Ligand Effects of Ruthenium 2,2′-Bipyridine and 1,10-Phenanthroline Complexes on the Electrochemical Reduction of CO_2

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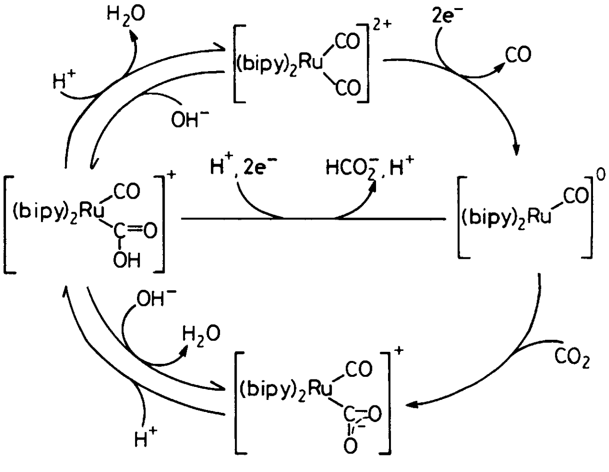
Electrochemical reduction of CO_2 catalysed by $[RuL^1(L^2)(CO)_2]^{2+}$ [L^1,L^2 = (bipy)$_2$, (bipy)(dmbipy), (dmbipy)$_2$, or (phen)$_2$], $[Ru(phen)_2(CO)Cl]^+$ (phen = 1,10-phenanthroline), and $[RuL(CO)_2Cl_2]$ [L = 2,2′-bipyridine (bipy) or 4,4′-dimethyl-2,2′-bipyridine (dmbipy)] were carried out by controlled-potential electrolysis at −1.30 V *vs.* saturated calomel electrode in acetonitrile–water (4:1, v/v), MeOH, or MeCN–MeOH (4:1, v/v). In acetonitrile–water (4:1, v/v) no difference in activities between the catalysts was observed, however in MeOH the amounts of carbon monoxide produced became larger than those of HCO_2^- upon introduction of the dmbipy ligand. This is attributed to the equilibrium constants among the reaction intermediates $[RuL^1(L^2)(CO)_2]^{2+}$, $[RuL^1(L^2)(CO)\{C(O)OH\}]^+$, and $[RuL^1(L^2)(CO)(CO_2^-)]^+$ which become smaller on substitution of bipy by dmbipy, because of the donor property of the CH_3 group.

Carbon dioxide fixation has received considerable attention in connection with the problems of lack of fuels, resources, and energies, and of the increase in carbon dioxide concentrations in air. Electrochemical reduction of CO_2 has been noted as one practical method, however for selective reduction of CO_2 without evolution of H_2 effective electrocatalysts are required. There have been many reports concerning electrochemical reduction of CO_2 catalysed by transition-metal complexes,[1–14] and the products obtained shown to depend on the nature not only of the central metal ions but also of ligands attached. For instance, complexes of Ni and Co with macrocycles,[1] palladium phosphine complexes,[2] and pyridine complexes of Re,[3] Ru,[4] and Rh[5] as catalysts are known to generate CO in the electrochemical reduction of CO_2. On the other hand, catalysts for formation of HCO_2^- are reported to be rhodium phosphine complexes,[6] phthalocyanine complexes and macrocycles of Co and Ni,[7] a palladium-based electrode,[8] ruthenium bipyridine complexes,[9] and iron–sulphur clusters.[10] Other products in the reduction are HCHO,[11] MeOH,[12] and CH_4,[13] all of which are produced by solid metal catalysts, except for $K_2Fe[Fe(CN)_6]$ which affords MeOH.[12a] Thus, the electrochemical reduction of CO_2 can be controlled by changing the metal ion and/or the ligand of transition-metal catalysts. While a variety of transition-metal ions has been examined there are only a few reports concerning the effect of ligands on the catalytic activity of transition-metal complexes.[14]

We have reported that $[Ru(bipy)_2(CO)_2]^{2+}$ (bipy = 2,2′-bipyridine) catalysed electrochemical reduction of CO_2 in aqueous dimethylformamide (dmf) solutions to afford CO and HCO_2^- as CO_2 reduction products under acidic and basic conditions, respectively,[4] and that HCO_2^- formed selectively in MeCN containing weak acids such as dimethylamine hydrochloride and phenol.[9] The reaction mechanisms were explained as shown in the Scheme;[4] $[Ru(bipy)_2(CO)_2]^{2+}$ is electrochemically reduced by two electrons to give $[Ru(bipy)_2(CO)]$ with CO elimination, and $[Ru(bipy)_2(CO)]$ reacts with CO_2 to give the σ-CO_2 complex, $[Ru(bipy)_2(CO)(CO_2^-)]^+$. Generation of $[Ru(bipy)_2(CO)(CO_2^-)]^+$ was confirmed spectroscopically under controlled-potential electrolysis at −1.10 V *vs.* saturated calomel electrode (s.c.e.) of a CO_2-saturated dmf solution of $[Ru(bipy)_2(CO)_2]^{2+}$. The complex $[Ru(bipy)_2(CO)(CO_2^-)]^+$ reacts with protons to afford $[Ru(bipy)_2(CO)\{C(O)OH\}]^+$ and $[Ru(bipy)_2(CO)_2]^{2+}$ under alkaline and acidic conditions, respectively. The former is reduced to give HCO_2^- and the latter evolves CO and regenerates $[Ru(bipy)_2(CO)]$. Therefore, the equilibrium reactions among $[Ru(bipy)_2(CO)_2]^{2+}$, $[Ru(bipy)_2(CO)\{C(O)OH\}]^+$, and $[Ru(bipy)_2(CO)(CO_2^-)]^+$ are important as regards the selectivity of the reaction products, CO and HCO_2^-.



Scheme.

We describe here the electrochemical reduction of CO_2 catalysed by ruthenium complexes of bipyridine derivatives, bipy, 4,4′-dimethyl-2,2′-bipyridine (dmbipy), and 1,10-phenanthroline (phen), and the ligand effects of the ruthenium complexes on the equilibrium reactions between the ruthenium complexes and OH^-, the electrochemical properties of those ruthenium complexes, and the electrochemical reduction of CO_2 catalysed by those ruthenium complexes.

Experimental

Materials.—The complexes $[Ru(bipy)(CO)_2Cl_2]$, $[Ru(dmbipy)(CO)_2Cl_2]$, $[Ru(bipy)_2(CO)_2][PF_6]_2$, and $[Ru(dmbipy)_2(CO)_2][PF_6]_2$ were prepared according to the literature.[15] Tetrabutylammonium hydroxide was purchased as a methanol solution and used without further purification; $NBu^n_4ClO_4$ prepared by the reaction of NBu^n_4Br with $HClO_4$ in water was recrystallized five times from diethyl ether–acetone. Methanol was purified by distillation with sodium methoxide under a nitrogen atmosphere. Acetonitrile was purified by distillation over P_2O_5 four times before use, and stored under a nitrogen atmosphere. Mercury used as a working electrode was washed successively with aqueous HCl and aqueous $NaBH_4$ and then distilled under reduced pressure.

Preparations.—$[Ru(bipy)(dmbipy)(CO)_2][PF_6]_2\cdot 0.5Me_2CO$. An ethanol–water (10:7, v/v; 170 cm^3) solution containing $[Ru(dmbipy)(CO)_2Cl_2]$ (0.41 g, 1.0 mmol) and 2,2′-bipyridine (0.18 g, 1.2 mmol) was refluxed under N_2 for 24 h. After cooling to room temperature, ethanol in the solution was evaporated to half volume *in vacuo*, and the resulting precipitates of unreacted $[Ru(dmbipy)(CO)_2Cl_2]$ and 2,2′-bipyridine were filtered off. To the filtrate was added an aqueous NH_4PF_6 solution to give a precipitate, which was recrystallized twice with acetone–ether as yellow crystals; 53% yield, $\nu(C{\equiv}O)$ 2 024 and 2 076 cm^{-1} (Found: C, 37.50; H, 2.85; N, 6.85. Calc. for $C_{25.5}H_{23}F_{12}N_4O_{2.5}P_2Ru$: C, 37.60; H, 2.75; N, 6.95%).

$[Ru(phen)_2(CO)_2][PF_6]_2$. An aqueous 90% formic acid solution (50 cm^3) of $RuCl_3\cdot nH_2O$ (1.0 g) was refluxed under N_2 for 5 h. The resulting clear orange solution was allowed to stand at room temperature, and evaporated to dryness under reduced pressure to afford an orange solid, which was dissolved in water–ethanol (1:4, v/v) containing 1,10-phenanthroline (1.0 g, 5.5 mmol). Then the solution was refluxed under N_2 for 2 h, followed by cooling to 0 °C to give an orange precipitate of $[Ru(phen)(CO)_2Cl_2]$. The crude product thus obtained and 1,10-phenanthroline (1.0 g, 5.5 mmol) was dissolved in water–ethanol (2:1, v/v, 100 cm^3), and heated under reflux for 24 h. To the solution was added a concentrated aqueous solution of NH_4PF_6 at room temperature to yield an off-white precipitate, which was purified by recrystallization from acetone–ether; 78% yield, $\nu(C{\equiv}O)$ 2 060 and 2 110 cm^{-1} (Found: C, 38.75; H, 2.15; N, 7.10. Calc. for $C_{26}H_{16}F_{12}N_4O_2P_2Ru$: C, 38.65; H, 2.00; N, 6.95%).

$[Ru(phen)_2(CO)Cl]PF_6$. A dmf solution (20 cm^3) containing $RuCl_3\cdot nH_2O$ (1.0 g, 3.8 mmol), 1.10-phenanthroline (1.4 g, 7.7 mmol), and LiCl (1.5 g, 35 mmol) was refluxed under N_2 for 8 h. After cooling to room temperature, the solution was mixed with acetone (100 cm^3) and allowed to stand overnight at 0 °C to give a precipitate of $[Ru(phen)_2Cl_2]$, which was collected by filtration, washed with ether and then water, and dried *in vacuo*. The product $[Ru(phen)_2Cl_2]\cdot 2H_2O$ (1.0 g, 1.8 mmol) thus obtained was dissolved in 90% HCO_2H (30 cm^3) and the solution was refluxed under N_2 for 6 h. After cooling to room temperature the solution was evaporated to dryness. The residue was dissolved in water, and an aqueous solution of NH_4PF_6 was added to afford a solid, which was collected by filtration and recrystallized from acetone–ether; $\nu(C{\equiv}O)$ 1 962 cm^{-1} (Found: C, 44.40; H, 2.75; N, 8.00. Calc. for $C_{25}H_{16}ClF_6N_4OPRu$: C, 44.80; H, 2.40; N, 8.35%).

Physical Measurements.—Equilibrium constants were determined by spectrophotometry and potentiometric titration at 25 °C, and the calculations were made according to the literature.[16] Electrochemical measurements were carried out in a Pyrex cell (30 cm^3) equipped with a working electrode, a platinum auxiliary electrode, a s.c.e., and a nozzle for bubbling N_2 or CO_2. The working electrodes used were a platinum microelectrode (area 0.20 cm^2) and a glassy carbon electrode (0.07 cm^2), both of which were polished well with abrasive paper 2000 and washed with distilled water several times before use. Cyclic voltammograms were obtained by the use of a Hokuto Denko HA-301 potentiostat, a Hokuto Denko HB-107A function generator, and a Yokogawa Electric Inc. 3077 X-Y recorder. The concentrations of CO_2 in MeCN were determined on a Shimadzu GC-7A gas chromatograph equipped with a 2-m column filled with Gaschropack 54 and using N_2 as a carrier gas.

Electrochemical Reductions of CO_2.—The reductions of CO_2 in CO_2-saturated acetonitrile–water (4:1, v/v), MeOH, or MeCN–MeOH (4:1, v/v) solutions containing ruthenium complexes (5.0×10^{-4} mol dm^{-3}) and $NBu^n_4ClO_4$ (0.10 mol dm^{-3}) were carried out by controlled-potential electrolysis at − 1.30 V *vs.* s.c.e. at a mercury electrode. The electrolysis cell consisted of three compartments: one for a mercury working electrode (3.1 cm^2), the second, separated from the working electrode cell by a Nafion membrane, for a platinum auxiliary electrode (*ca.* 3 cm^2), and the third for an s.c.e. reference electrode. The volumes of these compartments were 35, 25, and 8 cm^3, respectively, and the first two were connected to volumetric flasks with stainless-steel tubes (inside diameter = 0.4 mm). At a fixed interval of coulombs consumed in the reduction, 0.1-cm^3 portions of gas were sampled from the gaseous phases of both the working-electrode compartment and the volumetric flask with a pressure-locked syringe (Precision Sampling). Gaseous products were analysed on a Shimadzu GC-3BT gas chromatograph equipped with a 2-m column filled with molecular sieve 13X and using He as a carrier gas for the determination of CO, and on a Shimadzu GC-7A gas chromatograph equipped with a 2-m column filled with Unibeads 1S and using N_2 as a carrier gas for the determination of H_2 and $CO_2{}^-$. The volume of gas evolved in the reduction was determined from the change in the meniscus in the volumetric flask connected to the working-electrode compartment. The analysis of the solution was performed by sampling each 0.1-cm^3 portion from the working-electrode compartment through a septum cap by syringe techniques at a fixed interval of coulombs consumed. The amount of $HCO_2{}^-$ produced in the solution was determined with a Shimadzu IP-2A isotachophoretic analyser using an aqueous solution of β-alanine (0.02 mol dm^{-3}), HCl (0.01 mol dm^{-3}), and Triton X-100 (0.2%) as a leading electrolyte and an aqueous caproic (hexanoic) acid (0.01 mol dm^{-3}) solution as terminal electrolyte.

Results and Discussion

Equilibrium Reactions among $[RuL^1(L^2)(CO)_2]^{2+}$, $[RuL^1(L^2)(CO)\{C(O)OH\}]^+$, *and* $[RuL^1(L^2)(CO)(CO_2{}^-)]^+$.—The electronic absorption spectra of $[Ru(bipy)(dmbipy)(CO)_2]^{2+}$ in an aqueous solution (pH 5.31) and upon addition of an aqueous KOH solution are shown in Figure 1, which reveals that the bands at 251, 301, and 311 nm observed in the acidic medium are weakened with increasing pH, new bands appearing at 277, 343, and 422 nm with isosbestic points at 259, 296, and 322 nm. Similar spectra are observed for an aqueous $[Ru(dmbipy)_2(CO)_2]^{2+}$ solution; upon increasing the pH value, the absorption bands at 248, 301, and 313 nm disappeared and now bands at 268, 342, and 428 nm appeared with isosbestic points at 256, 296, and 322 nm, as shown in Figure 2. The spectral changes of both complexes are essentially consistent with that of the corresponding bis(2,2′-bipyridine) complex, $[Ru(bipy)_2(CO)_2]^{2+}$; in alkaline media one of the carbonyl groups of $[Ru(bipy)_2(CO)_2]^{2+}$ is attacked by OH^- to give $[Ru(bipy)_2(CO)\{C(O)OH\}]^+$ [equation (1)], which undergoes

$$[Ru(bipy)_2(CO)_2]^{2+} + OH^- \xrightleftharpoons{K_1} [Ru(bipy)_2(CO)\{C(O)OH\}]^+ \quad (1)$$

$$[Ru(bipy)_2(CO)\{C(O)OH\}]^+ + OH^- \xrightleftharpoons{K_2} [Ru(bipy)_2(CO)(CO_2{}^-)]^+ + H_2O \quad (2)$$

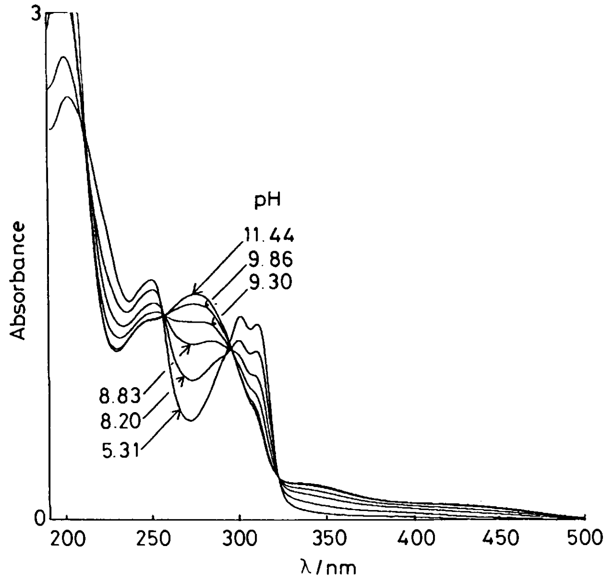


Figure 1. Electronic absorption spectra of [Ru(bipy)(dmbipy)(CO)$_2$]$^{2+}$ (5.0 × 10^{-5} mol dm^{-3}) in water at various pH (25 °C)

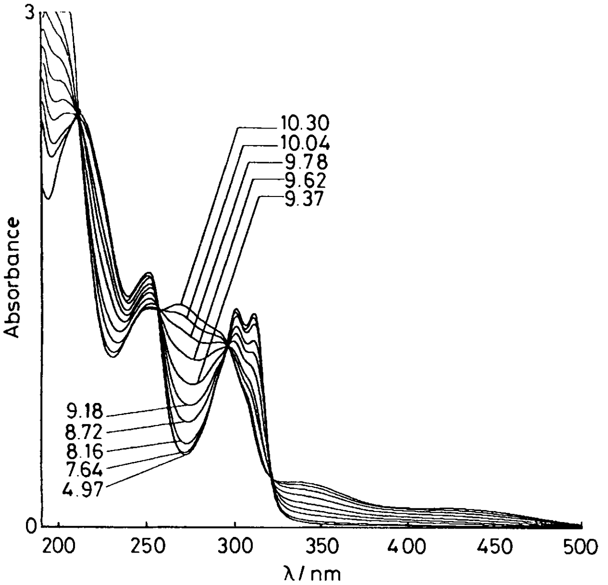


Figure 2. Electronic absorption spectra of [Ru(dmbipy)$_2$(CO)$_2$]$^{2+}$ (5.0 × 10^{-5} mol dm^{-3}) in water at various pH (25 °C)

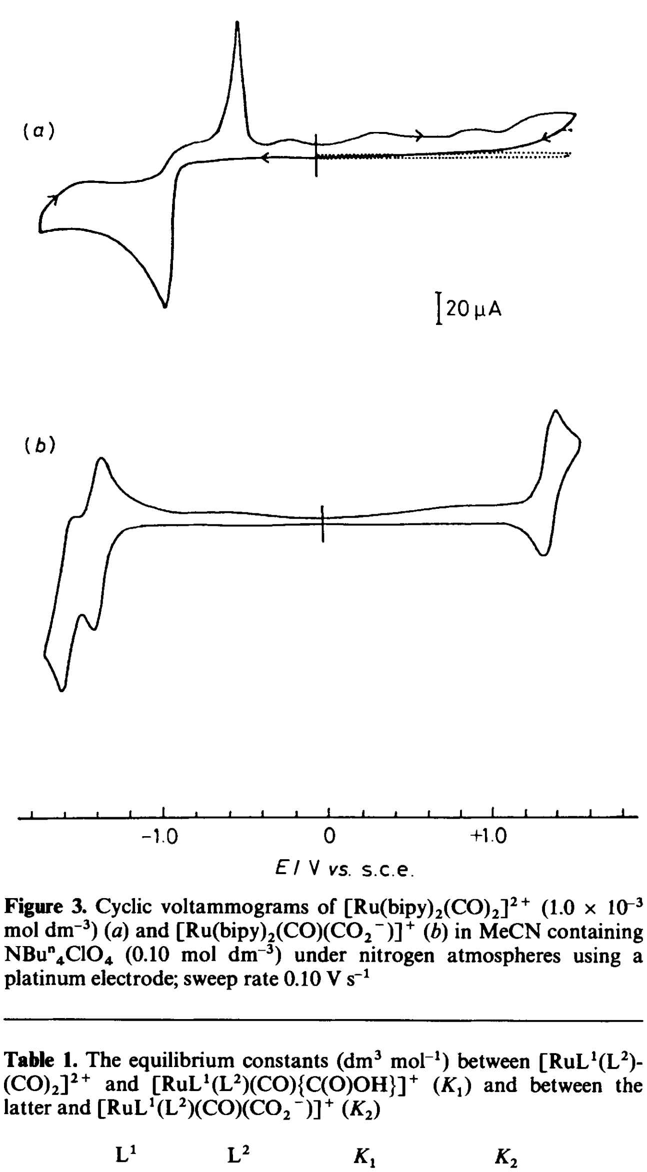


Figure 3. Cyclic voltammograms of [Ru(bipy)$_2$(CO)$_2$]$^{2+}$ (1.0 × 10^{-3} mol dm^{-3}) (*a*) and [Ru(bipy)$_2$(CO)(CO$_2^-$)]$^+$ (*b*) in MeCN containing NBu$^n_4$ClO$_4$ (0.10 mol dm^{-3}) under nitrogen atmospheres using a platinum electrode; sweep rate 0.10 V s^{-1}

Table 1. The equilibrium constants (dm^3 mol^{-1}) between [RuL^1(L^2)(CO)$_2$]$^{2+}$ and [RuL^1(L^2)(CO){C(O)OH}]$^+$ (K_1) and between the latter and [RuL^1(L^2)(CO)(CO$_2^-$)]$^+$ (K_2)

L^1	L^2	K_1	K_2
bipy	bipy	1.32 × 10^5	2.27 × 10^4 *
bipy	dmbipy	3.96 × 10^4	9.08 × 10^3
dmbipy	dmbipy	4.41 × 10^4	4.64 × 10^3

* H. Ishida, K. Tanaka, M. Morimoto, and T. Tanaka, *Organometallics*, 1986, **5**, 724.

deprotonation to afford [Ru(bipy)$_2$(CO)(CO$_2^-$)]$^+$ [equation (2)].[17] The equilibrium constants between [RuL^1(L^2)(CO)$_2$]$^{2+}$ and [RuL^1(L^2)(CO){C(O)OH}]$^+$ (K_1), and between the latter and [RuL^1(L^2)(CO)(CO$_2^-$)]$^+$ (K_2), evaluated from titration curves are listed in Table 1. Both the equilibrium constants become smaller upon introduction of 4,4′-dimethyl-2,2′-bipyridine with an electron-donating CH$_3$ group as a ligand in place of 2,2′-bipyridine.

Electrochemical Properties of Ruthenium Species.—The cyclic voltammograms of [Ru(bipy)$_2$(CO)$_2$]$^{2+}$ in MeCN under a nitrogen atmosphere are shown in Figure 3(*a*); there is an irreversible cathode peak around −1.03 V *vs.* s.c.e. and some anode peaks in the range −1.0 to +1.5 V, of which the peak around −0.47 V is strong. These anodic currents may correspond to oxidation of the reduction products of [Ru(bipy)$_2$(CO)$_2$]$^{2+}$, because no anode peak is observed when the scanning was conducted in the range 0 to +1.5 V *vs.* s.c.e. [dotted line in Figure 3(*a*)]. The cathode peak of [Ru(bipy)$_2$(CO)$_2$]$^{2+}$ at −1.03 V *vs.* s.c.e. is shifted to more negative potentials upon introduction of a dmbipy ligand in place of bipy and the potentials exhibited by [RuL^1(L^2)(CO)$_2$]$^{2+}$ [L^{1}L^2 = (bipy)$_2$, (bipy)(dmbipy), (dmbipy)$_2$, or (phen)$_2$] in MeCN are more negative than those in dmf, as listed in Table 2.

The cyclic voltammogram of [Ru(bipy)$_2$(CO)$_2$]$^{2+}$ in the presence of a high concentration of CO$_2$ (0.255 mol dm^{-3}) gives a large cathodic current around −1.6 V *vs.* s.c.e. as shown in Figure 4(*a*). This large current is attributed to the electrochemical reduction of CO$_2$ catalyzed by [Ru(bipy)$_2$(CO)$_2$]$^{2+}$. On the other hand, the cyclic voltammogram of the same complex in the presence of a low concentration of CO$_2$ (0.012 mol dm^{-3}) shows two shoulders at −1.41 and −1.60 V *vs.* s.c.e. with a large cathode current around −1.70 V [Figure 4(*b*)].

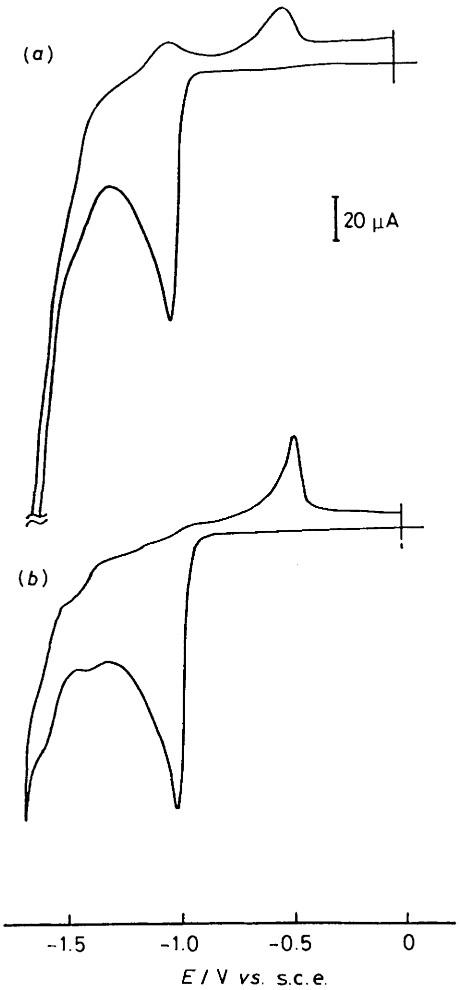


Figure 4. Cyclic voltammograms of $[Ru(bipy)_2(CO)_2]^{2+}$ (1.0×10^{-3} mol dm^{-3}) in MeCN containing $NBu^n_4ClO_4$ (0.10 mol dm^{-3}) in the presence of CO_2 [0.255 (*a*), 0.012 mol dm^{-3} (*b*)] using a platinum electrode; sweep rate 0.10 V s^{-1}

Table 2. Peak potentials of the irreversible reduction in the cyclic voltammograms of $[RuL^1(L^2)(CO)_2]^{2+}$ *

L^1	L^2	E_p/ V *vs.* s.c.e.	Solvent
bipy	bipy	−0.95	dmf
		−1.03	MeCN
bipy	dmbipy	−1.05	dmf
		−1.13	MeCN
dmbipy	dmbipy	−1.05	dmf
		−1.13	MeCN
phen	phen	−1.07	MeCN

* 1.0×10^{-3} mol dm^{-3} $[RuL^1(L^2)(CO)_2]^{2+}$, 0.10 mol dm^{-3} $NBu^n_4ClO_4$, sweep rate 0.10 V s^{-1}.

These two shoulders may be due to the reduction of an intermediate, Ru–CO_2 complex. On the other hand, the equimolar and twice molar addition of NBu^n_4OH to a MeCN solution of $[Ru(bipy)_2(CO)_2]^{2+}$ affords $[Ru(bipy)_2(CO)\{C(O)OH\}]^+$ and $[Ru(bipy)_2(CO)(CO_2^-)]^+$, respectively. The cyclic voltammogram of $[Ru(bipy)_2(CO)(CO_2^-)]^+$ under a nitrogen atmosphere shows two cathodic redox couples and an anodic couple [Figure 3(*b*)]. The cyclic voltammogram of $[Ru(bipy)_2(CO)(CO_2^-)]^+$ is the same as that of $[Ru(bipy)_2(CO)\{C(O)OH\}]^+$, however further addition of NBu^n_4OH resulted in decomposition of the ruthenium complex; the colour of the solution turned from orange to green. The ion $[Ru(bipy)_2(CO)(CO_2)]^+$ shows two cathodic peaks at −1.40 and −1.60 V *vs.* s.c.e.; the former is pseudo-reversible having −1.37 V as the $E_{p/2}$ value and the latter is irreversible, while the anodic couple having $E_{p/2}$ +1.40 V *vs.* s.c.e. is pseudo-reversible.* The reduction peak potentials around −1.40 and −1.60 V *vs.* s.c.e. agree closely with those in the cyclic voltammograms of $[Ru(bipy)_2(CO)_2]^{2+}$ at low concentration of CO_2, as shown in Figure 4(*b*). This result also supports the formation of $[Ru(bipy)_2(CO)(CO_2)]^+$ as an intermediate of the present CO_2 fixation, in addition to the spectroscopic result.[4] The first one-electron reduction potentials of $[RuL^1(L^2)(CO)(CO_2^-)]^+$ [L^1L^2 = $(bipy)_2$, (bipy)(dmbipy), $(dmbipy)_2$, or $(phen)_2$] are also shifted to negative values upon introducing dmbipy ligands, as listed in Table 3, though the values obtained in MeCN are slightly more negative than those in dmf.

Cyclic Voltammograms of $[RuL(CO)_2Cl_2]$ (L = bipy *or* dmbipy).—Monobipyridine complexes of rhenium, $[Re(bipy)(CO)_3X]$ (X = Br or Cl), are known to catalyze electrochemical reduction of CO_2,[3] while no catalytic activity has been reported for the corresponding ruthenium complexes. The cyclic voltammogram of $[Ru(bipy)(CO)_2Cl_2]$ in MeCN exhibits an irreversible cathode peak at −1.21 V *vs.* s.c.e. and a weaker anode peak at −0.42 V under N_2, as shown in Figure 5. The complex $[Ru(dmbipy)(CO)_2Cl_2]$ shows a similar cyclic voltammogram though the potentials are shifted to negative values; an irreversible cathode peak at −1.38 V and an anode peak at −0.60 V *vs.* s.c.e. The complex $[Ru(bipy)(CO)_2Cl_2]$ in MeCN under a carbon dioxide atmosphere displays a strong cathode peak around −1.85 V *vs.* s.c.e., which is more negative than that of $[Ru(bipy)_2(CO)_2]^{2+}$, and rather close to the reduction potential (−2.0 V *vs.* s.c.e.) of CO_2 without any catalyst. In view of this result, the activation of CO_2 by $[Ru(bipy)(CO)_2Cl_2]$ may be less effective than that by $[Ru(bipy)_2(CO)_2]^{2+}$. The cyclic voltammogram in acetonitrile-water (9:1, v/v) under a carbon dioxide atmosphere, however, shows a large cathodic current around −1.2 V *vs.* s.c.e., which may correspond to reduction of CO_2. Thus, $[Ru(bipy)(CO)_2Cl_2]$ may function as a catalyst for the electrochemical reduction of CO_2, in particular being efficient in acetonitrile-water (9:1, v/v).

Electrochemical Reduction of CO_2 *Catalyzed by Ruthenium Complexes.*—The reductions of CO_2 were performed in acetonitrile-water (4:1 v/v) solutions containing several ruthenium complexes (Table 4) by controlled-potential electrolysis at −1.30 V *vs.* s.c.e. The current densities in the electrolysis are almost the same (2—3 mA cm^{-2}) between the ruthenium complexes with 2,2′-bipyridine and 4,4′-dimethyl-2,2′-bipyridine, while they are influenced by stirring speed. The electrochemical reduction of CO_2 proceeds catalytically in the presence of either ruthenium complex, while the rate of reduction is somewhat slow when the ruthenium complexes with 1,10-phenanthroline are used as catalysts. The only reduction product is carbon monoxide in either case, and the amount is independent of the catalyst (Table 4).

The electrochemical reduction of CO_2 also proceeds in MeOH, however the reduction product is not only carbon monoxide but also formic acid, as shown in Table 5, and the

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* The reversibilities of the cathodic and anodic couples were examined at various scan rates. They are good below 0.3 V s^{-1}, but become poor above this value.

Table 3. Reduction potentials of $[RuL^1(L^2)(CO)(CO_2^-)]^+$ *

L^1	L^2	$E_{p/2}$/ V *vs.* s.c.e.	Solvent
bipy	bipy	−1.26	dmf
		−1.37	MeCN
bipy	dmbipy	−1.38	dmf
		−1.45	MeCN
dmbipy	dmbipy	−1.40	dmf
		−1.48	MeCN
phen	phen	−1.38	MeCN

* 1.0×10^{-3} mol dm^{-3} $[RuL^1(L^2)(CO)_2]^{2+}$, 2.0×10^{-3} mol dm^{-3} NBu^n_4OH, 0.10 mol dm^{-3} $NBu^n_4ClO_4$, sweep rate 0.10 V s^{-1}.

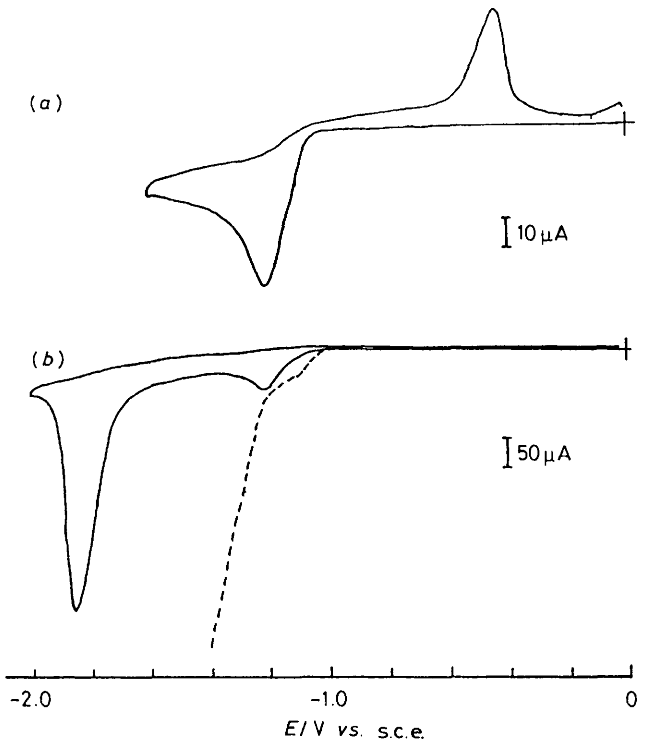

Figure 5. Cyclic voltammograms of $[Ru(bipy)(CO)_2Cl_2]$ (1.0×10^{-3} mol dm^{-3}) in MeCN (——) and acetonitrile–water (9:1, v/v) (– – – –) containing $NBu^n_4ClO_4$ (0.10 mol dm^{-3}) under (*a*) nitrogen and (*b*) carbon dioxide atmospheres using a glassy carbon electrode; sweep rate 0.10 V s^{-1}

Table 4. The electrochemical reduction of CO_2 catalyzed by ruthenium complexes in acetonitrile–water (4:1, v/v)[a]

Catalyst	Amount of product[b] CO/μ mol
$[Ru(bipy)_2(CO)_2]^{2+}$	209 (67.2)
$[Ru(bipy)(dmbipy)(CO)_2]^{2+}$	223 (71.8)
$[Ru(dmbipy)_2(CO)_2]^{2+}$	203 (65.3)
$[Ru(phen)_2(CO)_2]^{2+}$	191 (61.5)
$[Ru(phen)_2(CO)Cl]^+$	207 (66.6)
$[Ru(bipy)(CO)_2Cl_2]$	273 (87.8)
$[Ru(dmbipy)(CO)_2Cl_2]$	205 (66.0)

[a] −1.30 V *vs.* s.c.e. at a mercury electrode (3.3 cm^2); 60 C consumed. [b] Current efficiency (%) in parentheses.

Table 5. Electrochemical reduction of CO_2 catalyzed by ruthenium complexes in MeOH[a]

Catalyst	Amount of product[b]/μmol	
	CO	HCO_2^-
$[Ru(bipy)_2(CO)_2]^{2+}$	81 (26.1)	154 (49.5)
$[Ru(bipy)(dmbipy)(CO)_2]^{2+}$	106 (34.2)	123 (39.8)
$[Ru(dmbipy)_2(CO)_2]^{2+}$	139 (44.7)	101 (32.5)
$[Ru(phen)_2(CO)_2]^{2+}$[c]	108 (34.7)	76 (24.5)
$[Ru(phen)_2(CO)Cl]^+$[c]	123 (39.6)	40 (12.9)
$[Ru(bipy)(CO)_2Cl_2]$	85 (27.3)	117 (37.7)
$[Ru(dmbipy)(CO)_2Cl_2]$	122 (39.2)	83 (26.8)

[a] −1.30 V *vs.* s.c.e., at a mercury electrode (3.3 cm^2); 60 C consumed. [b] Current efficiency (%) in parentheses. [c] In MeCN–MeOH (4:1, v/v).

current densities are relatively low (*ca.* 0.5—1.0 mA cm^{-2}). The ions $[Ru(phen)_2(CO)_2]^{2+}$ and $[Ru(phen)_2(CO)Cl]^+$ are not soluble in MeOH, therefore the reactions catalyzed by the complexes were conducted in MeCN–MeOH (4:1, v/v). The amounts of the products are dependent on the catalyst; carbon monoxide increases and formic acid decreases with increasing donor property of the ligand. For instance, the amount of carbon monoxide generated increases in the order $[Ru(bipy)_2(CO)_2]^{2+}$ < $[Ru(bipy)(dmbipy)(CO)_2]^{2+}$ < $[Ru(dmbipy)_2(CO)_2]^{2+}$, whereas that of formic acid decreases in the same order. The amount of carbon monoxide also increased in the order; $[Ru(bipy)(CO)_2Cl_2]$ < $[Ru(dmbipy)(CO)_2Cl_2]$.

The mechanisms for the electrochemical reduction of CO_2 using $[Ru(bipy)(dmbipy)(CO)_2]^{2+}$ and $[Ru(dmbipy)_2(CO)_2]^{2+}$ as catalysts may be the same as that with $[Ru(bipy)_2(CO)_2]^{2+}$. The change in product distribution may be associated with equilibrium reactions among $[RuL^1(L^2)(CO)_2]^{2+}$, $[RuL^1(L^2)(CO)\{C(O)OH\}]^+$, and $[RuL^1(L^2)(CO)(CO_2^-)]^+$ (L^1, L^2 = bipy, dmbipy, or phen); the equilibrium concentration of $[RuL^1(L^2)(CO)_2]^{2+}$ becomes small on replacing the dmbipy ligand for L^1 and L^2 by bipy, because of the donor property of the CH_3 group. Thus, the amount of carbon monoxide generated became large on introducing the dmbipy ligand when the electrochemical reduction of CO_2 was conducted in MeOH. On the other hand, the absence of differing reactivity between catalysts in acetonitrile–water (4:1, v/v) may be explained by that water is a strong acid in MeCN and the equilibrium concentration of $[Ru(bipy)_2(CO)\{C(O)OH\}]^+$ is very small.

The electrochemical reduction of CO_2 catalyzed by $[Ru(bipy)(CO)_2Cl_2]$ or $[Ru(dmbipy)(CO)_2Cl_2]$ gives a result similar to that obtained with ruthenium bis(bipyridine) complexes. In order to obtain information on the active species in the catalytic system, electrochemical spectra of $[Ru(bipy)(CO)_2Cl_2]$ and $[Ru(dmbipy)(CO)_2Cl_2]$ were measured in MeCN, resulting in the decomposition of the ruthenium complexes. On the other hand, measurement of electronic absorption spectra of $[Ru(bipy)(CO)_2Cl_2]$ and $[Ru(dmbipy)(CO)_2Cl_2]$ in water has indicated that these complexes irreversibly react with OH^- leading to dissociation of the chloride or CO ligand. Thus, further study may be required to elucidate the active species in the present reduction of CO_2 by mono(bipyridine) catalysts.

In conclusion, the amounts of carbon monoxide become large on introducing the dmbipy ligand in the catalyst $[RuL^1(L^2)(CO)_2]^{2+}$ [L^1L^2 = $(bipy)_2$, (bipy)(dmbipy), or $(dmbipy)_2$] for the electrochemical reduction of CO_2 in MeOH. This is attributed to the equilibrium constants among $[RuL^1(L^2)(CO)_2]^{2+}$, $[RuL^1(L^2)(CO)\{C(O)OH\}]^+$, and $[RuL^1L^2(CO)(CO_2^-)]^+$ which become smaller on replacing the bipy ligand for L^1 and L^2 by dmbipy, because of the donor property of the

CH_3 group. This report is the first to describe ligand effects on the product selectivity in the electrochemical reduction of CO_2 catalyzed by transition-metal complexes.

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