Selective formation of HCO_2^- and $C_2O_4^{2-}$ in electrochemical reduction of CO_2 catalyzed by mono- and di-nuclear ruthenium complexes

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Electrochemical reduction of carbon dioxide catalyzed by mono- and di-nuclear ruthenium complexes produced HCO_2H with trace amounts of CO and $C_2O_4^{2-}$ in the presence and absence of H_2O, respectively, in MeCN.

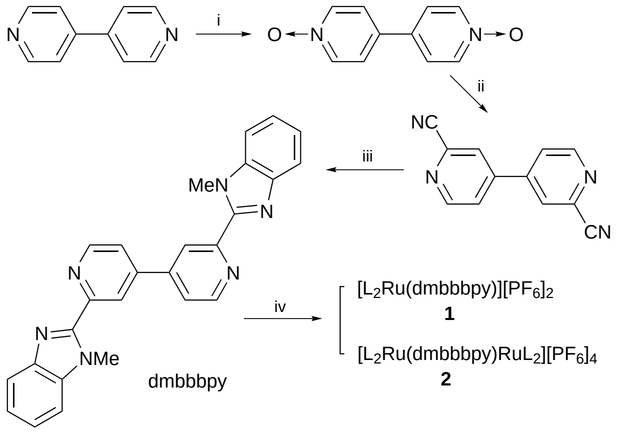
Reduction of CO_2 accompanied by carbon–carbon bond formation is highly desired because the electrochemical reduction of CO_2 catalyzed by metal complexes usually produces only CO and/or HCO_2H.[1–6] A key process for the activation of CO_2 on metals is how to create coordinately unsaturated low valent metal centers under mild conditions. We have found that $[(CpM)_3(\mu_3\text{-}S)_2]^{2+}$ (M = Co, Rh, Ir)[7] catalyzes electrochemical reduction of CO_2 to produce oxalate selectively, where the reaction sites for the first catalytic formation of $C_2O_4^{2-}$ are presumed to be created by an M–M bond cleavage upon the two-electron reduction of these M_3S_2 clusters. Metal complexes with unsymmetrical chelating rings may also provide sites for activation of CO_2 by dechelation in the electrochemical reduction of CO_2. We introduced 2,2′-bis(1-methylbenzimidazol-2-yl)-4,4′-bipyridine (dmbbbpy) as an unsymmetrical chelating ligand into a $Ru(bpy)_2$ moiety to aim not only to create reaction sites by opening the chelate ring but also to accumulate electrons into the ligand required in the reduction of CO_2. Here, we report almost selective HCO_2H and $C_2O_4^{2-}$ formation depending on the presence and the absence of H_2O in electrochemical reduction of CO_2 catalyzed by mono- and di-nuclear Ru complexes.

Scheme 1 shows the synthetic route for 2,2′-bis(1-methylbenzimidazol-2-yl)-4,4′-bipyridine (dmbbbpy) and the mono- and di-nuclear ruthenium complexes. Mono- (**1**) and di-nuclear Ru complexes (**2**) were synthesized by the reaction of $[Ru(bpy)_2Cl_2]$ with dmbbbpy with mol ratios of 1 : 1 and 2 : 1, respectively, in ethylene glycol. Both complexes were purified by column chromatography and characterized by electrospray MS and elemental analyses.

The cyclic voltammogram (CV) of **1** exhibited three reversible one electron redox couples at $E_{1/2}$ = −1.45, −1.75 and −1.99 V in MeCN resulting from dmbbbpy and two bpy based reductions, respectively. Complex **2** also showed three reversible redox couples with a small positive shift (0.2 V) of the dmbbbpy based redox wave. Introduction of CO_2 by bubbling into the solutions of **1** and **2** results in an increase in the cathodic currents at potentials more negative than −1.60 and −1.50 V, respectively, indicating that two-electron reduced forms of **1** and **2** have an ability to catalyze the reduction of CO_2 (Fig. 1).

Controlled potential electrolysis of **1** and **2** (0.2–0.3 mmol dm^{-3}) at −1.65 and −1.55 V (*vs.* Ag/AgCl) was conducted in CO_2 saturated MeCN (20 ml) in the presence of H_2O (0.5 ml). After 91 C was passed in the electrolysis of **1**,† HCO_2^- was produced with a current efficiency (η) of 89% together with a trace amount of CO (η = 2–3%). On the other hand, the similar electrochemical reduction of CO_2 in dry MeCN selectively produced oxalate‡ with an η of 64% without forming HCO_2^- and CO after 50 C was passed in the electrolysis. The electrochemical reduction of CO_2 catalyzed by **2** also generated almost selectively HCO_2^- (η = 90%) and $C_2O_4^{2-}$ (η = 70%) in the presence and the absence of H_2O, respectively, under similar conditions.

The reaction of CO_2 catalyzed by **1** was monitored in an IR cell with KBr windows equipped with a gold mesh for the working electrode, a platinum wire for a counter electrode and an Ag/AgCl reference electrode.[8] Reductive electrolysis at −1.65 V§ of **1** in CO_2-saturated CD_3CN solution resulted in the appearance of three bands at 1684, 1633 and 1603 cm^{-1} [Fig. 2(*b*)]. Reoxidation at −0.70 V causes the disappearance of the 1684 and 1603 cm^{-1} bands, while the 1633 cm^{-1} band assigned to $C_2O_4^{2-}$ remained unchanged. The three bands at 1684, 1633 and 1603 cm^{-1} shifted to 1638, 1600 and 1540 cm^{-1}, respectively, under similar electrolysis using $^{13}CO_2$



Scheme 1 Synthesis route for the bridging ligand, Ru mono- and di-nuclear complexes. *Reagents and conditions*: i, $MeCO_2H + H_2O_2$; ii, $(MeO)_2SO_2$, KCN; iii, *N*-methyl-1,2-phenylenediamine; iv, $[RuL_2Cl_2]$ (L = bpy).

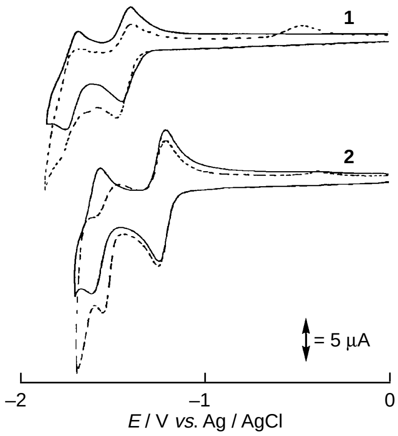


Fig. 1 Cyclic voltammograms of 0.3 mM **1** or **2** in 0.1 M NBu_4BF_4MeCN at glassy carbon electrode (id = 3.0 mm) under N_2 (——) and CO_2 (------) atmospheres. Scan rate = 50 mV s^{-1}.

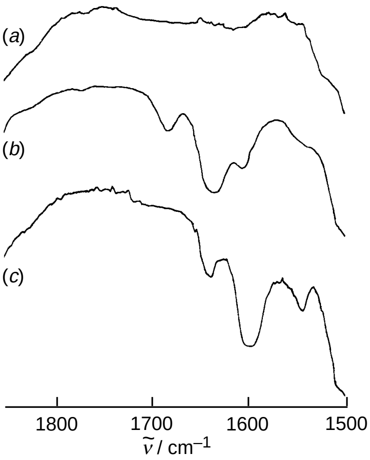


Fig. 2 IR spectra of **1** (0.8 mM) during a thin-cell bulk electrolysis in CD_3CN with $LiBF_4$. (*a*) Starting scan, (*b*) using $^{12}CO_2$, (*c*) using $^{13}CO_2$.

[Fig. 2(*c*)]. The bands at 1638 and 1540 cm^{-1} also disappeared upon reoxidation at -0.70 V suggesting that a CO_2 adduct probably formed by an attack of two molecules of CO_2 to the two-electron reduced form of **1** which acts as a precusor to oxalate in the electrochemical reduction of CO_2 in dry MeCN.

It is noteworthy that any interaction between reduced forms of $[Ru(bpy)_2L]^{2+}$ (L = bpy or 2-pyridyl-1-methylbenzimidazole¶) and CO_2 was not observed at all in the CV in MeCN. Indeed, these complexes have no ability to catalyze the electrochemical reduction of CO_2 under controlled potential electrolysis even at -1.80 V in the absence or presence of H_2O in MeCN. Moreover, $[Ru(bpy)_2(CO)X]^{n+}$ (n = 2, X = CO; n = 1, X = Cl)[9] works as an effective catalyst producing CO and/or HCO_2H in the electrochemical reduction of CO_2 under protic conditions, but the complex readily decomposes in the similar reduction of CO_2 in the absence of proton donor. Savéant and coworkers have shown that aromatic nitriles and esters with redox potentials more negative than -1.93 V mediate electrochemical reduction of CO_2 affording oxalate. The reaction is explained by an electrophilic attack of CO_2 to oxygen or nitrogen of the anion radicals followed by homolytic cleavage of the $ArX–CO_2^-$ [X = OC(O)R, CN] bond and the subsequent coupling of free $CO_2^{\cdot -}$.[10] On the other hand, the IR spectra of **1** showed the two $\nu(CO_2)$ bands (1684, 1603 cm^{-1}) assignable to the precursor for oxalate under electrolysis at -1.65 V, suggesting that oxalate generation in the present study does not result from dimerization of free $CO_2^{\cdot -}$. If two-electron reduction of **1** and **2** causes dechelation of dmbbbpy, the resultant five-coordinate Ru and monodentate dmbbbpy$^-$ may provide two binding sites for an attack of CO_2, which would facilitate a coupling reaction of CO_2 affording oxalate. Thus, dmbbbpy of **1** and **2** greatly contributes to the first selective formation of $C_2O_4^{2-}$ and HCO_2^- depending upon the absence and the presence of H_2O, respectively, in the electrochemical reduction of CO_2.

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Footnotes and References

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† HCO_2H was characterized using an isotachophoretic analyzer and ^{13}C NMR spectroscopy.

‡ Oxalate was characterized using an isotachophoretic analyzer [GC–MS (diester derivative, by esterification with diazomethane)] and ^{13}C NMR spectroscopy.

§ Electrolysis of **1** at potentials more negative than -1.75 V resulted in rapid growth of the 1633 cm^{-1} band so that electrolysis was conducted at -1.65 V to detect the emergence of the 1684 and 1603 cm^{-1} bands clearly.

¶ $[Ru(bpy)_2L]^{2+}$ (L = 2-pyridyl-1-methylbenzimidazole) was prepared and characterized by electrospray MS and elemental analyses.

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