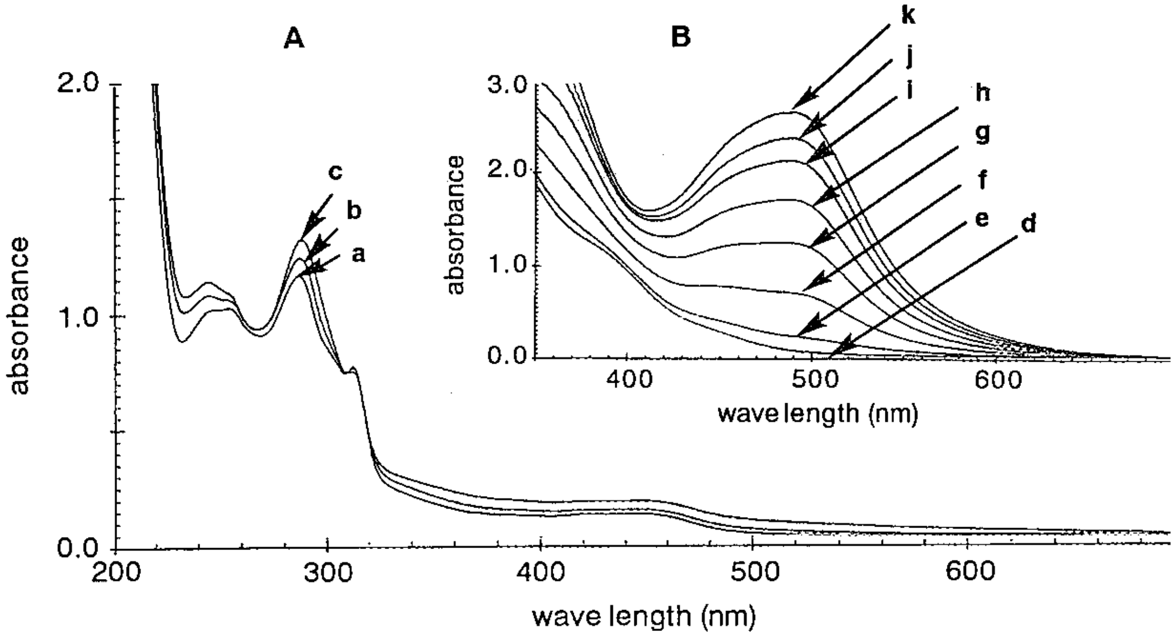

Figure 2. Electronic absorption spectra of $[Ru(NO_2)(CO)(bpy)_2]PF_6$ (5.50×10^{-5} mol dm^{-3} (A) and 4.08×10^{-4} mol dm^{-3} (B)) in CH_3CN in the presence of various concentrations of Bu_4NOH: 0 (a and d); 1.73 (b); 3.46 (c); 2.04 (e); 3.06 (f); 4.04 (g); 5.10 (h); 6.08 (i); 7.10 (j); 8.16 $\times 10^{-4}$ mol dm^{-3} (k).

$(bpy)_2]^+$. On the other hand, when $[Ru(NO_2)(CO)(bpy)_2]PF_6$ was allowed to react with 20 equiv of Bu_4NOH in MeOH, the reaction product exhibited only a strong band at 1574 cm^{-1} without any $\nu(NO_2)$ band. These observations suggest that $[Ru(NO_2)(CO)(bpy)_2]^+$ reversibly is converted into $[Ru(C(O)OH)(NO_2)(bpy)_2]$ in low OH^- concentrations in MeOH (eq 6),[22] while $[Ru(NO_2)(CO)(bpy)_2]^+$ decomposes in the presence of a large excess of OH^- presumably by dissociation of NO_2^- from unstable $[Ru(C(O)O)(NO_2)(bpy)_2]^-$.

$$[Ru(NO_2)(CO)(bpy)_2]^+ + OH^- \rightleftharpoons [Ru(C(O)OH)(NO_2)(bpy)_2] \quad (6)$$

As similar to the lability of the $Ru\text{-}NO_2^-$ bond of $[Ru(NO_2)(CO)(bpy)_2]^+$ in the presence of a large excess of OH^- in MeOH, treatment of $[Ru(NO_2)(CO)(bpy)_2]PF_6$ with an excess amount of gaseous HCl or aqueous HCl (10 mol/dm^3) in CH_3OH caused loss of the NO_2^- ligand, and $[RuCl(CO)(bpy)_2]PF_6$ was selectively formed in a ca. 80% yield. On the basis of the fact that $[Ru(NO_2)(CO)(bpy)_2]PF_6$ undergoes no substitution reaction by either $Na^{15}NO_2$ or Et_4NCl in MeOH, the formation of $[RuCl(CO)(bpy)_2]^+$ in the reaction of $[Ru(NO_2)(CO)(bpy)_2]^+$ with HCl may result from fission of the $Ru\text{-}NO_2^-$ bond after protonation of NO_2^- of $[Ru(NO_2)(CO)(bpy)_2]^+$ in MeOH. In fact, the IR spectra of the crude products obtained from the reaction of $[Ru(NO_2)(CO)(bpy)_2]PF_6$ with H_2SO_4 in MeOH showed two strong bands at 1968 and 1911 cm^{-1} assignable to the $\nu(C{\equiv}O)$ and $\nu(N{\equiv}O)$ of $[Ru(CO)(bpy)_2(NO)]^{3+}$. Regeneration of $[Ru(NO_2)(CO)(bpy)_2]^+$ on exposure of $[Ru(CO)(bpy)_2(NO)]^{3+}$ to air (moisture) also implies that the NO ligated on a Ru(II) atom is more acidic than a CO ligand.

Chapter III

Structure Difference in *cis*-Bis(2,2'-bipyridine)(η^1(C)-carbon dioxide)carbonylruthenium, *cis*-Bis(2,2'-bipyridine)(carbonyl)hydroxycarbonylruthenium, and *cis*-Bis(2,2'-bipyridine)dicarbonylruthenium

Introduction

Since the first characterization of $[Ni(PCy_3)_2(\eta^2\text{-}CO_2)]$,[3c] a variety of CO_2-metal complexes with η^1-,[8] η^2-,[9] μ_2-,[10] and μ_3-[11] CO_2 modes have been prepared. In high oxidation metal complexes, the $\eta^1(C)\text{-}CO_2$ mode may be thermodynamically unstable due to an electronic repulsion between positively charged CO_2 carbon and metal atoms. The $\eta^1(C)\text{-}CO_2$ mode, on the other hand, is favored by the charge transfer interaction from the d_{z^2} orbital of the low oxidation metals such as Rh(I) and Co(I) to the π^* orbital of CO_2,[23] and is considered to be more suitable than other modes as active species in the reduction of CO_2 to CO and/or HCOOH, since $[M(\eta^1(C)\text{-}CO_2)]^{n+}$ would be smoothly converted to $[M(C(O)OH)]^{(n+1)+}$ and $[M(CO)]^{(n+2)+}$. Despite intensive studies on catalytic CO_2 reduction by using homogeneous catalysts[5] in recent years, there are only two $\eta^1(C)\text{-}CO_2$ complexes,[8] which have been determined the molecular structure by X-ray analysis. It is, therefore, highly desired to elucidate the molecular structures of a series of $\eta^1(C)\text{-}CO_2$, hydroxycarbonyl, and carbonyl metal complexes as possible active species in photo- and electrochemical CO_2 reductions.

The comparison of the molecular structures of $[Ru(CO_2)(CO)(bpy)_2]$, $[Ru(C(O)OH)(CO)(bpy)_2]^+$ and $[Ru(CO)_2(bpy)_2]^{2+}$ may give fundamental information with respect to the smooth conversion among CO, C(O)OH, and CO_2 on the Ru atom. This chapter describes the molecular structures of $[Ru(CO)_2(bpy)_2]^{2+}$, $[Ru(C(O)OCH_3)(CO)(bpy)_2]^+$ as a model compound of $[Ru(C(O)OH)(CO)(bpy)_2]^+$, and $[Ru(CO_2)(CO)(bpy)_2]$.

Experimental Section

Materials $[Ru(CO)_2(bpy)_2](PF_6)_2$ and $[Ru(C(O)OH)(CO)(bpy)_2]PF_6$ were prepared according to literatures[24,14] $[Ru(C(O)OCH_3)(CO)(bpy)_2]B(C_6H_5)_4\cdot CH_3CN$ for X-ray structure analysis was similarly prepared as $[Ru(C(O)OCH_3)(CO)(bpy)_2]PF_6$[14] A methanolic Bu_4NOH solution (0.347 M) was used without further purification. CH_3OH was dried over molecular sieves(4A). CH_3CN was distilled over calcium hydride.

Preparation of $[Ru(CO_2)(CO)(bpy)_2]\cdot 3H_2O$ A methanolic solution (5 cm^3) of Bu_4NOH (0.347 M) was added to a stirred H_2O/C_2H_5OH solution (100 cm^3, 1:1 v/v) of $[Ru(CO)_2(bpy)_2](PF_6)_2$ (602 mg) . Slow evaporation of the resulting reddish yellow solution gave red crystals, which were washed with CH_3CN, and dried under reduced

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A part of this work is published in *Organometallics* **1992**, *11*, 1450 and *Organometallics* **1992**, *11*, 3171, and in press in *Inorg. Chem.*

pressure. Calcd for $C_{22}H_{22}N_4O_6Ru$: C, 48.98; H, 4.11; N, 10.38. Found: C, 48.86; H, 3.99; N, 10.37. Yield 340 mg (80%). Infrared spectrum (KBr) ν(C≡O) 1911 cm^{-1} and $\nu(CO_2)$ 1428, 1242 cm^{-1}. ^{13}C NMR (67.8 MHz, MeOH-*d4*) δ 203.9 and 210.2 (CO_2 and CO), 158.2, 157.7, 157.1, 156.6, 155.9, 155.8, 150.0, 149.1, 140.0, 139.9, 139.8, 137.8, 127.9, 127.7, 127.5, 127.4, 124.7, 124.6, 124.2, 123.6 (bpy).

^{13}C NMR Data for $[Ru(C(O)OH)(CO)(bpy)_2]PF_6$ in CD_3CN δ 201.5 and 205.1 (CO and hydroxycarbonyl) ; δ 158.3, 157.2, 156.7, 156.4, 156.1, 150.5, 148.6, 141.0, 140.8, 140.8, 139.6, 128.7, 128.6, 128.4, 128.2, 125.6, 125.3, 124.9, 124.4 (bpy).

Physical Measurements and Product Analysis Infrared spectra were obtained on a Shimadzu DR8000 spectrophotometer. ^1H and ^{13}C NMR were obtained on a JEOL EX270 spectrometer. Elemental analyses were carried out at Chemical Materials Center of Institute for Molecular Science.

X-Ray Crystallographic Studies The reflections of X-ray analysis were collected by θ-2θ technique ($0 < 2\theta < 55°$ for $[Ru(CO_2)(CO)(bpy)_2]\cdot 3H_2O$ and $[Ru(CO)_2(bpy)_2](PF_6)_2$, and $0 < 2\theta < 50°$ for $[Ru(C(O)OCH_3)(CO)(bpy)_2]B(C_6H_5)_4\cdot CH_3CN$ on an Enraf-Nonius CAD4-GX21 automated four-circle diffractometer with Mo Kα radiation (0.7107Å). The 2370 and 3770 for $[Ru(CO_2)(CO)(bpy)_2]\cdot 3H_2O$ and $[Ru(CO)_2(bpy)_2](PF_6)_2$, respectively, independent reflections with $|F_o| > 4\sigma|F_o|$, and 7219 for $[Ru(C(O)OCH_3)(CO)(bpy)_2]B(C_6H_5)_4\cdot CH_3CN$ with $|F_o| > 2\sigma|F_o|$ were used for the structure refinement. All the calculations were carried out on a HITAC-M680H computer, using a UNICS III program. The structures were solved by the heavy-atom method. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions and included in the structure factor calculations. The data for crystal structures analysis are shown in Table III. The selected bond distances and angles of $[Ru(CO_2)(CO)(bpy)_2]\cdot 3H_2O$, $[Ru(C(O)OCH_3)(CO)(bpy)_2]B(C_6H_5)_4\cdot CH_3CN$, and $[Ru(CO)_2(bpy)_2](PF_6)_2$ are shown in Tables IV, V, and VI.

Table III. Data for Crystal Structure Analysis of $[Ru(CO_2)(CO)(bpy)_2]\cdot 3H_2O$, $[Ru(C(O)OCH_3)(CO)(bpy)_2]B(C_6H_5)_4\cdot CH_3CN$, and $[Ru(CO)_2(bpy)_2](PF_6)_2$.

formula	$C_{22}H_{22}N_4O_6Ru$	$C_{49}H_{42}BN_5O_3Ru$	$C_{22}H_{16}F_{12}N_4O_2P_2Ru$
fw	539.51	860.77	759.39
a, Å	8.672 (2)	9.548 (3)	12.034 (2)
b, Å	12.279 (1)	13.004 (5)	16.434 (3)
c, Å	20.820 (4)	17.743 (4)	13.925 (3)
a, deg.	90.00	77.26 (3)	90.00
b, deg.	97.48 (6)	74.89 (2)	94.88 (1)
c, deg.	90.00	83.64 (3)	90.00
Z; *V*, $Å^3$	4, 2190.1 (7)	2, 2071.1 (12)	4, 2743.9 (9)
space group	$P2_1/n$	*P*-1	$P2_1/c$
D_{calcd}, g/cm^3	1.64	1.38	1.84
θ range, deg.	<27.5	<25	<27.5
no. of data used ($\lvert F_o\rvert > 4\sigma\lvert F_o\rvert$)$^{a)}$	2370	7219	3770
no. of variables	299	532	389
final *R*(*F*)/*RW*(*F*),$^{b)}$%	7.1/7.9	4.5/4.5	6.9/8.1

a) $|F_o| > 2\sigma|F_o|$ for $[Ru(bpy)_2(CO)(C(O)OCH_3)]B(C_6H_5)_4\cdot CH_3CN$. b) $R(F) = (\Sigma||F_o|-|F_c||)/\Sigma|F_o|$. $RW(F) = [\Sigma W(|F_o|-|F_c|)^2]/\Sigma W|F_o|^2$.

Table IV. Selected Bond distances (Å) and Bond Angles (deg) for $[Ru(CO_2)(CO)(bpy)_2]\cdot 3H_2O$.

Ru-C1	2.064 (13)	C1-Ru-C2	88.5 (6)	N1-Ru-N2	77.6 (4)
Ru-C2	1.815 (14)	C1-Ru-N1	88.7 (5)	N2-Ru-N3	88.5 (4)
Ru-N1	2.073 (10)	C1-Ru-N2	86.6 (4)	N3-Ru-N4	76.9 (4)
Ru-N2	2.133 (10)	C1-Ru-N3	172.6 (5)	N4-Ru-N1	167.0 (4)
Ru-N3	2.204 (10)	C1-Ru-N4	97.7 (5)	Ru-C1-O1	118.5 (9)
Ru-N4	2.105 (10)	C2-Ru-N1	96.7 (5)	Ru-C1-O2	120.6 (10)
C1-O1	1.245 (16)	C2-Ru-N2	172.7 (5)	O1-C1-O2	120.9 (12)
C1-O2	1.283 (15)	C2-Ru-N3	96.9 (5)	Ru-C2-O3	178.8 (11)
C2-O3	1.145 (17)	C2-Ru-N4	94.7 (5)		

Table V. Selected Bond Distances (Å) and Bond Angles (deg) for $[Ru(C(O)OCH_3)(CO)(bpy)_2]B(C_6H_5)_4\cdot CH_3CN$.

Ru-C1	2.042 (6)	C1-Ru-C2	88.5 (3)	C2-Ru-N1	95.6 (2)
Ru-C2	1.800 (7)	C1-Ru-N1	89.8 (2)	C2-Ru-N2	172.9 (2)
Ru-N1	2.070 (5)	C1-Ru-N2	89.1 (2)	C2-Ru-N3	98.8 (2)
Ru-N2	2.105 (5)	C1-Ru-N3	169.9 (2)	C2-Ru-N4	91.4 (2)
Ru-N3	2.151 (5)	C1-Ru-N4	95.9 (2)	Ru-C1-O1	125.4 (5)
Ru-N4	2.093 (5)	N1-Ru-N2	77.7 (2)	Ru-C1-O2	115.4 (4)
C1-O1	1.191 (8)	N2-Ru-N3	84.5 (2)	O1-C1-O2	119.2 (6)
C1-O2	1.344 (8)	N3-Ru-N4	77.0 (2)	C1-O2-C3	116.4 (6)
O2-C3	1.463 (9)	N4-Ru-N1	171.1 (2)	Ru-C2-C3	176.5 (6)
C2-O3	1.154 (8)				

Table VI. Selected Bond Distances (Å) and Bond Angles (deg) for $[Ru(CO)_2(bpy)_2](PF_6)_2$.

Ru-C1	1.865 (10)	C1-Ru-C2	88.8 (4)	N4-Ru-N1	169.5 (3)
Ru-C2	1.906 (9)	C1-Ru-N1	97.9 (3)	C2-Ru-N1	89.5 (3)
Ru-N1	2.095 (6)	C1-Ru-N2	93.9 (3)	C2-Ru-N2	175.9 (3)
Ru-N2	2.102 (6)	C1-Ru-N3	175.7 (3)	C2-Ru-N3	93.1 (3)
Ru-N3	2.073 (7)	C1-Ru-N4	88.7 (3)	C2-Ru-N4	98.9 (3)
Ru-N4	2.083 (6)	N1-Ru-N2	78.2 (3)	Ru-C1-O1	176.4 (8)
C1-O1	1.144 (12)	N2-Ru-N3	84.5 (2)	Ru-C2-O2	177.2 (7)
C2-O2	1.125 (11)	N3-Ru-N4	78.0 (2)		

Results and Discussion

Isolation of $[Ru(CO_2)(CO)(bpy)_2]\cdot 3H_2O$ A colorless H_2O/C_2H_5OH (1:1 v/v) solution of $[Ru(CO)_2(bpy)_2](PF_6)_2$ rapidly changed to yellow on an addition of an equimolar amount of a methanolic Bu_4NOH. Concentration of the solution afforded $[Ru(C(O)OH)(CO)(bpy)_2]PF_6$ as a yellow solid, which shows strong ν(C≡O) and ν(C=O) bands at 1946 and 1619 cm^{-1}.[14] These bands were shifted to 1904 and 1586 cm^{-1} after the hydroxycarbonyl complex was dissolved in $CH_3OH/CH_3CN/H_2{}^{18}O$ (5:2:1 v/v) for 30 min. On the other hand, the H_2O /

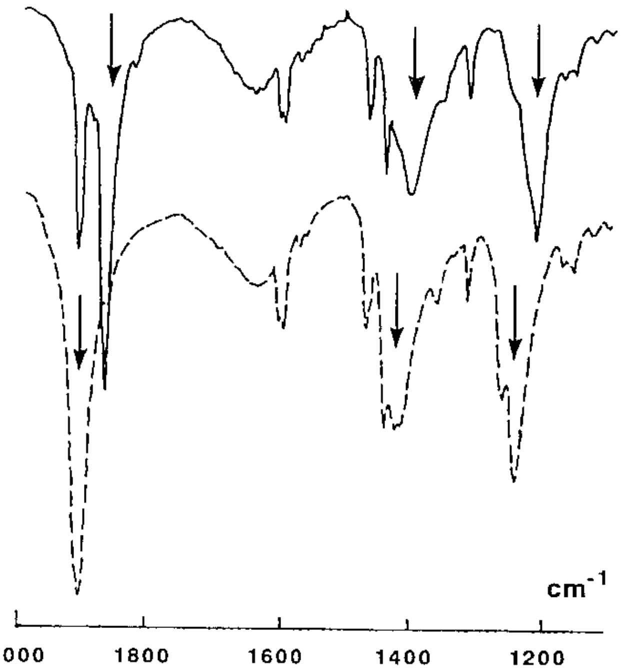


Figure 3. Infrared spectra (KBr) of $[Ru(CO_2)(CO)(bpy)_2]$ (a dotted line) and the sample isolated from CH_3OH / $H_2{}^{18}O$ (99% enriched, 5:1 v/v, a solid line).

C_2H_5OH (1:1 v/v) solution of $[Ru(CO)_2(bpy)_2](PF_6)_2$ turned to reddish yellow by an addition of 2 equiv of Bu_4NOH. Slow evaporation of the reddish yellow solution gave red single crystals of $[Ru(CO_2)(CO)(bpy)_2]\cdot 3H_2O$. The infrared spectrum of $[Ru(CO_2)(CO)(bpy)_2]\cdot 3H_2O$ shows the ν(C≡O) band at 1911 cm^{-1} and the $\nu(CO_2)$ bands at 1428 and 1242 cm^{-1} (Figure 3). The $\nu(CO_2)$ bands are relatively low wavenumber compared with those of $\eta^1(C)$-CO_2 complexes reported so far; 1610 and 1210 cm^{-1} for $[Rh(\eta^1(C)\text{-}CO_2)Cl(diars)_2]$,[8a] and 1650 and 1280 cm^{-1} for $[Co(pr\text{-}salen)KCO_2\cdot THF]_n$[8b]. It is worthy to note that both $\nu(CO_2)$ and ν(C=O) bands of $[Ru(\eta^1(C)\text{-}CO_2)(CO)(bpy)_2]$ were shifted to 1869, 1407 and 1213 cm^{-1} after the complex was dissolved in $CH_3OH/H_2{}^{18}O$ (99% enriched, 5:1 v/v) for 3 h. Thus, the oxygen atoms of both CO_2 and CO of $[Ru(CO_2)(CO)(bpy)_2]$ are replaced by that of $H_2{}^{18}O$ (Figure 3, eq 7).

$$[Ru(CO_2)(CO)(bpy)_2] + 3H_2{}^{18}O \rightleftharpoons [Ru(C^{18}O_2)(C^{18}O)(bpy)_2] + 3H_2O \quad (7)$$

X-Ray Structure Analysis A comparison of the molecular structures of $[Ru(CO)_2(bpy)_2]^{2+}$, $[Ru(C(O)OH)(CO)(bpy)_2]^+$, and $[Ru(CO_2)(CO)(bpy)_2]$ is particularly interesting in the view point of the smooth conversion among those complexes in H_2O. Although colorless and red single crystals of $[Ru(CO)_2(bpy)_2](PF_6)_2$ and $[Ru(CO_2)(CO)(bpy)_2]\cdot 3H_2O$ suitable for X-ray crystal analysis were obtained successfully, attempts to grow single crystals of $[Ru(C(O)OH)(CO)(bpy)_2]^+$ were unsuccessful. The crystal structure of $[Ru(C(O)OCH_3)(CO)(bpy)_2]B(C_6H_5)_4\cdot CH_3CN$, therefore, was determined as a model compound of $[Ru(C(O)OH)(CO)(bpy)_2]^+$ based on the view that the molecular structure of $[Ru(C(O)OH)(CO)(bpy)_2]^+$ can be safely presumed by that of $[Ru(C(O)OCH_3)(CO)(bpy)_2]^+$. The molecular structures of $[Ru(CO_2)(CO)(bpy)_2]\cdot 3H_2O$, $[Ru(C(O)OCH_3)(CO)(bpy)_2]B(C_6H_5)_4\cdot CH_3CN$, and $[Ru(CO)_2(bpy)_2](PF_6)_2$ are shown in Figures 4, 5, and 6. Two bpy ligands of three complexes are in cis-position, and the bond distances and angles of bpy ligands are similar to those observed in the other bpy ruthenium complexes, reported so far.[17] So, the structural difference in the present complexes is focused on the $Ru(CO)_2$, $Ru(CO)(C(O)OCH_3)$, and $Ru(CO)(CO_2)$ moieties (Figure 7). Although the bond distances of the C1-O1 (1.144 (12) Å) and C2-O2 bonds (1.125 (11) Å) for $[Ru(CO)_2(bpy)_2]^{2+}$ are not so difference from those of the C2-O3 for $[Ru(C(O)OCH_3)(CO)(bpy)_2]^+$ and $[Ru(CO_2)(CO)(bpy)_2]$ (1.154 (8) and 1.145 (17) Å, respectively), the

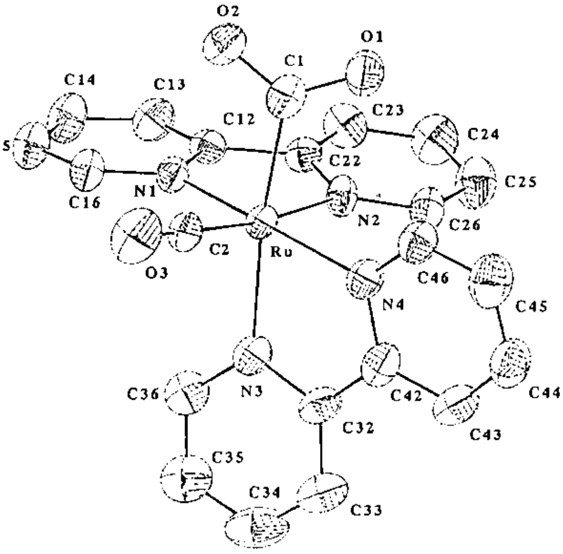


Figure 4. Molecular Structure of $[Ru(CO_2)(CO)(bpy)_2]$.

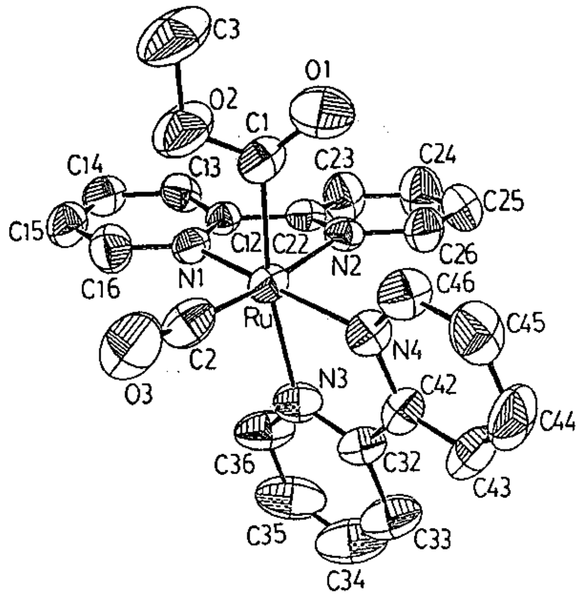


Figure 5. Molecular Structure of $[Ru(C(O)OCH_3)(CO)(bpy)_2]^+$.

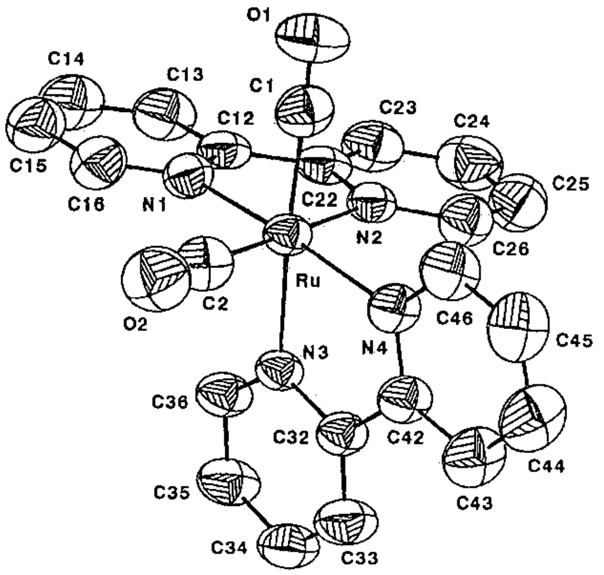


Figure 6. Molecular Structure of $[Ru(CO)_2(bpy)_2]^{2+}$.

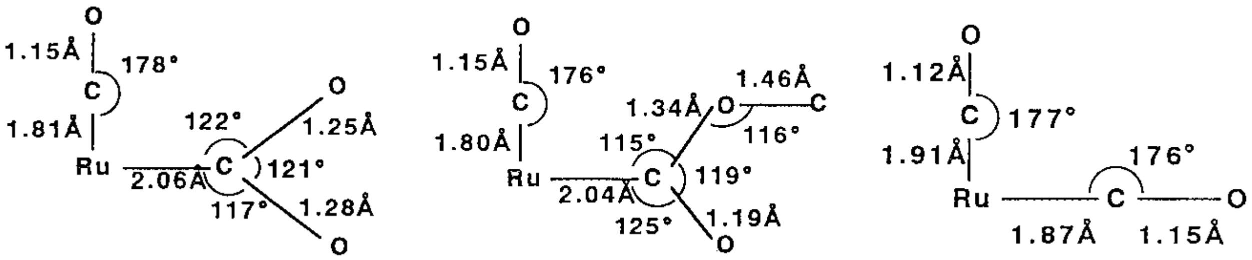


Figure 7. The bond distances and angles of $Ru(CO)(CO_2)$, $Ru(CO)(C(O)OCH_3)$, and $Ru(CO)_2$ moieties.

wavenumber of ν(C≡O) bands of the CO ligand decreases in the order; $[Ru(CO)_2(bpy)_2]^{2+}$ (2093 and 2039 cm^{-1}), $[Ru(C(O)OCH_3)(CO)(bpy)_2]^+$ (1960 cm^{-1}), and $[Ru(CO_2)(CO)(bpy)_2]$ (1911 cm^{-1}). This may be correlated with the difference in the electron donor ability of CO, CO_2CH_3, and CO_2 ligands. In accordance with this, both Ru-N2 (trans to CO) and Ru-N3 (trans to CO, CO_2CH_3, or CO_2) bond distances for the present complexes have a tendency to lengthen in the same order; $[Ru(CO)_2(bpy)_2]^{2+}$ (2.102 (6) and 2.073 (7) Å), $[Ru(C(O)OCH_3)(CO)(bpy)_2]^+$ (2.105 (5) and 2.151 (5) Å), and $[Ru(CO_2)(CO)(bpy)_2]$ (2.133 (10) and 2.204 (10) Å).

The most interesting features in $[Ru(C(O)OCH_3)(CO)(bpy)_2]^+$ and $[Ru(CO_2)(CO)(bpy)_2]$ are the bond lengths and angles of the $Ru\text{-}CO_2$ fragments. The Ru-C1 bond distance of the former is 2.042 (6) Å with Ru-C1-O1 (125.4 (5)°), Ru-C1-O2 (115.4 (4)°), and O1-C1-O2 (119.2 (6)°), and that of the latter is 2.064 (13) Å with Ru-C1-O1 (118.5 (9)°), Ru-C1-O2 (120.6 (10)°), and O1-C1-O2 (120.9 (12)°). The $Ru\text{-}CO_2$ bond distance of $[Ru(\eta^1(C)\text{-}CO_2)(CO)(bpy)_2]$ is close to CO_2-metal distances of $[Rh(\eta^1(C)\text{-}CO_2)Cl(diars)_2]$[8a] and $[Co(pr\text{-}salen)KCO_2{\cdot}THF]_n$,[8b] and the $Ru\text{-}CO_2CH_3$ bond length of $[Ru(C(O)OCH_3)(CO)(bpy)_2]^+$ is also similar to metal-CO_2CH_3 ones of other methoxycarbonyl metal complexes.[25] Although a double bond character has been suggested in the $W\text{-}CO_2$ bond of $[W(CO)_5(\eta^1(C)\text{-}CO_2)]^{2-}$,[26] the fact that the Ru-C1 distance of $[Ru(C(O)OCH_3)(CO)(bpy)_2]^+$ is shorter than that of $[Ru(\eta^1(C)\text{-}CO_2)(CO)(bpy)_2]$ suggests that a multi-bond character of the Ru-CO_2 bond is not always larger than the Ru-$C(O)OCH_3$ one. A difference in the C1-O1 (1.245 (16) Å) and C1-O2 (1.283 (15) Å) bond distances of $[Ru(CO_2)(CO)(bpy)_2]\cdot 3H_2O$ may be associated with a difference in the number of hydrogen bondings of O2 with two water (O4 and O5''), and that of O1 with another water (O6) (see below). It is, however, worthy to note that the C1-O1 (1.245 (16) Å) and C1-O2 (1.283 (15) Å) bond distances of $[Ru(\eta^1(C)\text{-}CO_2)(CO)(bpy)_2]$ are intermediate between those of $[Ru(C(O)OCH_3)(CO)(bpy)_2]^+$ (1.191 (8) and 1.344 (8) Å), and the average of the C1-O1 and C1-O2 bond distances of the former (1.264 Å) is almost consistent with that of the latter (1.268 Å). The C1-O1 and C1-O2 bonds of $[Ru(CO_2)(CO)(bpy)_2]$, therefore, are approximated by 1.5 bond order, and one extra electron-pair involved in $[Ru(CO_2)(CO)(bpy)_2]$ resulting from dissociation of the terminal proton of $[Ru(C(O)OH)(CO)(bpy)_2]^+$ may be mainly localized in the CO_2 ligand rather than delocalized over the $RuCO_2$ moiety.

The increase in the electron density of the CO_2 moiety of $[Ru(CO_2)(CO)(bpy)_2]\cdot 3H_2O$ compared with that of $[Ru(C(O)OH)(CO)(bpy)_2]^+$ may be compensated by the existence of the extended three-dimensional network of hydrogen bondings observed between the complex and three water molecules (Figure 8). Each water molecule is connected by three hydrogen bondings; e.g., O4 (water) is connected to O2 (CO_2), O5 (water), and O6 (water) with distances of 2.711 (14), 2.800 (14), and 2.751 (14)Å, respectively. Similarly, O5 is connected to O2 (CO_2), O4 (water), and O6 (water) with distances of 2.764 (14), 2.800 (14), and 2.870 (14) Å, respectively, and O6 is connected to O1 (CO_2), O4 (water) and O5 (water) with 2.653 (15), 2.751 (15), and 2.870 (14) Å, respectively. The hydrogen bonding network of $[Ru(CO_2)(CO)(bpy)_2]\cdot 3H_2O$ results in a distinct difference in the solubility of hydrated and anhydrous $[Ru(CO_2)(CO)(bpy)_2]$; $[Ru(CO_2)(CO)(bpy)_2]\cdot 3H_2O$ is only soluble in H_2O, CH_3OH, and C_2H_5OH, and almost insoluble in CH_3CN, DMSO, and DMF, while anhydrous $[Ru(CO_2)(CO)(bpy)_2]$ prepared similarly in dry CH_3CN is quite soluble in most organic solvents.

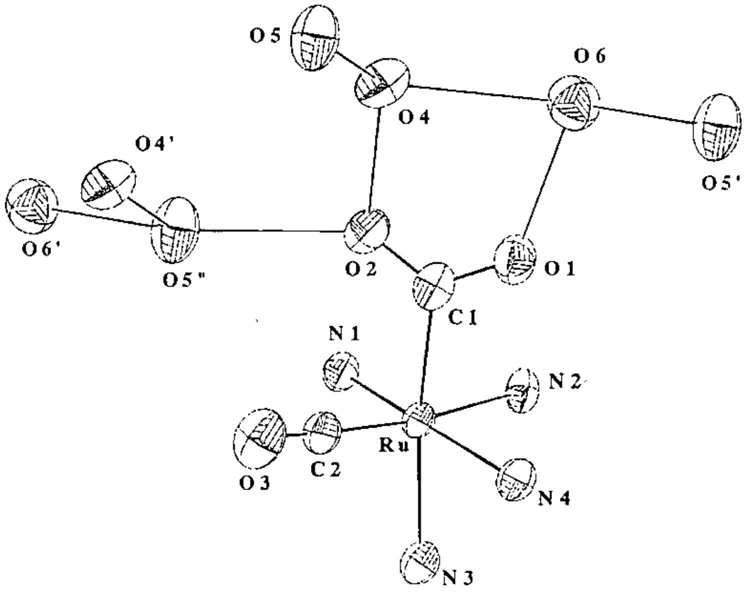


Figure 8. Three-dimensional network of hydrogen bondings of $[Ru(CO_2)(CO)(bpy)_2]\cdot 3H_2O$.

Chapter IV

Reactivity of the CO_2 Ligand in *cis*-Bis(2,2'-bipyridine)(η^1(C)-carbon dioxide)carbonylruthenium

Introduction

The conversion of the M-η^1(C)-CO_2 moiety to M-CO through the M-C(O)OH in protic media is the key reaction in the photo- and electrochemical CO_2 reduction catalyzed by transition metal complexes. Such the conformational change has been elucidated by X-ray analysis of a series of $[Ru(CO_2)(CO)(bpy)_2]$, $[Ru(C(O)OCH_3)(CO)(bpy)_2]^+$, and $[Ru(CO)_2(bpy)_2]^{2+}$. A proton abstraction from a C-H bond of organic molecules by η^1(C)-CO_2 moiety of $[Ru(CO_2)(CO)(bpy)_2]$ is also interesting in the viewpoint of the elucidation of not only the nucleophilicity of the CO_2 molecules activated on metals but also the reactivity of $[Ru(C(O)OH)(CO)(bpy)_2]^+$ toward the resulting carbanions. On the basis of the fact that most of the reaction products are limited to C1 compounds and a new carbon-carbon formation has hardly been achieved in electro- and photochemical CO_2 reduction so far, the reaction of the Ru-C(O)OH moiety with carbanions may lead to a new synthetic route for a C-C bond formation in the electrochemical CO_2 reduction. This chapter describes the reaction of $[Ru(CO_2)(CO)(bpy)_2]$ with acidic protons of organic molecules.

Experimental Section

Materials $[Ru(CO)_2(bpy)_2](PF_6)_2$ was prepared according to literature procedure.[24] TCNE was sublimed prior to use. Malononitrile, dimethyl malonate, succinonitrile, fumaronitrile, 1,2-dibromoethylene, dimethyl acetylenedicarboxylate, methyl acrylate, iodomethane, and a methanolic solution of Bu_4NOH (0.347 M) were used without further purification. Commercially available 1,2-diiodoethane was purified by washing a diethylether solution of 1,2-diiodoethane with aqueous sodium thiosulfate, aqueous sodium hydrogencarbonate, and water. Then, the diethylether solution was dried with sodium sulfate. After evaporation of the solvent, 1,2-diiodoethane was used for a reaction. Methanol was dried over molecular sieves(4A). Acetonitrile was distilled over calcium hydride.

Reaction of $[Ru(CO_2)(CO)(bpy)_2]\cdot 3H_2O$ with CH_3I A CD_3CN/CD_3OD solution (0.6 cm^3, 1:1 v/v) containing $[Ru(CO_2)(CO)(bpy)_2]\cdot 3H_2O$ (22.2 mg) and iodomethane (5.9 mg) was standing for 3 hr under an N_2 atmosphere. ^1H and ^{13}C NMR spectra of the resulting solution was consistent with those of $[Ru(C(O)OCH_3)(CO)(bpy)_2]B(C_6H_5)_4$ in the same solvent. ^1H NMR (270 MHz, MeOH-d_4) δ 3.36 (s) (the methyl proton) ; ^{13}C NMR (67.8 MHz, MeOH-d_4) δ 202.2 and 206.8 (CO and methoxycarbonyl) ; δ158.0, 156.9, 156.5, 156.2, 155.7, 150.6, 149.0, 140.7, 140.6, 140.5, 139.3, 128.5, 128.5, 128.2, 128.0, 125.4, 125.1, 124.6, 124.2 (bpy) ; δ 49.9 (the methyl group).

Reaction of [Ru(CO$_2$)(CO)(bpy)$_2$]·3H$_2$O with H$_2$C(CN)$_2$ H$_2$C(CN)$_2$ (33.4 mg, 0.51 mmol) was added to a suspension of [Ru(CO$_2$)(CO)(bpy)$_2$]·3H$_2$O (24.7 mg, 0.046 mmol) in CH$_3$CN (3.6 cm^3). The suspension was stirred for 18 h at room temperature. The reddish suspension changed to an orange one during the time. An insoluble orange [Ru(C(O)C(CN)$_2$)(CO)(bpy)$_2$]·0.5H$_2$O was obtained by filtration, and washed with CH$_3$CN and CH$_3$OH, and then dried *in vacuo.* Calcd. for $C_{25}H_{17}N_6O_{2.5}Ru$: C, 55.35; H, 3.16; N, 15.49. Found: C, 55.32; H, 3.20; N, 15.40. Yield 20 mg (80%). Infrared spectrum (KBr) ν(C≡O) 1926 cm^{-1}, ν(C=O) 1428 cm^{-1}, ν(C≡N) 2172, 2149 cm^{-1}.

Reaction of [Ru(CO$_2$)(CO)(bpy)$_2$]·3H$_2$O with H$_2$C(C(O)OCH$_3$)$_2$ H$_2$C(C(O)OCH$_3$)$_2$ (200 mg, 1.52 mmol) was added to a suspension of [Ru(CO$_2$)(CO)(bpy)$_2$]·3H$_2$O (28.9 mg, 0.054 mmol) in CH$_3$CN (1.0 cm^3), and the suspension was stirred for 12 h. The reddish yellow suspension changed to an orange solution during the time. Slow evaporation of the solution gave orange microcrystals. After excess of H$_2$C(C(O)OCH$_3$)$_2$ was removed by washing with diethylether, [Ru(C(O)CH(C(O)OH)$_2$)(CO)(bpy)$_2$]OH·3H$_2$O was obtained. Yield 70%. Calcd. for $C_{25}H_{26}N_4O_{10}Ru$: C, 46.65; H, 4.07; N, 8.71. Found: C, 46.58; H, 4.07; N, 8.45. Infrared spectrum (KBr) ν(C≡O) 1950 cm^{-1}, ν(C=O) 1732, 1601 cm^{-1}.

Reaction of [Ru(CO$_2$)(CO)(bpy)$_2$]·3H$_2$O with TCNE TCNE (17.4 mg, 0.136 mmol) was added to a methanolic solution (5 cm^3) of [Ru(CO$_2$)(CO)(bpy)$_2$]·3H$_2$O (72.1 mg, 0.134 mmol) under an N$_2$ atmosphere. The solution was stirred for 5 min at room temperature and then concentrated to about 1 cm^3 under reduced pressure. On cooling the solution to -20 °C, [Ru(C(O)OC(OCH$_3$)$_2$CH(CN)$_2$)(CO)(bpy)$_2$]OH crystallized out of the solution. The product separated by filtration was washed with diethylether and dried *in vacuo.* Calcd. for $C_{28}H_{24}N_6O_6Ru$: C, 52.41; H, 3.77; N, 13.10. Found: C, 52.25; H, 3.68; N, 13.21. Infrared spectrum (KBr) ν(C≡O) 1960 cm^{-1}, ν(C=O) 1632 cm^{-1}, ν(C-O) 1050 cm^{-1}, ν(C≡N) 2195, 2164 cm^{-1}. ^{13}C NMR (67.8 MHz, DMF-*d*$_7$) δ 202.9 (s) and 201.9 (s) (carbonyl); δ 118.8 (s), 116.7 (s) and 115.7 (s) (C(CN)$_2$); δ 50.0(s), 49.4 (s) and 49.1 (s) (methoxy and methine); δ 123-158 (20 signals of bpy).

Reaction of [Ru(CO$_2$)(CO)(bpy)$_2$]·3H$_2$O with ICH$_2$CH$_2$I A methanolic solution (12 cm^3) containing [Ru(CO$_2$)(CO)(bpy)$_2$]·3H$_2$O (46.5 mg, 0.086 mmol) and ICH$_2$CH$_2$I (122 mg, 0.433 mmol) was stirred for 10 h under an N$_2$ atmosphere in dark. A dark brown [RuI(CO)(bpy)$_2$]I$_3$ precipitated was collected by filteration and washed with a small amount of methanol and diethylether. Yield 75%. Calcd. for $C_{21}H_{16}I_4N_4ORu$: C, 26.58; H, 1.70; N, 5.90. Found: C, 26.55; H, 1.75; N, 5.83. Infrared spectrum (KBr) ν(C≡O) 1950 cm^{-1}.

Physical Measurements and Product Analysis Infrared spectra were obtained on a Shimadzu DR8000 spectrometer. ^{1}H and ^{13}C NMR were obtained on a JEOL EX270 spectrometer. Elemental analyses were carried out at Chemical Materials Center of Institute for Molecular Science. Quantitative analyses of CO$_2$ and CH$_2$=CH$_2$ were carried out on a Shimadzu GC-8A gas chromatograph equipped with a 3 m column filled with Unibeads 1S using He as a carrier gas. Electrochemical measurements were performed in a pyrex cell equipped with a glassy carbon working electrode, a Pt auxiliary electrode, an Ag/AgCl reference electrode, and a nozzle for bubbling of N_2 or CO_2. Cyclic voltammograms were obtained by use of a Hokuto Denko HR-101B potentiostat, a Hokuto Denko HB-107A function generator, and a Yokokawa Electric Inc. 3077 X-Y recorder.

Results and Discussion

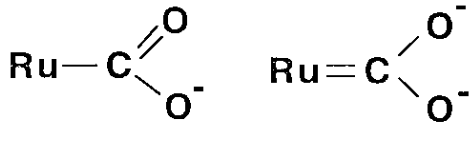
Reaction of $[Ru(CO_2)(CO)(bpy)_2]$ with CH_3OH The ^{13}C NMR spectrum of $[Ru(CO)_2(bpy)_2](PF_6)_2$ showed the CO carbon at δ 190.3 in CD_3CN, and the CO and CO_2 signals of $[Ru(CO_2)(CO)(bpy)_2]\cdot 3H_2O$ were observed at δ 203.9 and 210.2 in CD_3OD. An addition of an equimolar amount of a methanolic solution of Bu_4NOH to the $[Ru(CO)_2(bpy)_2](PF_6)_2$ solution resulted in a complete disappearance of the δ 190.3 signal, and the CO and COOH carbons of $[Ru(C(O)OH)(CO)(bpy)_2]^+$ appeared at δ 201.5 and 205.1 with 19 signals of two non-equivalent bpy ligands. Such selective formation of $[Ru(C(O)OH)(CO)(bpy)_2]^+$ in the reaction of an equimolar amount of OH^- with $[Ru(CO)_2(bpy)_2]^{2+}$ in CH_3CN is quite contrast to that in H_2O, where $[Ru(C(O)OH)(CO)(bpy)_2]^+$ always exists as an equilibrium mixture with either $[Ru(CO)_2(bpy)_2]^{2+}$ or $[Ru(CO_2)(CO)(bpy)_2]$, or both of them. A further addition of a methanolic solution of Bu_4NOH (about 1.2 molar excess) to the CH_3CN solution of $[Ru(CO)_2(bpy)_2](PF_6)_2$ caused an appearance of two signals of δ 203.9 and 210.2 of $[Ru(CO_2)(CO)(bpy)_2]$ in addition to the δ 201.5 and 205.1 signals of $[Ru(C(O)OH)(CO)(bpy)_2]^+$.[27] This result indicates that the conversion between $[Ru(C(O)OH)(CO)(bpy)_2]^+$ and $[Ru(CO_2)(CO)(bpy)_2]$ in CD_3CN/CD_3OD is very slow compared with that in H_2O.

Cooper et al. have demonstrated that $[W(CO)_5(\eta^1(C)\text{-}CO_2)]^{2-}$ produced in the reaction of $W(CO)_6$ with Li under CO_2 at -78 °C in THF undergoes an oxide-abstraction reaction by CO_2 to regenerate $W(CO)_6$ at room temperature (eq 8) and shows the $\eta^1(C)$-CO_2 carbon at δ 225 in the ^{13}C NMR spectrum.[26] Such an unusual oxide-abstraction reaction by CO_2 may be rationalized by a strong nucleophilicity of the oxygen atom of the

$$[W(CO)_5(\eta^1(C)\text{-}CO_2)]^{2-} \ + \ CO_2 \longrightarrow W(CO)_6 \ + \ CO_3^{2-} \quad (8)$$

CO_2 ligand. On the other hand, $[Ru(CO_2)(CO)(bpy)_2]$ does not react with CO_2 and the chemical shift of the $\eta^1(C)$-CO_2 carbon is observed at fairly high magnetic field compared with that of $[W(CO)_5(CO_2)]^{2-}$. These results suggest that $[Ru(CO_2)(CO)(bpy)_2]$ exists as the deprotonated form (**1**) of $[Ru(C(O)OH)(CO)(bpy)_2]^+$ rather than the Fischer-type carbene form (**2**) (Scheme I), although the Ru-CO_2 bond distance of $[Ru(CO_2)(CO)(bpy)_2]$ (2.064 Å) is close to metal-

Scheme I



1 **2**

carbon bonds of Ru carbene complexes reported so far (2.09 Å).[28]

In contrast to eq 8, $[Ru(CO_2)(CO)(bpy)_2]$ is quite stable in CH_3OH at room temperature, as described above. The ^{13}C NMR of $[Ru(CO_2)(CO)(bpy)_2]\cdot 3H_2O$ in CO_2-saturated CD_3OH, however, revealed the formation of both $[Ru(C(O)OH)(CO)(bpy)_2]^+$ (δ 201.5 and 205.1) and $CD_3OC(O)O^-$ (δ 161.4), and neither $[Ru(CO_2)(CO)(bpy)_2]$ nor $[Ru(CO)_2(bpy)_2]^{2+}$ was detected in the solution. The absence of $[Ru(CO)_2(bpy)_2]^{2+}$ in the CO_2-saturated CD_3OH indicates that $[Ru(CO_2)(CO)(bpy)_2]$ does not undergo an oxide-abstraction reaction by CO_2. On the basis of the pK_a=9.5 of $[Ru(C(O)OH)(CO)(bpy)_2]^+$, protonation of $[Ru(CO_2)(CO)(bpy)_2]$ affording $[Ru(C(O)OH)(CO)(bpy)_2]^+$ in CO_2-saturated CD_3OH is explained by an enhancement of the acidity of CD_3OH due to concomitant formation of $CD_3OCO_2^-$ (9). It is worthy to note that a selective conversion of $[Ru(CO_2)(CO)(bpy)_2]$ to $[Ru(C(O)OH)(CO)(bpy)_2]^+$ can not be attained in aqueous conditions, since $[Ru(C(O)OH)(CO)(bpy)_2]^+$ invariably exists as an equilibrium mixture of $[Ru(CO_2)(CO)(bpy)_2]$ and $[Ru(CO)_2(bpy)_2]^{2+}$ in H_2O. The conversion of $[Ru(CO_2)(CO)(bpy)_2]$ to $[Ru(C(O)OH)(CO)(bpy)_2]^+$ in CO_2-saturated CH_3OH was also observed in a

$$[Ru(CO_2)(CO)(bpy)_2] + CH_3OH + CO_2 \longrightarrow [Ru(C(O)OH)(CO)(bpy)_2]^+ + CH_3OCO_2^- \qquad (9)$$

cyclic voltammogram (CV); the CV of $[Ru(CO_2)(CO)(bpy)_2]\cdot 3H_2O$ shows an irreversible anodic wave at +0.53 V *vs.* Ag/AgCl (a solid line in Figure 9(a)) and a strong cathodic current at potential more negative than -1.25 V in CH_3OH under an N_2 atmosphere (a solid line in Figure 9(b)). The anodic +0.53 V wave completely disappears in CO_2-saturated CH_3OH (a dotted line in Figure 9(a)) and the reduction of CO_2 takes place at potentials more negative than -1.18 V (a dotted line in Figure 9(b)). Those results may make clear the roles of $[Ru(CO_2)(CO)(bpy)_2]$ and $[Ru(C(O)OH)(CO)(bpy)_2]^+$ in a previous electrochemical CO_2 reduction catalyzed by $[Ru(CO)_2(bpy)_2]^{2+}$, where $[Ru(C(O)OH)(CO)(bpy)_2]^+$ resulting from $[Ru(CO_2)(CO)(bpy)_2]$ functions as the active species for the formation of $HCOO^-$ in CO_2-saturated CH_3OH.[29]

Reactions of $[Ru(CO_2)(CO)(bpy)_2]$ with Organic Compounds Having Active Hydrogens A proton abstraction from a C-H bond by the $\eta^1(C)$-CO_2 moiety of $[Ru(CO_2)(CO)(bpy)_2]$ is much more interesting than that of hydroxy proton of methanol, since the resulting carbanion may react with the hydroxycarbonyl carbon of $[Ru(C(O)OH)(CO)(bpy)_2]^+$ to form a carbon-carbon bond. Although no reaction took place between $[Ru(CO_2)(CO)(bpy)_2]\cdot 3H_2O$ and $NCCH_2CH_2CN$ in CH_3OH, the reaction of $[Ru(CO_2)(CO)(bpy)_2]\cdot 3H_2O$ with $H_2C(C(O)OCH_3)_2$ afforded $[Ru(C(O)CH(C(O)OCH_3)_2)(CO)(bpy)_2]^+$ in CH_3OH. The reaction was monitored by the ^{13}C NMR spectra of $[Ru(CO_2)(CO)(bpy)_2]\cdot 3H_2O$ in the presence of 30 equiv[30] of $H_2C(C(O)OCH_3)_2$ in CD_3OD/CD_3CN (1:2 v/v). The mixture showed two signals at δ 170.6 (s) and 171.8 (s), and a triplet signal at δ 44.8 (t) due to the formation of a C-D bond (J (^{13}C-D) =19.3 Hz) in

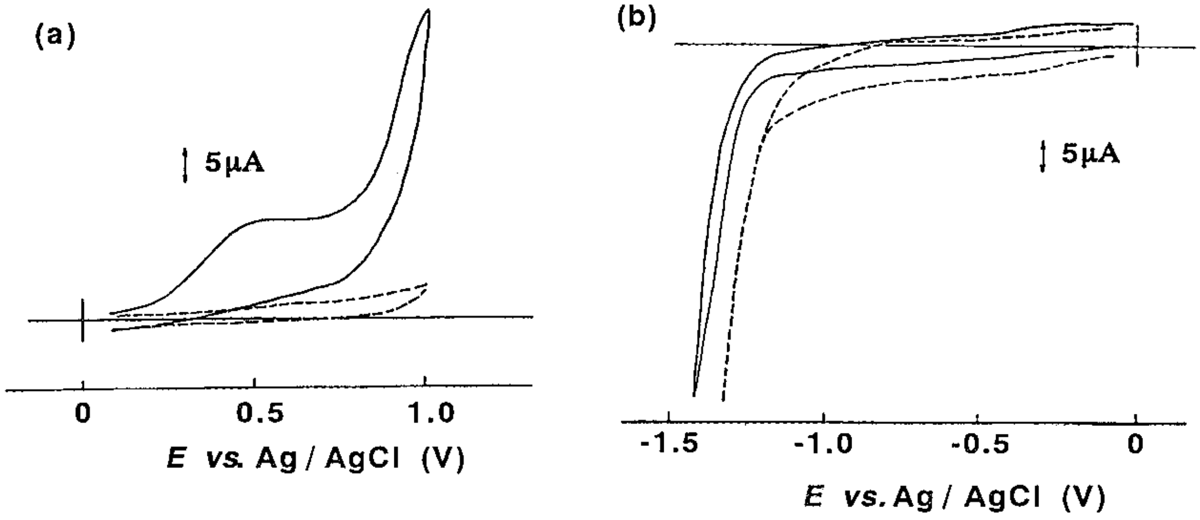
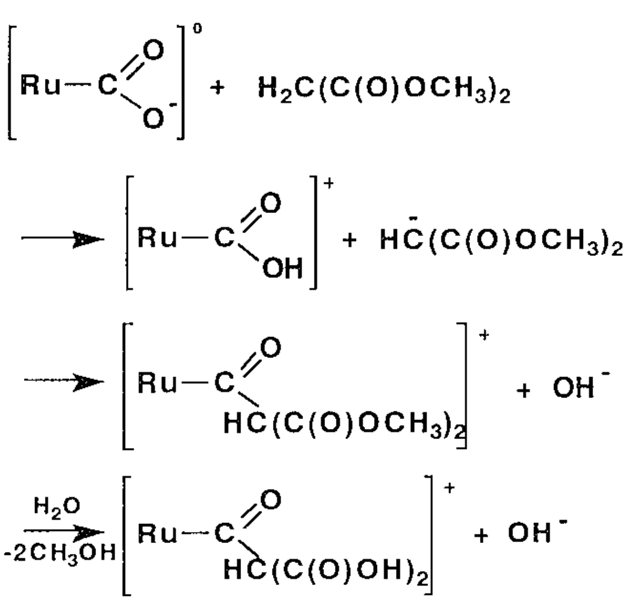


Figure 9. Cyclic voltammogram of $[Ru(CO_2)(CO)(bpy)_2] \cdot 3H_2O$ in CH_3CN containing 0.1M Bu_4NBF_4 as a supporting electrolyte under N_2 (solid lines) and CO_2 (dotted lines). $dE/dt = 100$ mV/s.

the vicinity of the strong carboxylate (δ 167.5 (s)) and methylene (δ 41.1 (s)) signals of free $H_2C(C(O)OCH_3)_2$. In addition, the δ 203.9 (s) and 210.2 (s) signals of $[Ru(CO_2)(CO)(bpy)_2]$ completely disappeared, and two signals appeared at δ 201.5 (s) and 205.3 (s). This result suggests that $[Ru(C(O)CD(C(O)OCH_3)_2)(CO)(bpy)_2]^+$ is formed in the solution. The reaction of $[Ru(CO_2)(CO)(bpy)_2]$ with $H_2C(C(O)OCH_3)_2$, therefore, may proceed *via* abstraction of a methylene proton of $H_2C(C(O)OCH_3)_2$ by the η^1(C)-CO_2 moiety of $[Ru(CO_2)(CO)(bpy)_2]$, followed by a replacement of OH^- in the hydroxycarbonyl group of $[Ru(C(O)OH)(CO)(bpy)_2]^+$ by $[HC(C(O)OCH_3)_2]^-$ with generating $[Ru(C(O)CH(C(O)OCH_3)_2)(CO)(bpy)_2]OH$. The fact that $[Ru(C(O)CH(C(O)OH)_2)(CO)(bpy)_2]OH$ was obtained as the final reaction product indicates that $[Ru(C(O)CH(C(O)OCH_3)_2)(CO)(bpy)_2]OH$ underwent a hydrolysis reaction presumably due to either OH^- or H_2O[31] during the purification (Scheme II). As similar to $[Ru(C(O)OH)(CO)(bpy)_2]^+$, $[Ru(C(O)CH(C(O)OH)_2)(CO)(bpy)_2]OH$ rapidly was converted to $[Ru(CO)_2(bpy)_2]^{2+}$ in a quantitative yield by treatment with acidic water (pH 2).

Scheme II



The reaction of $[Ru(CO_2)(CO)(bpy)_2]$ with $H_2C(CN)_2$ is very rapid compared with the reaction with $H_2C(C(O)OCH_3)_2$. A reddish yellow suspension of $[Ru(CO_2)(CO)(bpy)_2]$ in

CH_3CN rapidly changed to an orange suspension by an addition of 10 equiv of $H_2C(CN)_2$. The product was insoluble in usual solvents such as DMF, CH_3CN, CH_3OH and H_2O. The IR spectrum of the product showed $\nu(C{\equiv}O)$ and $\nu(C{=}O)$ bands at 1926 and 1428 cm^{-1}, respectively, and two $\nu(C{\equiv}N)$ bands were observed at 2172 and 2149 cm^{-1}. In addition, the reaction product suspended in acidic H_2O (pH 2.0) also gave $[Ru(CO)_2(bpy)_2]^{2+}$ quantitatively. Combined with these results and the elemental analysis, the orange product may be $[Ru(C(O)C(CN)_2)(CO)(bpy)_2]$ rather than $[Ru(C(O)\text{-}CH(CN)_2)(CO)(bpy)_2]^+$. From analogy with the reaction with $H_2C(C(O)OCH_3)_2$, the initial reaction product may be the latter, which presumably dissociates a methine proton by the presence of strong electron-withdrawing two cyano group.[32] The reaction of $[Ru(CO_2)(CO)(bpy)_2]$ with $H_2C(CN)_2$, therefore, may be expressed by eq 10.

$$[Ru(CO_2)(CO)(bpy)_2] + (NC)_2CH_2 \longrightarrow [Ru(C(O)C(CN)_2)(CO)(bpy)_2] + H_2O \quad (10)$$

The Reaction of $[Ru(CO_2)(CO)(bpy)_2]$ with Alkyl Iodides In comparison with eq 8 and 9, the nucleophilicity of the CO_2 ligand of $[Ru(CO_2)(CO)(bpy)_2]$ may be much less than that of $[W(CO)_5(\eta^1(C)\text{-}CO_2)]^{2-}$. It has been ,however, reported that a neutral $\eta^1(C)\text{-}CO_2$ complex $[IrCl(dmpe)_2(\eta^1(C)\text{-}CO_2)]$ can be converted to the corresponding methoxycarbonyl complex $[IrCl(C(O)OCH_3)(dmpe)_2]FSO_3$ by a treatment with a strong methylation agent such as CH_3FSO_3.[33] In the present study, $[Ru(C(O)OCH_3)(CO)(bpy)_2]I$, which shows methyl proton at δ 3.36 (s) in CD_3OD on a ^1H (270 MHz) NMR spectrum, was quite smoothly obtained in the reaction of $[Ru(CO_2)(CO)\text{-}(bpy)_2]\cdot 3H_2O$ with CH_3I in CH_3OH (eq 11). It is worthy to note that $[Ru(C(O)OCH_3)(CO)\text{-}(bpy)_2]^+$ can be also synthesized by the reaction of $[Ru(CO)_2(bpy)_2]^{2+}$ with CH_3ONa in CH_3OH (eq 12).[14] Thus, $[Ru(C(O)OCH_3)(CO)(bpy)_2]^+$ can be prepared not only by an electrophilic attack of CH_3I to $[Ru(CO_2)(CO)(bpy)_2]$ but also by a nucleophilic attack of CH_3O^- to $[Ru(CO)_2(bpy)_2]^{2+}$.

$$[Ru(CO_2)(CO)(bpy)_2] + CH_3I \longrightarrow [Ru(C(O)OCH_3)(CO)(bpy)_2]I \quad (11)$$

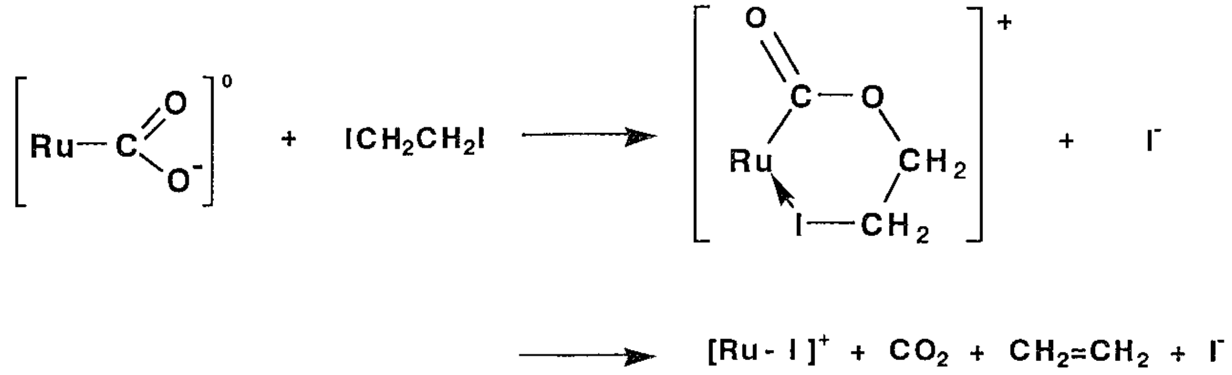
$$[Ru(CO)_2(bpy)_2]^{2+} + CH_3O^- \longrightarrow [Ru(C(O)OCH_3)(CO)(bpy)_2]^+ \quad (12)$$

In contrast to the reaction with CH_3I, $[Ru(CO_2)(CO)(bpy)_2]\cdot 3H_2O$ reacted with two moles of ICH_2CH_2I in CH_3OH to generate $[RuI(CO)(bpy)_2]I_3$, CO_2, and 2 moles of $CH_2{=}CH_2$ in a quantitative yield (eq 13). The initial reaction product of eq 13 may be

$$[Ru(CO_2)(CO)(bpy)_2] + 2ICH_2CH_2I \longrightarrow [RuI(CO)(bpy)_2]I_3 + CO_2 + 2CH_2{=}CH_2 \quad (13)$$

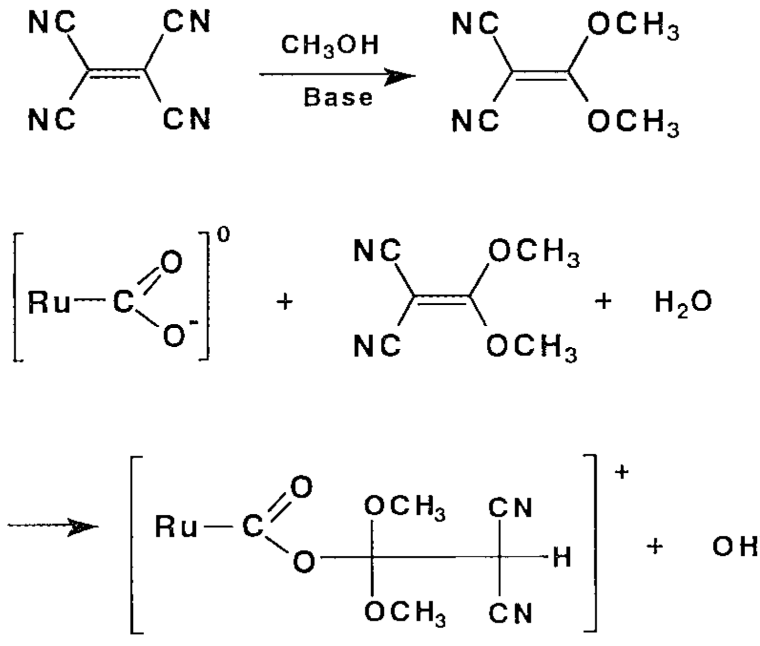
$[Ru(C(O)OCH_2CH_2I)(CO)(bpy)_2]^+$ and I^- from analogy with the reaction with CH_3I. An intramolecular nucleophilic attack of terminal iodine of $[Ru(C(O)OCH_2CH_2I)(CO)(bpy)_2]^+$ to Ru may afford $[RuI(CO)(bpy)_2]^+$ with liberating $CH_2{=}CH_2$ (Scheme III). Another $CH_2{=}CH_2$ evolution in eq 13 apparently results from the reaction of I^- with ICH_2CH_2I, since vigorous $CH_2{=}CH_2$ evolution took place by an addition of KI or NaI to a methanolic solution of ICH_2CH_2I.

Scheme III



Reaction of $[Ru(CO_2)(CO)(bpy)_2]$ with TCNE Neither dimethyl acetylenedicarboxylate, fumaronitrile, 1,2-dibromoethylene nor methyl acrylate reacted with $[Ru(CO_2)(CO)(bpy)_2]\cdot 3H_2O$ in CH_3OH. On the other hand, TCNE smoothly reacted with $[Ru(CO_2)(CO)(bpy)_2]\cdot 3H_2O$ under an N_2 atmosphere to give air-unstable yellow microcrystals of $[Ru(C(O)OC(OCH_3)_2CH(CN)_2)(CO)(bpy)_2]OH$, which showed two methoxy carbons and a methine carbon at δ 49.1 (s), 49.4 (s) and 50.0 (s), two cyano carbons and $-O-{}^*C(CN)_2-$ at δ 115.7 (s), 116.7 (s) and 118.8 (s), and two carbonyl carbons at δ 201.9 and 202.9 in the ^{13}C NMR in $(CD_3)_2NC(O)D$. The replacement of two CN groups of TCNE by CH_3O groups in the product may be explained by the fact of a smooth conversion of TCNE to 1,1-dicyano-2,2-dimethoxyethylene in the presence of weak base such as urea in CH_3OH.[34] The IR spectra of the product displayed ν(C≡O) and ν(C=O) bands at 1960 and 1632 cm^{-1} together with

Scheme IV



ν(C≡N) bands at 2164 and 2195 cm^{-1}. The new C-O bond involved in the product may be $[Ru(C(O)OC(OCH_3)_2CH(CN)_2)(CO)(bpy)_2]^+$ rather than $[Ru(C(O)OC(CN)_2CH-(OCH_3)_2)(CO)(bpy)_2]^+$ by considering the Michael-type addition and the polarization of $(NC)_2C=C(OCH_3)_2$ (Scheme IV). The product also underwent a smooth hydrolysis in acidic water (pH 2) to form $[Ru(CO)_2(bpy)_2]^{2+}$ quantitatively.

This chapter reveals the nucleophilicity of the η^1(C)-CO_2 moiety of $[Ru(CO_2)(CO)(bpy)_2]$. The Ru-CO_2 bond of $[Ru(CO_2)(CO)(bpy)_2]$ may be expressed by the resonance structure **1** of Scheme I, and neither spectroscopical data nor the reactivity of $[Ru(CO_2)(CO)(bpy)_2]$ gives any positive evidence for the contribution of the structure **2** of Scheme I.

Chapter V

Nucleophilicity of CO_2 in Protic Media —— Competitive Addition of CO_2 and Proton to Reduced Quinones

Introduction

There is a matter of controversy about the initial stage of the reduction of CO_2 catalyzed by transition metal complexes; which of proton or CO_2 attacks on low valent coordinatively unsaturated metal centers. In the former, formato complexes (M-OC(O)H) are produced by insertion of CO_2 to the resulting M-H bond (eq 14),[5f] while metal carboxylates (M-C(O)OH) would be generated by protonation of M-CO_2 in the latter (eq 15).[12] Both metal-formato and -carboxylato complexes are reasonable precursors for the formation of formic acid, and generation of CO has been ascribed to an irreversible reduction of metal-carbonyl complexes resulted from dehydroxylation of M-C(O)OH complexes.[12] The question, however, has been raised whether CO_2 attacks on metals or not in aqueous solutions because of lack of any data concerning the acidity of CO_2 in protic media. This chapter describes a competitive electrophilic addition of CO_2 and proton to reduced quinones in CH_3CN/H_2O and CH_3OH from the viewpoint of the elucidation of the relative acidity of CO_2 and proton in those media.

$$[M]^{n+} \xrightarrow{H^+} [M\text{-}H]^{(n+1)+} \xrightarrow{CO_2} [M\text{-}OC(O)H]^{(n+1)+} \qquad (14)$$

$$[M]^{n+} \xrightarrow{CO_2} [M\text{-}CO_2]^{n+} \xrightarrow{H^+} [M\text{-}C(O)OH]^{(n+1)+} \qquad (15)$$

Experimental Section

Electrochemical measurements were performed in a pyrex cell equipped with a glassy carbon working electrode, a Pt auxiliary electrode, an Ag/AgCl reference electrode, and a nozzle for bubbling of N_2 or CO_2. Cyclic voltammograms were obtained by use of a Hokuto Denko HR-101B potentiostat, a Hokuto Denko HB-107A function generator, and a Yokokawa Electric Inc. 3077 X-Y recorder.

Results and Discussion

The CV of TMQ shows two reversible $[TMQ]^{0/-}$ and $[TMQ]^{-/2-}$ redox couples at $E_{1/2}$ = -0.75 and -1.31 V *vs.* Ag/AgCl in dry CH_3CN (a solid line in Figure 10(a)). Introduction of CO_2 to the CH_3CN solution (0.24M) results in the increase of the cathodic peak current of the $[TMQ]^{0/-}$ couple and a strong anodic wave appeared at 0.05 V (a dotted

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A part of this work is in press in *Chem. Lett.*

line in Figure 10(a)). The original $[TMQ]^{0/-}$ and $[TMQ]^{-/2-}$ redox couples are completely regenerated with the same peak current intensities upon removing CO_2 by bubbling N_2 for 20 min. This result clearly indicates that $[TMQ]^{2-}$ forms a CO_2 adduct, as similar to the 1:2 adduct between 9,10-phenanthrenequinone dianion and CO_2.[35] Quite similarly, the CV of 2,6-di-t-butyl-1,4-benzoquinone, methyl-1,4-benzoquinone, 1,4-benzoquinone, and 1,4-naphtoquinone exhibited irreversible two-electron cathodic and anodic waves around -0.6 and 0 V in CO_2-saturated CH_3CN (Table VII). Thus, those quinone dianions $[Q_1]^{2-}$ form 1:2 adducts with CO_2 (eq 16) in CH_3CN.

$$Q_1 + 2e^- + 2CO_2 \rightleftharpoons [Q_1\cdot 2CO_2]^{2-} \quad (16)$$

CO_2 gives no effect on the reversible (0/1-) redox couple of TCQ at $E_{1/2}$ = 0.12 V, but causes 90 and 350 mV anodic shifts of the cathodic and anodic waves of the $[TCQ]^{-/2-}$ couple as compared with those in CH_3CN under N_2 (compare a solid line with a dotted one in Figure 10(b)). This implies that the acidity of CO_2 is not strong enough to attack

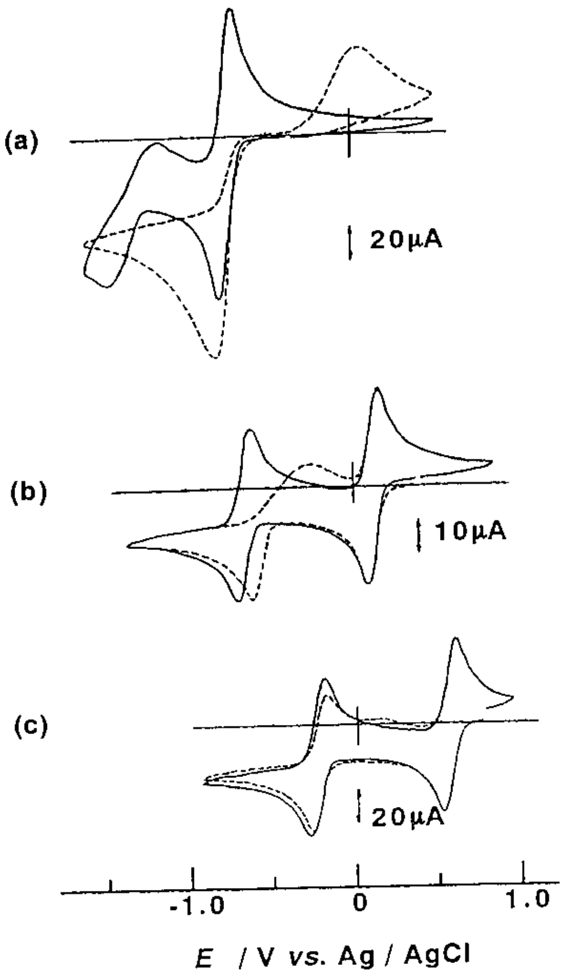

Figure 10. Cyclic voltammogram of TMQ (3.40 mM, (a)), TCQ (1.16 mM, (b)), and DDQ (1.89 mM, (c)) under N_2 (solid lines) and CO_2 (dotted lines) in CH_3CN containing Bu_4NBF_4 (0.1M). dE/dt = 100 mV/s: working electrode; glassy carbon.

Table VII. Electrochemical data of quinones in CH_3CN [a)].

		$Q + e^- \rightleftharpoons Q^-$		$Q^- + e^- \rightleftharpoons Q^{2-}$		see b)	
type	quinones	E_{pc}	E_{pa}	E_{pc}	E_{pa}	E_{pc}	E_{pa}
Q_1	2,6-di-t-butyl-1,4-benzo-	-0.68	-0.60	-1.46	-1.32	-0.69	0.10
Q_1	TMQ	-0.78	-0.70	-1.35	-1.17	-0.79	-0.02
Q_1	methyl-1,4-benzo-	-0.51	-0.44	-1.18	-0.98	-0.52	0.13
Q_1	1,4-benzo-	-0.49	-0.36	-1.27	-0.96	-0.55	0.21
Q_2	1,4-naphtoquinone	-0.60	-0.53	-1.19	-1.07	-0.63	-0.10
Q_2	TCQ	0.08	0.15	-0.69	-0.60	-0.60	-0.25
Q_2	TBQ	0.02	0.08	-0.72	-0.64	-0.65	-0.27
-	DDQ	0.51	0.60	-0.30	-0.21	-0.29 [c)]	0.16 [c)]

a) V *vs.* Ag/AgCl. ; dE/dt = 100 mV/s. b) $Q_1 + 2e^- + 2CO_2 \rightleftharpoons [Q_1\cdot 2CO_2]^{2-}$; $Q_2^- + e^- + CO_2 \rightleftharpoons [Q_2\cdot CO_2]^-$. c) weak interaction.

on a radical anion of TCQ. TBQ showed quite similar redox behavior under N_2 and CO_2 (Table VII). Dubois et al. has proposed a new CO_2 carrier system by using the $[TCQ]^{-/2-}$ redox couple in organic solvents (eqs 17 and 18).[36]

$$Q_2 + e^- \rightleftharpoons Q_2^- \tag{17}$$

$$Q_2^- + e^- + CO_2 \rightleftharpoons [Q_2 \cdot CO_2]^{2-} \tag{18}$$

DDQ also displays two reversible $[DDQ]^{0/-}$ and $[DDQ]^{-/2-}$ couples at $E_{1/2} = 0.56$ and -0.24 V in CH_3CN under N_2 (a solid line in Figure 10(c)). A weak anodic wave appears at +0.18 V at the expense of the peak current of the anodic wave of the $[DDQ]^{-/2-}$ couple under CO_2 (a dotted line in Figure 10(c)). The +0.18 V anodic wave disappears by bubbling N_2 for 5 min, suggesting the interaction of DDQ^{2-} with CO_2. Based on the small change in the CV of DDQ under N_2 and CO_2, the interaction of DDQ^{2-} with CO_2 is extremely weak as compared with $[Q_1]^{2-}$ and $[Q_2]^{2-}$. It is worthy to note that quinones having cathodic waves of the $[Q]^{0/-}$ and $[Q]^{-/2-}$ couples at potentials more negative than -0.5 V show strong affinity for CO_2, and the interaction increases in the order $[DDQ]^{2-} << [Q_2]^{2-} << [Q_1]^{2-}$. To evaluate the acidity of CO_2 in protic media, the redox behavior of TMQ in CH_3CN/H_2O and MeOH under CO_2 was investigated, since those solvents are widely used as a proton source in electrochemical CO_2 reductions. The (1-/2-) couples of Q_1 undergo pronounced anodic shifts as compared with the (0/1-) couple with increasing amount of H_2O in CH_3CN.[37] In accordance with this, two couples of cathodic and anodic waves of TMQ appear at -0.65 and -0.53 V in CH_3CN/H_2O (9:1 v/v, a solid line in Figure 11(a)), as described elsewhere.[37] Similarly, TMQ also shows only a pair of cathodic and anodic waves at -0.56 and -0.06 V in CH_3OH (a solid line in Figure 11(b)). Based on the anodic peak potentials of $[TMQ \cdot 2H]^0$ at +0.59 and +0.60 V in CH_3CN/H_2O (9:1 v/v) and CH_3OH, respectively, the main species of TMQ dianion may be $[TMQ \cdot H]^-$ in those media (eqs 19 and 20).[38] On the other hand, the cathodic and anodic waves of TMQ are observed at -0.64 and +0.29 V, and -0.52 and +0.33 V in CO_2-saturated CH_3CN/H_2O (9:1 v/v) and CH_3OH, respectively (dotted lines in Figure 11).

$$TMQ + 2e^- + H^+ \rightleftharpoons [TMQ \cdot H]^- \tag{19}$$

$$TMQ + 2e^- + 2H^+ \rightleftharpoons [TMQ \cdot 2H]^0 \tag{20}$$

There are four possible CO_2 adducts ($[TMQ \cdot H \cdot CO_2]^-$, $[TMQ \cdot H \cdot CO_2H]^0$, $[TMQ \cdot CO_2 \cdot CO_2H]^-$, and $[TMQ \cdot (CO_2H)_2]^0$) except for $[TMQ \cdot 2H]^0$ existing in strong acidic solutions. Both $[TMQ \cdot H \cdot CO_2]^-$ and $[TMQ \cdot H \cdot CO_2H]^0$ would be produced by an addition of CO_2 to $[TMQ \cdot H]^-$, although the existence of $[TMQ \cdot H \cdot CO_2H]^0$ generated by protonation of $[TMQ \cdot H \cdot CO_2]^-$

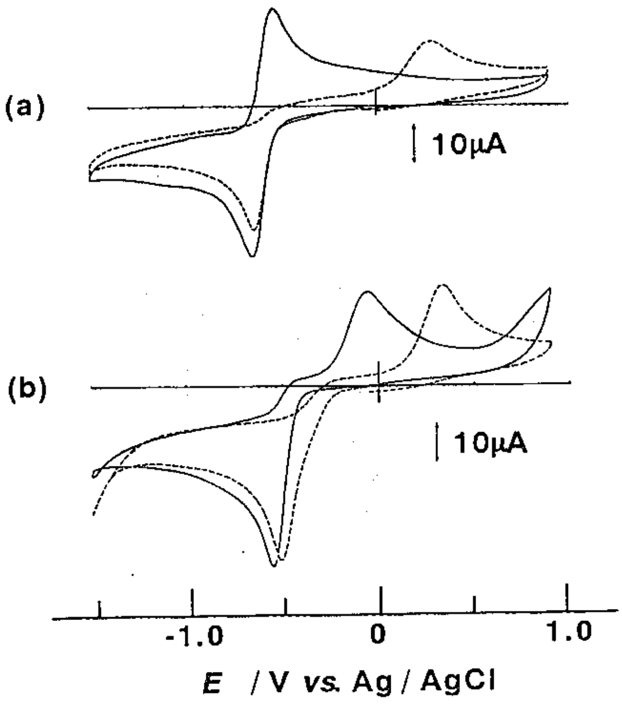

Figure 11. Cyclic voltammogram of TMQ (0.96 mM, (a); 1.22mM, (b)) under N_2 (solid lines) and CO_2 (dotted lines) in CH_3CN / H_2O (9:1 v/v) (a) and CH_3OH (b), containing Bu_4NBF_4 (0.1 M). dE/dt = 100 mV / s: working electrode; glassy carbon.

may be doubtful from the comparison of the basicity between $[TMQ{\cdot}H]^-$ and $[TMQ{\cdot}H{\cdot}CO_2]^-$. The other two, $[TMQ{\cdot}CO_2{\cdot}CO_2H]^-$ and $[TMQ{\cdot}(CO_2H)_2]^0$, are formed by protonation of $[TMQ{\cdot}2CO_2]^{2-}$. Thus, the three possible CO_2 adducts apparently result from an electrophilic attack of CO_2 to either $[TMQ]^{2-}$ or $[TMQ{\cdot}H]^-$. It is, therefore, concluded that the acidity of CO_2 is almost equivalent or stronger than that of hydroxy proton of CH_3CN/H_2O (9:1 v/v) and CH_3OH under CO_2. If the selectivity of eqs 14 and 15 is mainly controlled by the acidity of CO_2, the reaction of eq 15 rather than eq 14 is liable to occur in CH_3CN/H_2O (9:1 v/v) and CH_3OH.

Chapter VI
Conclusions

To evaluate a relative acidity of CO and NO ligated on metal complexes, $[Ru(NO_2)(CO)(bpy)_2]PF_6$ was prepared and analyzed the structure. The CO ligand of $[Ru(NO_2)(CO)(bpy)_2]^+$ undergoes a reversible nucleophilic attack of OH^- to form, while neither $[Ru(CO)(bpy)_2(NO_2H)]^{2+}$ nor $[Ru(CO)(bpy)_2(NO)]^{3+}$ was formed by the treatment of $[Ru(NO_2)(CO)(bpy)_2]^+$ with HCl. This observation suggests that the Ru-NO or Ru-NO_2H moiety has more acidic character than the Ru-CO one.

The molecular structures of $[Ru(CO)_2(bpy)_2](PF_6)_2$, $[Ru(C(O)OCH_3)(CO)(bpy)_2]$-$BPh_4 \cdot CH_3CN$ as a model of $[Ru(C(O)OH)(CO)(bpy)_2]^+$, and $[Ru(\eta^1(C)\text{-}CO_2)(CO)(bpy)_2] \cdot 3H_2O$ were determined. On the basis of the fact that the Ru-$C(O)OCH_3$ bond distance of $[Ru(C(O)OCH_3)(CO)(bpy)_2]^+$ is shorter than the Ru-CO_2 one of $[Ru(\eta^1(C)\text{-}CO_2)(CO)(bpy)_2]$, a multi-bond character of the Ru-CO_2 bond is not larger than the Ru-$C(O)OCH_3$ bond. One extra electron pair involved in $[Ru(\eta^1(C)\text{-}CO_2)(CO)(bpy)_2]$ resulting from dissociation of the terminal proton of $[Ru(C(O)OH)(CO)(bpy)_2]^+$ may, therefore, localize mainly in the CO_2 ligand. The increase in the electron density of the CO_2 moiety is effectively compensated by the extended three-dimensional network of hydrogen bondings between the CO_2 ligand and three water molecules in $[Ru(\eta^1(C)\text{-}CO_2)(CO)(bpy)_2] \cdot 3H_2O$.

The basicity of $\eta^1(C)\text{-}CO_2$ moiety of $[Ru(\eta^1(C)\text{-}CO_2)(CO)(bpy)_2]$ is strong enough to abstract an active hydrogen of malonic acid and malononitrile (R-H). The resulting $[Ru(C(O)OH)(CO)(bpy)_2]^+$ further reacts with those carbanions (R^-) to form the Ru-C(O)R moiety with generating a new C-C bond.

Interaction of CO_2 with reduced quinones was examined in CH_3CN, CH_3CN/H_2O (9:1 v/v), and CH_3OH to evaluate the nucleophilicity of CO_2 in protic media. Predominant carboxylation of TMQ dianion in CO_2-saturated CH_3OH and CH_3CN/H_2O (9:1 v/v) implies that the acidity of CO_2 is strong enough to attack basic sites even in these protic media, although there has been a controversy about the formation of either M-CO_2 or M-H complex in the reaction of CO_2 with low valence metal complexes in protic media. The above result reasonably explains the presence of M-$\eta^1(C)\text{-}CO_2$ complexes as the reaction intermediate in catalytic cycles of photo- and electrochemical CO_2 reduction catalyzed by transition metal complexes.

The present work could give the information concerning the structural changes in the conversion from CO_2 to CO on metal complexes and the relative nucleophilicities of CO_2 and protons in protic media, for the first time.

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Acknowledgments

The author would like to express his gratitude to Professor Koji Tanaka and Dr. Hirotaka Nagao for their continuous guidance and encouragement.

Thanks are due to Professor Yoshihiko Kushi and Dr. Tatsuya Kawamoto of Osaka University for their advice on X-ray analysis in Chapter II.

Thanks are due to Professor Shie-Ming Peng and Mr. Biing-Chiau Tzeng of National Taiwan University for their advice on X-ray analysis in Chapter III.

Thanks are also extended to Mr. Nobutoshi Komeda, Miss Hide Kambayashi, Mr. Tetsunori Mizukawa, Dr. Ryo Miyamoto, and Mr. Yoshinori Kushi for their collaboration. Many thanks are due to all the members of the Coordination Chemistry Laboratories in Institute for Molecular Science.

Thanks are due to Mr. Toshizaburo Oga, Mr. Akitaka Kimura, and Mr. Hitoshi Itani of Sumitomo Rubber Industry Co. Ltd. for their kindness.

Thanks are due to my dear parents for their kindness.

The present work is partially supported by Grant-in-Aid for Scientific Research No. 03453105 from the Ministry of Education, Science and Culture.