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Stabilization of $[Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)]$ and unprecedented reversible oxide transfer reactions from CO_3^{2-} to $[Ru(bpy)_2(CO)_2]^{2+}$ and from $[Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)]$ to CO_2

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Abstract

Unusual thermal stability of $[Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)]$ (**1**) as a metal–η^1-CO_2 complex was examined both in solid state and in solution. Compound **1** dissolves in CH_3CN containing $LiCF_3SO_3$. Interaction between Li^+ and the η^1-CO_2 group enhances an electron flow from Ru to the CO_2 ligand and greatly contributes to the stabilization of the Ru–η^1-CO_2 bond. The reaction of $[Ru(bpy)_2(CO)_2](PF_6)_2$ with $[Crown\cdot K]_2CO_3$ in dry CH_3CN selectively produced **1** through the 1:1 adduct with the RuC(O)–OCO_2 moiety. Stoichimetric formation of **1** from the 1:1 adduct is also assisted by $[Crown\cdot K]^+$ as a Lewis acid. Similarly, the reaction of $[Ru(bpy)_2(CO)_2](PF_6)_2$ with $(Me_4N)_2CO_3$ in DMSO gave the 1:1 adduct in the initial stage, which gradually changed to a metalloanhydride complex, $[Ru(bpy)_2(CO)((CO)_2O)]$ due to the absence of Lewis acids to stabilize **1**, since an addition of $LiCF_3SO_3$ to the solution gave $[Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)]$ quantitatively. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Much attention has been devoted to activation of CO_2 on metal complexes [1]. Although a variety of metal complexes are shown to be active as catalyst precursors in the reduction of CO_2 [2], metal–η^1-CO_2 complexes ($[M\text{–}\eta^1\text{-}CO_2]^{n+}$) are generally accepted as key intermediates in the CO_2/CO conversion in both protic and aprotic conditions [3]. In the presence of proton donors, $[M\text{–}\eta^1\text{-}CO_2]^{n+}$ is transformed to $[M\text{–}CO]^{(n+2)+}$ through $[M\text{–}C(O)OH]^{(n+1)+}$ (Eq. (1)) [4]. In aprotic solutions, transformation of CO_2 to CO on metals is caused by oxygen and oxide transfer reactions from metal–CO_2 to various acceptors such as CO_2 [5], another metal–CO_2 [6], adjacent oxophilic metals [7] and PR_3 ligands [8]. Among these reactions, oxide transfer from metal–CO_2 to CO_2 (Eq. (2)), that requires no additional reactant in the CO_2/CO conversion, is utilized in the electrochemical reduction of CO_2 catalyzed by metal complexes (Eq. (3)) [9].

$$[M\text{–}\eta^1\text{-}CO_2]^{n+} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} [M\text{–}C(O)OH]^{(n+1)+} \times \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} [M\text{–}CO]^{(n+2)+} \quad (1)$$

$$[M(CO_2)]^{n+} + CO_2 \rightarrow [M\text{–}CO]^{(n+2)+} + CO_3^{2-} \quad (2)$$

$$2CO_2 + 2e^- \rightarrow CO + CO_3^{2-} \quad (3)$$

Stability of metal–η^1-CO_2 bonds will be enhanced by an increase of an electron donor ability of central metals, since a metal–η^1-CO_2 bond is formed by an overlap of the filled dz^2 orbital of d^8 metals and the empty CO_2 π^* orbital. Accordingly, an η^1-CO_2 group of metal complexes often behaves as a nucleophile to form multi-nuclear complexes with μ_2- and μ_3-CO_2 bridges [10]. Moreover, highly reduced metal–η^1-CO_2 complexes such as $[W(CO)_5(\eta^1\text{-}CO_2)]^{2-}$ and $[CpFe(CO)_2(\eta^1\text{-}CO_2)]^-$ are thermally labile and readily undergo oxide transfer reactions by CO_2 to generate $W(CO)_6$ and $[CpFe(CO)_3]^+$, respectively (Eq. (2)) ([5]a,b). Similarly, $[Ru(bpy)_2(qu)(CO)]^{2+}$ is produced through $[Ru(bpy)_2(qu)(\eta^1\text{-}CO_2)]^0$ in the reaction of $[Ru(bpy)_2(qu)(CH_3CN)]^0$ (qu = quinoline) with CO_2 at

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low temperature ([5]c). In contrast to the highly reactive $[Ru(bpy)_2(qu)(\eta^1\text{-}CO_2)]^0$, an analogous $[Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)]^0$ is quite stable and does not react with CO_2 under normal conditions. Such a difference in the reactivity between $[Ru(bpy)_2(qu)(\eta^1\text{-}CO_2)]^0$ and $[Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)]^0$ is correlated with the basicity of the $\eta^1\text{-}CO_2$ group. Basicity of metal–$\eta^1\text{-}CO_2$ complexes is evaluated from pK_a values of metal–C(O)OH complexes as their conjugated acids, though isolation of metal–$\eta^1\text{-}CO_2$ complexes is still rare ([1]e). The value of metal–C(O)OH reported so far is in a range from 2.5 to over 14 [1], suggesting that the amount of electrons transferred from metals to CO_2 group varies in a wide range, which must greatly influence the reactivity of metal–$\eta^1\text{-}CO_2$ complexes. This paper reports on the origin of thermal stability of $Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)$ (**1**), and the first reversible oxide transfer reactions from **1** to CO_2 and from CO_3^{2-} to $[Ru(bpy)_2(CO)_2]^{2+}$ ($\mathbf{3^{2+}}$).

2. Experimental

2.1. Materials

Sodium carbonate and 18-crown-6 were purchased from Nacalai Tesque and used as received. CH_3OH, CH_3CN, DMF and DMSO were distilled over CaH_2 twice prior to use. $[Ru(bpy)_2(CO)_2](PF_6)_2$ ([3]b), $[Ru(bpy)_2(H_2O)_2](PF_6)_2$ [11] and $Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)\cdot 3H_2O$ [12] were prepared according to the literatures.

2.2. Preparation of $[Ru(bpy)_2(^{13}CO)(H_2O)](PF_6)_2$

A red 2-methoxyethanol solution (20 ml) of $[Ru(bpy)_2(H_2O)_2](PF_6)_2$ (2.0 g) was stirred at 90°C in a 50 ml Schlenk tube under atmospheric pressure of ^{13}CO for 24 h. The resulted pale yellow solution was reduced to half in volume under vacuo. An addition of 3 M excess amounts of an aqueous $NaPF_6$ solution gave a yellow precipitate of $[Ru(bpy)_2(^{13}CO)(H_2O)](PF_6)_2$ in an 80% yield. IR (KBr) 1931 cm^{-1} ($\nu(^{13}CO)$).

2.3. Preparation of $[Ru(bpy)_2(^{13}CO)(^{12}CO)](PF_6)_2$

A suspension of $[Ru(bpy)_2(^{13}CO)(H_2O)](PF_6)_2$ (1.0 g) in H_2O (20 ml) was vigorously stirred in an autoclave at 140°C under ^{12}CO pressure (20 kg cm^{-2}) for 12 h. After the solution was cooled to room temperature, treatments with 3 M amounts of an aqueous $NaPF_6$ gave a white precipitate of $[Ru(bpy)_2(^{13}CO)(^{12}CO)](PF_6)_2$ in a 60% yield. IR (KBr) 2077 and 2008 cm^{-1} ($\nu(^{13}CO)$), 2089 and 2037 cm^{-1} ($\nu(^{12}CO)$), ^{13}C-NMR (CD_3CN) $\delta = 190.4$ ppm (Ru–CO). Prolonged reaction time gave a mixture of $[Ru(bpy)_2(^{13}CO)(^{12}CO)](PF_6)_2$ and $[Ru(bpy)_2(^{12}CO)_2](PF_6)_2$. IR (KBr) 2091 and 2037 cm^{-1} ($\nu(^{12}CO)$).

2.4. Preparation of $(Me_4N)_2CO_3$

After a CH_3OH solution (30 ml) of $Me_4NOH\cdot 5H_2O$ (200 mg) was dried over a molecular sieve 3A, dry CO_2 was bubbled slowly into the solution for 48 h. The solvent was evaporated under reduced pressure to a minimal portion. Sonication of the crude product in dry DMF (20 ml) for 1 h precipitated white $(Me_4N)_2CO_3$, which was filtered, washed with diethylether, and then dried in vacuo for 24 h. To protect from moisture, $(Me_4N)_2CO_3$ was stored under N_2.

2.5. Preparation of $(18\text{-crown-}6\cdot K)_2CO_3$ ($[Crown\cdot K]_2CO_3$)

Potassium carbonate (500 mg) was added to a CH_3OH (50 ml) solution of 18-crown-6 (2.44 g), and the suspension was sonicated until K_2CO_3 completely dissolved into the MeOH solution. The resulting solution was evaporated under reduced pressure to a minimal portion. An addition of diethylether gave $[Crown\cdot K]_2CO_3$ as a white precipitate. The product was washed with diethylether for several times and dried in vacuo for 24 h. To protect from moisture the obtained $[Crown\cdot K]_2CO_3$ was stored under N_2.

2.6. Thermolysis of $[Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)]\cdot 3H_2O$ in CH_3CN under N_2

Sonication of red crystals of $[Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)]\cdot 3H_2O$ in CD_3CN at 80°C under N_2 gave a yellow solution with the evolution of CO_2. The ^1H-NMR of the CD_3CN solution showed the Ru–H signal of $[Ru(bpy)_2(CO)(H)]^+$ ($\delta = -11.8$ ppm) [13] in an 80% intensity based on bpy signals.

2.7. Thermolysis of $[Ru(bpy)_2(CO)(CO_2)]\cdot 3H_2O$ in CH_3CN under air

Thermolysis of ^{13}C (50%) labeled $[Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)]\cdot 3H_2O$ in dry CH_3CN at 75°C under air gave a blue solution in 15 min and ^{13}C labeled $[Ru(bpy)_2(CO_3)]$ [14] gradually precipitated in an 80% yield. ^{13}C-NMR, $\delta = 168$ ppm (CO_3); IR (KBr) 1587 cm^{-1} $\nu(C{=}O)$, FAB Mass ($m/z = 473$, M).

2.8. Physical measurements

IR spectra were obtained on a Shimadzu FTIR-8100 spectrophotometer. ^1H- and ^{13}C-NMR spectra were measured on a JEOL EX270 (270 MHz) spectrometer. Electronic absorption spectra were recorded on a

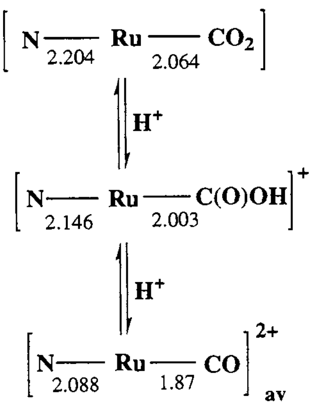


Fig. 1. The Ru–X (X = CO_2, C(O)OH, CO) and Ru–N (*trans* to Ru–X) bond distances (Å) of **1**·$3H_2O$, **2**(CF_3SO_3)(H_2O) and **3**(PF_6)$_2$.

Hewlett Packard 8452A diode array spectrophotometer. Rate constants of the reaction of $[Ru(bpy)_2(CO)_2](PF_6)_2$ with $(Me_4N)_2CO_3$ in DMSO were obtained on a UNISOFU RSP601 stopped-flow spectrophotometer.

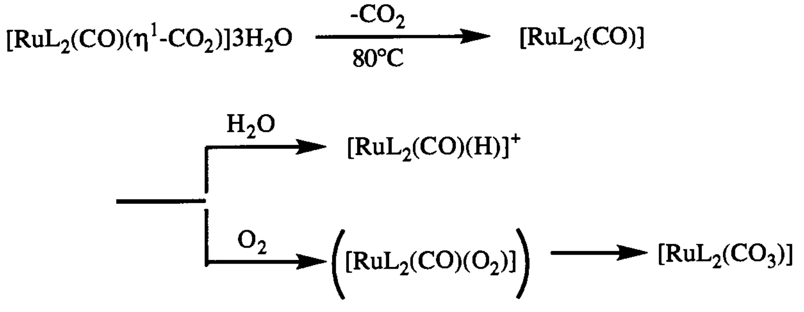
3. Results and discussion

3.1. Stability of $[Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)]$ (1) in solutions

Despite the importance of metal–η^1-CO_2 complexes as active catalysts in photo- and electrochemical reduction of CO_2 catalyzed by metal complexes, the reactivity of metal–η^1-CO_2 group is not fully understood due to thermal lability of most of those complexes [1]. Molecular structures of three metal–η^1-CO_2 complexes, Co(Pro-salen)K(η^1-CO_2)THP [15], $RhCl(diars)_2(\eta^1\text{-}CO_2)$ [16] and $Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)\cdot 3H_2O$ (**1**·$3H_2O$) [12], have been determined by X-ray analysis. Red crystals of **1**·$3H_2O$ show unusual thermal stability as a metal–η^1-CO_2 complex since the complex is stable to air and soluble in protic solvents such as H_2O, CH_3OH and C_2H_5OH. In H_2O, **1** exists as an equilibrium mixture with $[Ru(bpy)_2(CO)(C(O)OH)]^+$ (**2**$^+$) and $[Ru(bpy)_2(CO)_2]^{2+}$ (**3**$^{2+}$) (Eq. (4)) ([3]a,b). The molecular structures of **1**·$3H_2O$ [12], **2**$^+$ [17] and **3**$^{2+}$ [12] determined by X-ray analysis revealed that the Ru–X (X = CO, C(O)OH, CO_2) bond distance is elongated in the order of **3**$^{2+}$ < **2**$^+$ < **1** (Fig. 1). This trend is associated with a decrease of a π acidity in the order of CO > COOH > CO_2 ligands, though a double bond character in W–η^1-CO_2 bond has been suggested in $[W(CO)_5(\eta^1\text{-}CO_2)]^{2-}$ ([5]b). In addition, the view that metal–η^1-CO_2 bond is composed of σ-donation from dz^2 orbital of a central metal to CO_2, also supports less π-bond character of the Ru–CO_2 bond of **1** compared with the Ru–C(O)OH bond of **2**$^+$. The similar change in the Ru–N bond lengths in the order **3**$^{2+}$ < **2**$^+$ < **1** probably reflects the function of bpy as the σ-donor and π-acceptor ligand that effectively works as an electronic buffer toward the serious changes in the electronic configuration of Ru in these complexes. Two bpy ligands, therefore, would largely contribute to unusual thermal stability of not only **1**·$3H_2O$ but also **2**$^+$ compared with metal–η^1-CO_2 and metal–C(O)OH complexes reported so far [17].

$$[Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)] \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} [Ru(bpy)_2(CO_2)]^{2+} \qquad (4)$$

An ionic Ru–η^1-CO_2 complex, $[Cp(CO)_2Ru(CO_2)]$-Na, decomposes to $Cp(CO)_2Ru(H)$ in THF at 0°C [18]. Red crystals of **1**·$3H_2O$ are not soluble in aprotic solvents such as CH_3CN, DMSO and DMF. Thermolysis of **1**·$3H_2O$, therefore, was conducted in CH_3CN suspension under N_2 at 80°C. Under the conditions, **1**·$3H_2O$ decomposed to yellow $[Ru(bpy)_2(CO)(H)]^+$ in a 80% yield with evolving CO_2. This reaction is explained by CO_2 dissociation from **1**, followed by electrophilic attack of H_2O to the resultant $[Ru(bpy)_2(CO)]^0$ (Scheme 1). Similar thermolysis of **1**·$3H_2O$ under air also evolved CO_2 and $[Ru(bpy)_2(CO_3)]$ was formed in a 60% yield. The oxidation of the CO group of $[Ru(bpy)_2(CO)]^0$ by O_2 is explained by formation of $[Ru(bpy)_2(CO)(O_2)]^0$ as a reaction intermediate in the thermolysis, since a CO ligand of $Ir(CH_3)[P(p\text{-}tolyl)_3]_2(CO)(O_2)$ is smoothly oxidized to $Ir(CH_3)[P(p\text{-}tolyl)_3]_2(O_2CO)$ [19]. Similarly, a $Rh(O_2)(CO)$ species is proposed in oxidation of a CO ligand of $Rh_6(CO)_{16}(O_2)$ by O_2 [20]. It is worthy of note that no appreciable thermolysis of **1** was observed in H_2O (pH 11.0) at 100°C for 2 h under N_2 ([3]b). Such thermal stability



Scheme 1. Thermolysis of **1** under N_2 and air.

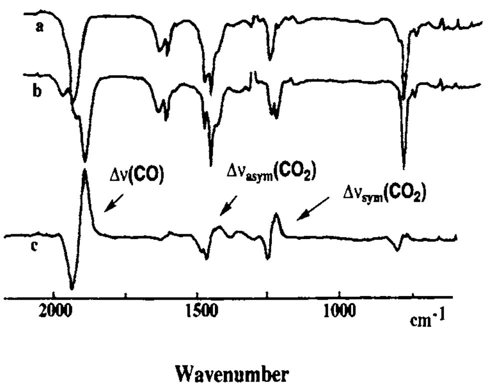


Fig. 2. IR spectra of $[Ru(bpy)_2(Cl_6O)(Cl_6O_2)]\cdot 3H_2O$ (a) and $[Ru(bpy)_2(Cl_8O)(Cl_8O_2)]\cdot 3H_2^{18}O$ (b) in CD_3CN containing 5 mole equivalents of $LiCF_3SO_3$, and the difference spectra (a-b) (c).

of **1** in H_2O compared with $\mathbf{1}\cdot 3H_2O$ suspended in CH_3CN is reasonably associated with hydrogen bondings between the η^1-CO_2 group and solvent molecules. Red crystals of $\mathbf{1}\cdot 3H_2O$ have 3-dimensional networks of hydrogen bondings among the oxygen atoms of the CO_2 ligand and the solvated water molecules [12], and these hydrogen bondings must be broken when the crystals dissolve into solvents. In protic solvents, solvent molecules make new hydrogen bond with the CO_2 ligand cleaving the 3-dimensional network. Hydrogen bondings between the η^1-CO_2 ligand of **1** and solvent molecules in protic solutions must induce an additional electron flow from Ru to CO_2 which would strengthen the Ru–CO_2 bond. In aprotic solvents, the solvent molecules have no ability to break the hydrogen bond network of $\mathbf{1}\cdot 3H_2O$. Once the hydrogen bond networks were destroyed by heating, the complex was destabilized and the Ru–CO_2 bond was cleaved. In connection with this, alkali metals which have an ability to interact with η^1-CO_2 group, are shown to stabilize anionic M–η^1-CO_2 complexes in the order of n-$Bu_4N^+ < K^+ < Na^+ < Li^+$ ([4]c, [15,21,22]). In fact, $\mathbf{1}\cdot 3H_2O$ suspended in CH_3CN soon became a clear yellow solution by an addition of about three equivalents of $LiCF_3SO_3$ to the suspension. The ^{13}C-NMR spectrum of the resultant yellow CD_3CN solution containing $\mathbf{1}\cdot 3H_2O$ and $LiCF_3SO_3$ displayed two peaks at 214.9 and 203.4 ppm assignable to the Ru–CO_2 and Ru–CO signals, respectively. The IR spectrum of the same CD_3CN solution showed strong two bands at 1467 and 1246 cm^{-1} assigned to ν_{asym} (CO_2) and ν_{sym} (CO_2) bands, respectively. These two bands shifted to 1422 and 1217 cm^{-1}, respectively, when $Ru(bpy)_2(C^{18}O)(\eta^1\text{-}C^{18}O_2)\cdot 3H_2^{18}O$ [12] was dissolved in CD_3CN containing $LiCH_3SO_3$ (Fig. 2). The 1467 and 1246 cm^{-1} bands of the ν_{asym} (CO_2) and ν_{sym} (CO_2) modes are quite close to those of $\mathbf{1}\cdot 3H_2O$ in KBr disks (1428 and 1242 cm^{-1}). It is worthy of note that interaction between $LiCF_3SO_3$ and the CO_2 group of **1** is strong enough to break the hydrogen bonding networks of the red crystals of $\mathbf{1}\cdot 3H_2O$, but the η^1-CO_2 structure of **1** remains intact in CH_3CN containing $LiCF_3SO_3$. The retention of the molecular structure of **1** in the yellow CH_3CN solution was also evidenced by the generation of $[Ru(bpy)_2(CO)_2]^{2+}$ ($\mathbf{3}^{2+}$) in a quantitative yield by an addition of two equivalents of CF_3COOH to the solution (Eq. (4)).

3.2. Oxide transfer reactions from CO_3^{2-} to $[Ru(bpy)_2(CO)_2]^{2+}$ and from $[Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)]$ to CO_2

Only the oxide transfer reaction from $[M\text{–}\eta^1\text{-}CO_2]^{n+}$ to CO_2 affording $[M\text{–}CO]^{(n+2)+}$ and CO_3 has been reported so far (Eq. (2)), and no example of the oxide transfer reaction from CO_3^{2-} to $[M\text{–}CO]^{(n+2)+}$ is demonstrated. Such irreversibility is believed to result from thermal lability of metal–η^1-CO_2 complexes compared with metal–CO ones. On the other hand, $\mathbf{3}^{2+}$ is reversibly converted to **1** through $[Ru(bpy)_2(CO)(C(O)\text{-}OH)]^+$ ($\mathbf{2}^+$) in H_2O (Eq. (4)). Moreover, **1** also is quite stable in CH_3CN as far as an appropriate Lewis acid such as $LiCF_3SO_3$ exists in the solutions. The oxide transfer from CO_3^{2-} to $\mathbf{3}^{2+}$ was conducted in dry CH_3CN, where proton assisted interconversion between $\mathbf{3}^{2+}$ and **1** (Eq. (4)) is reasonably neglected. A colorless CH_3CN solution of $\mathbf{3}(PF_6)_2$ rapidly turned to yellow in color (λ_{max} 390 nm (sh)) by an addition of an equimolar amount of $[Crown\cdot K]_2CO_3$ to the solution and then changed to a greenish red solution showing an absorption band at $\lambda_{max} = 586$ nm with a shoulder at 400 nm (Fig. 3).

The ^1H-NMR spectra of the greenish red CD_3CN solution shows magnetically nonequivalent two bpy ligands suggesting the formation of a *cis*-$Ru(bpy)_2$ moiety (Fig. 4). The solution also exhibited two signals at $\delta = 202.8$ and 201.8 ppm in the ^{13}C-NMR spectra, and the carbonyl signal of $\mathbf{3}^{2+}$ ($\delta = 190.4$ ppm) completely

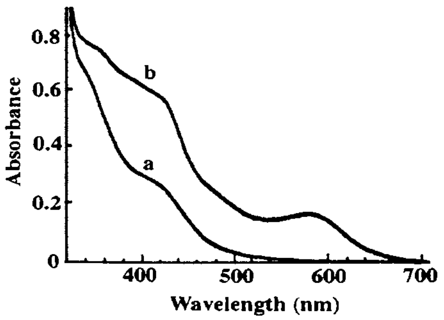


Fig. 3. Electronic absorption spectra of an equimolar mixture of $\mathbf{3}(PF_6)_2$ and $[Crown\cdot K]_2CO_3$ (2.68×10^{-4} M); right after mixing (a) and 30 min later (b) in CH_3CN.

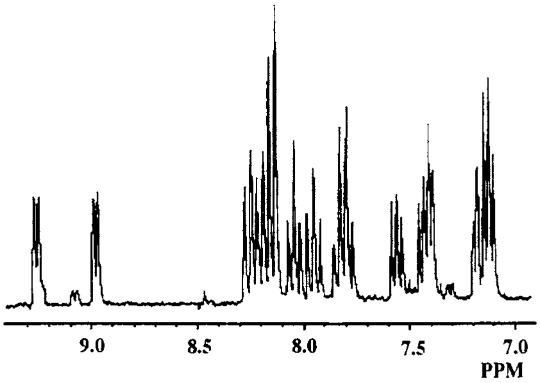


Fig. 4. ^{1}H-NMR spectrum of the final product of the reaction of $\mathbf{3}(PF_6)_2$ and $[Crown\cdot K]_2CO_3$ in CD_3CN.

disappeared in the spectra. These NMR spectra remained unchanged over one night at room temperature. The IR spectra of the greenish red solution displayed two strong new bands at 1968 and 1620 cm^{-1} besides the $\nu(CO_2)$ band of free CO_2 at 2342 cm^{-1} (Fig. 5). In the same operation using $[Ru(bpy)_2(^{12}CO)(^{13}CO)]^{2+}$, a new set of two bands were observed at 1921 and 1587 cm^{-1} in addition to the bands at 2342, 1968 and 1620 cm^{-1}. Appearance of the $\nu(^{12}CO_2)$ band but not the $\nu(^{13}CO_2)$ one of free CO_2 in the reaction of $[Ru(bpy)_2(^{12}CO)(^{13}CO)]^{2+}$ with $^{12}CO_3^{2-}$ makes evident the occurrence of oxide transfer from CO_3^{2-}, to $\mathbf{3}^{2+}$. Treatments of the final greenish red solution with two equimolar amount of CF_3COOH or $HClO_4$ regenerated colorless $\mathbf{3}^{2+}$ (IR, 2087 and 2043 cm^{-1}, and ^{13}C-NMR, $\delta = 190.4$ ppm) in an almost quantitative yield. The 1968 and 1620 cm^{-1} bands, therefore, are assigned to $\nu(C{\equiv}O)$ and ν_{asym} (CO_2) bands of **1** formed in the reaction (Eq. (7)), although these bands [23] were observed at 1969 and 1467 cm^{-1}, respectively, in a CH_3CN solution containing $\mathbf{1}\cdot 3H_2O$ and Li^+. The large difference in the ν_{asym} (CO_2) band of $[Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)]$ ($\Delta\nu = 153$ cm^{-1}) in the presence of Li^+ and $[Crown\cdot K]^+$ must reflect the stronger affinity of the former to the η^1-CO_2 ligand.

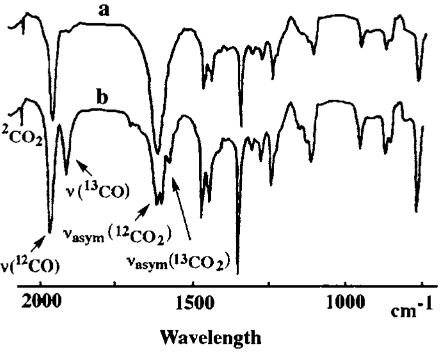


Fig. 5. IR spectra of the final product of the reactions of $[Crown\cdot K]_2CO_3$ with $\mathbf{3}(PF_6)_2$ (a) and with $[Ru(bpy)_2(CO)(^{13}CO)](PF_6)_2$ (b) in CH_3CN.

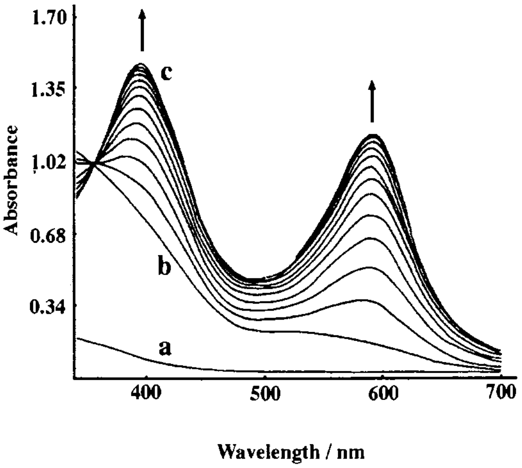


Fig. 6. Electronic absorption spectra of $\mathbf{3}(PF_6)_2$ (1.60×10^{-2} M) (a) and after an addition of $[(CH_3)_4N]_2CO_3$ (4.80×10^{-1} M) at 30 s intervals (from B to C) in DMSO.

$$[Ru(bpy)_2(CO_2)]^{2+} + CO_3^{2-} \rightarrow [Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)] + CO_2 \qquad (7)$$

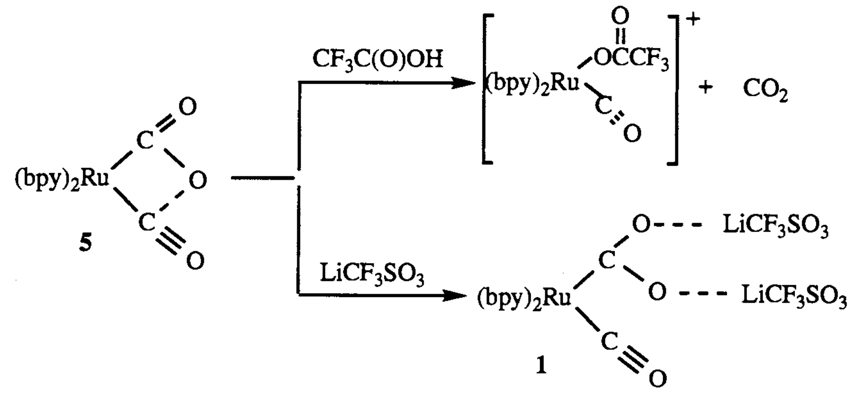
The greenish red CH_3CN solution of **1** prepared by the reaction of Eq. (7) did not change even after CO_2 is introduced into the solution by bubbling. Further addition of 5 M excess of $LiCF_3SO_3$ to the solution caused a gradual disappearance of the greenish red color and $\mathbf{3}^{2+}$ was regenerated with a precipitation of Li_2CO_3 (confirmed by IR spectra). It is worthy to note that $\mathbf{3}^{2+}$ was not formed at all by an addition of either $LiCF_3SO_3$ or CO_2 to the CH_3CN solution of **1**. Thus, the oxide transfer from **1** to CO_2 (Eq. (8)) is forced to proceed by

$$[Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)] + 2Li^+ + CO_2 \rightarrow [Ru(bpy)_2(CO)_2]^{2+} + Li_2CO_3 \qquad (8)$$

the removal of Li_2CO_3 out of the CH_3CN solution as a white precipitate. In fact, the oxide transfer from $[Crown\cdot K]_2CO_3$ to $\mathbf{3}^{2+}$ in CH_3CN (Eq. (7)) finished in a few minutes, while it took an almost 1 day to complete the oxide transfer from **1** to CO_2 in the presence of $LiCF_3SO_3$ in the same solvent (Eq. (8)).

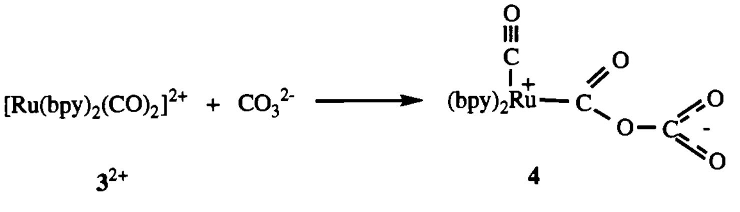
3.3. Reaction of $[Ru(bpy)_2(CO)_2]^{2+}$ ($\mathbf{3}^{2+}$) with $(Me_4N)_2CO_3$

The formation of **1** in the oxide transfer from CO_3^{2-} to $\mathbf{3}^{2+}$ would be largely influenced by the counter ion of carbonate, since the η^1-CO_2 group of **1** must be stabilized by interaction with Li^+ or $[Crown\cdot K]^+$ in CH_3CN. The oxide transfer reaction from $(Me_4N)_2CO_3$ to $\mathbf{3}^{2+}$ was also conducted since R_4N^+ is expected to have essentially no ability to stabilize metal–η^1-CO_2 complexes. Fig. 6 shows the change in the electronic absorption spectra of the reaction of $\mathbf{3}(PF_6)_2$ with

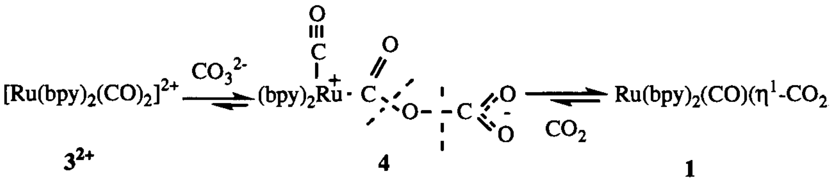


Scheme 2. Reactivity of **5**.

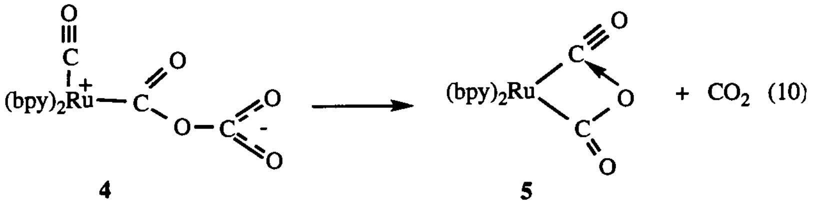
$(Me_4N)_2CO_3$ in DMSO [24]. Right after the mixing, a colorless DMSO solution rapidly changed to yellow, and a weak broad band appears around 540 nm with an increase in the absorbances at wavelengths shorter than 480 nm. Then, two absorption bands at 396 and 590 nm emerge and gradually increase in the intensities with an isosbestic point at 355 nm. The spectral change almost ceased in 5 min, and the color of the final solution became dark green. Although the final electronic absorption spectra of the DMSO solution was different from that of the reaction of $\mathbf{3}^{2+}$ with $[Crown\cdot K]_2CO_3$ in CH_3CN, the transient yellow solutions observed in both reactions gave the same electronic spectra. Both reactions, therefore, proceed through the same intermediate. Relatively long lifetime of the yellow intermediate in the reaction of $\mathbf{3}^{2+}$ with $(Me_4N)_2CO_3$ in DMSO enabled to measure the ^{13}C-NMR spectra of the species in the solvent. The ^{13}C-NMR spectra of the yellow solution appeared in the initial stage of the reaction of $Ru(bpy)_2(^{12}CO)(^{13}CO)](PF_6)_2$ with $[(CH_3)_4N]_2CO_3$ in d_6-DMSO displayed two signals at $\delta = 201.7$ and 205.2 ppm. These signals gradually disappeared and two new signals emerged at $\delta = 157.4$ and 161.4 ppm. Although the chemical shifts of the two signals of the final product are not assigned to CO and η^1-CO_2 ligands, those of the two signals initially emerged are almost same as those of $[Ru(bpy)_2(CO)(C(O)OH)]^+(\mathbf{2}^+)$ ($\delta =$ 201.5, 204.3 ppm) in DMSO. The yellow intermediate observed in the initial stage of the reaction is, therefore, the head-to-tail adduct (**4**) formed by a nucleophilic attack of CO_3^{2-} to carbonyl carbon of $\mathbf{3}^{2+}$). The reaction of (Eq. 9) $\mathbf{3}^{2+}$ with $[Crown\cdot K]_2CO_3$ producing **1** and CO_2 is reasonably explained by the dissociation of CO_2 from **4**. The final product (**5**) resulted from dissociation of CO_2 from **4** in the presence of Me_4N^+ in DMSO. However, it is different from **1** based on the ^{13}C-NMR chemical shift ($\delta = 157.4$ and 161.4 ppm). Treatment of the final dark green DMSO solution of **5** with an equimolar amount of CF_3COOH produced $[Ru(bpy)_2(CO)(OC(O)CF_3)]^+$ in an almost quantitative yield [25] with evolving $^{13}CO_2$ (confirmed by ^{13}C-NMR spectra) [26], indicating the fission of one of the Ru–CO bond of $\mathbf{3}^{2+}$. On the other hand, an addition of 5 M excess of $LiCF_3SO_3$ to the dark green DMSO solution of **5** resulted in a gradual change to yellow in color. After 10 h, the electronic spectrum of the yellow solution was consistent with that of **1** in the presence of $LiCF_3SO_3$ in CH_3CN. Indeed, the DMSO solution of **1** obtained from the dark green solution of **5** was allowed to react with 2 M excess of CF_3COOH produced colorless $\mathbf{3}^{2+}$ ($\delta = 195.3$ ppm) with a trace amount of $[Ru(bpy)_2(CO)(O(O)CF_3)]^+$ ($\delta = 198.4$ ppm). The facts that $[Ru(bpy)_2(CO)(OC(O)CF_3)]^+$ and **1** are selectively produced in the reactions of the dark green product (**5**) with CF_3COOH add $LiCF_3SO_3$, respectively, indicate that **5** is a configurational isomer of **1**, which is not stabilized by the interaction between the η^1-CO_2 group and Lewis acids. Based on theses observations, the most reasonable structure of the dark green product (**5**) is a metalloanhydride complex, $Ru(bpy)_2((CO)_2O)$, which is formed by the intramolecular attack of oxygen of the η^1-CO_2 group to the adjacent CO ligand of **1** (Eq. 10). The reactions of **5** with CF_3COOH and $LiCF_3SO_3$, therefore, is represented by Scheme 2. It is worthy of note that treatment of **1**



(9)



Scheme 3. Equilibrium among 3^{2+}, 4 and 1.



4 **5**

with CF_3COOH selectively produced 3^{2+}, while the same procedure of **5** gave $[Ru(bpy)_2(CO)(OC(O)CF_3)]^+$. Thus, a metalloanhydride complex, **5** is not suitable one for the CO_2/CO conversion. The complete conversion from **5** to **1** by the addition of $LiCF_3SO_3$ also indicates the strong stabilization of the η^1-CO_2 group by Li^+ even in DMSO. In fact, the reaction of 3^{2+} with $[Crown \cdot K]_2CO_3$ in d_6-DMSO gave the dark green solution via the yellow intermediate of **4**, but the ^{13}C-NMR spectrum of the DMSO solution showed four signals assignable to **1** ($\delta = 202.2$ and 201.4 ppm) and **5** ($\delta =$ 166.6 and 160.5 ppm) with nearly same intensities. Based on the fact that **1** is selectively produced in the reaction of 3^{2+} with $[Crown \cdot K]_2CO_3$ in CH_3CN, the formation of a mixture of **1** and **5** in the same reaction in DMSO apparently is caused by the decrease in the Lewis acidity of $[Crown \cdot K]^+$ in DMSO due to the strong solvation. Several attempts of isolation of **5** from DMSO solutions were not successful, but similar metalloanhydride complexes have been also proposed in ^{18}O scrambling between CO_2 and CO ligands of $[CpFe(CO)_2(\eta^1\text{-}CO_2)]^-$ ([4]a) and in the thermolysis reaction of $CpRu(CO)(CO_2)Na$ [18].

As depicted in the spectral change in the reaction of 3^{2+} with $(Me_4N)_2CO_3$ in DMSO (Fig. 6), the rate of the adduct formation (Eq. 9) is much faster than that of the cyclization with dissociation of CO_2 (Eq. 10). The rates of these reactions (Eq. 9 and 10) were separately determined by monitoring the increase in the absorbances at 355 and 590 nm, respectively, under pseudo first-order reaction conditions of 10–50 M excess of $(Me_4N)_2CO_3$ in DMSO. Plots of the observed rate constant for the adduct formation (Eq. 9) against the concentration of $(Me_4N)_2CO_3$ gave a straight line with the zero intercept, suggesting that the contribution of the backward reaction of Eq. 9 is negligible. The rate constant of the first step (k_1) was determined as 3.5×10^2 l mol^{-1} s^{-1} (25°C). Under the pseudo-first order reaction conditions, the observed rate constant of the second step was essentially independent on the concentrations of $(Me_4N)_2CO_3$, and the rate constant of the second step (k_2) is determined as 1.1×10^{-2} s^{-1} (25°C). The $\Delta H^{\neq}$ and $\Delta S^{\neq}$ calculated from the k_2 values obtained at 25, 30, 35, and 40°C were 134.3×10^3 J mol^{-1} and $+175.8$ J K^{-1} mol^{-1}, respectively. The large $\Delta S^{\neq}$ value for the second step suggests that the rate determining step is the dissociation of CO_2 from the 1:1 adduct of **4**. The fact that the rate of the dissociation of CO_2 from **4** in the presence of $[Crown \cdot K]^+$ in CH_3CN (Eq. (7)) is much faster than that in the presence of $(CH_3)_4N^+$ in DMSO (Eq. 10) also is indication of the stabilization of **1** by $[Crown \cdot K]^+$.

3.4. Direction of the oxide transfer

In the solid state, three water molecules of **1**·$3H_2O$ are linked to the η^1-CO_2 group and form three-dimensional hydrogen bonding networks. High stability of **1** in protic solvents also is ascribed to the formation of hydrogen bondings between the η^1-CO_2 group and solvent molecules. Solubilization of red crystals of **1**·$3H_2O$ into CH_3CN containing $LiCF_3SO_3$ is also associated with strong interaction between Li^+ and the η^1-CO_2 ligand. Similar to the hydrogen bondings between the η^1-CO_2 ligand and solvent molecules, the interaction with Li^+ must induce an additional electron flow from Ru to the CO_2 group and strengthen the Ru–CO_2 bond. The first requisite for the formation of **1** in aprotic solvents is the assist for the stabilization of the Ru–η^1-CO_2 bond by Lewis acids such as Li^+ and $[Crown \cdot K]^+$, otherwise a metalloanhydride complex of **5** is formed by an attack of oxygen of the η^1-CO_2 ligand to the carbonyl carbon of **1** due to the lack of the stabilization of the Ru–η^1-CO_2 bond. From the viewpoint of the acid-base equilibrium among **1**, $\mathbf{2}^+$ and 3^{2+} in H_2O (Eq. (4)), the basicity of **1** is considered to be weaker than CO_3^{2-} based on pK_a value of the conjugated acids of **2**$^+$ (9.5) ([3]b) and $HOCO_2^-$ (10.3) [27]. The 1:1 adduct (**4**) formation by an attack of oxygen of CO_3^{2-} to carbonyl carbon of **3**$^{2+}$ (Scheme 3), therefore, is also explained by an acid–base reaction. The smooth dissociation of CO_2 from **4** in the presence of Li^+ or [Crown·K]$^+$ in CH_3CN are associated with the stabilization of **1** by these Lewis acids. Thus, the counter ions of CO_3^{2-} play the key role in the first example of the oxide transfer from COd_3^{2-} to metal–CO producing metal–η^1-CO_2. The equilibrium between **4** and **1** (Scheme 3) shifts to the right under normal conditions due to weak basicity of **1**. In fact, CO_2 (1 atm) did not give any influence on the electronic absorption spectra of **1** in the presence of [Crown·K]$^+$ in CH_3CN, but the **3**$^{2+}$ was slowly produced by the oxide transfer from **1** to CO_2 when CO_3^{2-} is removed out of the solution as a precipitation of Li_2CO_3.

Both **1** and **3**$^{2+}$ work as the CO_2 carrier and the precursor to CO evolution in electro- [28] and photochemical reduction [29] of CO_2 in water, where **1** is rapidly converted to **3**$^{2+}$ through $[Ru(bpy)_2(CO)(C(O)OH)]^+$(**2**$^+$) (Eq. (4)). The equilibrium of between **3**$^{2+}$ and **1** via **4** in aprotic media, however, shifts to **1** (Scheme 3), which practically loses catalytic ability of **1** and **3**$^{2+}$ toward the reductive disproportionation reaction of CO_2 (Eq. (3)). Relatively weak basicity of the η^1-CO_2 of **1** results from the existence of π-acceptor ligands of two bpy and one CO group. Replacement of the CO ligand of **1** by qu (qu = quinoline) greatly enhances the basicity of the η^1-CO_2 ligand, since $Ru(bpy)_2(qu)(\eta^1\text{-}CO_2)$ is rapidly converted to $[Ru(bpy)_2(qu)(CO)]^{2+}$ under CO_2 atmosphere (Eq. (3)). As a result, $[Ru(bpy)_2(qu)(CO)]^{2+}$ works as an excellent catalyst in reductive disproportionation reduction of CO_2 to produce CO and CO_3^{2-} in CH_3CN under electrolysis conditions ([4]c). Thus, the direction of the conversion between CO_2 and CO on metals can be controlled by the adjustment of the basicity of the η^1-CO_2 ligands.

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[23] The $\nu_{sym}(CO_2)$ band of $[Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)]$ formed in the reaction of Eq. 7 was obscured by strong bands of $[Crown \cdot K]^+$ in CD_3CN.

[24] The reaction was conducted in DMSO due to extremely low solubility of $(Me_4N)_2CO_3$ in CH_3CN.

[25] The complex was characterized by the comparison of ^{13}C-NMR spectra with the authentic sample ($\delta = 198.4$ (Ru–CO)) and FAB-mass spectrum ($m/z = 555$, M).

[26] The amount of CO_2 evolved after the addition of CF_3COOH to the reaction mixture of $[Ru(bpy)_2(^{12}CO)_2]^{2+}$ and $(Me_4N)_2CO_3$ in DMSO was not detected by ^{13}C-NMR under the experimental conditions.

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