COMMUNICATIONS

Selective Production of Acetone in the Electrochemical Reduction of CO₂ Catalyzed by a Ru–Naphthyridine Complex

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Electrochemical reduction of CO_2 with metal complexes is a feasible technique for the utilization of CO_2 as a C_1 source, though the reduction products usually have been limited to CO and/or HCOOH. Metal-catalyzed reductive disproportionation of CO_2 [Eq. (1)] proceeds through oxide transfer from a metal – CO_2 moiety to CO_2 [Eq. (2)] followed by reductive cleavage of the resultant metal – CO bond.

$$2\operatorname{CO}_2 + 2e^- \longrightarrow \operatorname{CO} + \operatorname{CO}_3^{2-} \tag{1}$$

$$[M-CO_2]^{n+} + CO_2 \longrightarrow [M-CO]^{(n+2)+} + CO_3^{2-}$$

$$(2)$$

Acylation of the metal–CO bond would lead to a new methodology for carbon–carbon bond formation in the reduction of CO₂. Polypyridyl ruthenium carbonyl complexes such as $[Ru(bpy)_2(quinoline)(CO)]^{2+}$ and $[Ru(bpy)_{-}(terpyridine)(CO)]^{2+}$ (bpy = 2,2'-bipyridyl) work as catalysts for the reduction of CO₂ according to Equation (1),^[1] and one-electron reduction of these complexes causes a bathochromic shift of their $\nu(CO)$ bands by about 30–40 cm^{-1,[2]} The mononaphthyridine complex $[Ru(bpy)_2(napy)(CO)](PF_6)_2$ (1; napy = 1,8-naphthyridine) undergoes a pronounced bathochromic shift of the $\nu(CO)$ band ($\Delta \tilde{\nu} = 418 \text{ cm}^{-1}$) upon one-electron reduction due to nucleophilic attack of the nonbonded nitrogen atom of the monodentate napy ligand on the carbonyl carbon atom $[Eq. (3)].^{[3]}$



Such a metallacyclization would suppress the reductive cleavage of the Ru–CO bond (CO evolution), and enable reduction of the CO group derived from CO_2 . Here we report the first selective production of acetone in the electrochemical reduction of CO_2 catalyzed by $[Ru(bpy)(napy)_2(CO)_2](PF_6)_2$ (2) in the presence of $(CH_3)_4NBF_4$.

The two CO ligands of 2 are coordinated to Ru in *cis* positions, and the two napy moieties are linked to Ru in a monodentate manner, as depicted in the crystal structure (Figure 1).^[4]



Figure 1. Molecular structure of the dication of 2 with atom labeling.

The cyclic voltammogram of **1** (0.1 mmol L⁻¹) in DMSO in the presence of $(CH_3)_4NBF_4$ (0.1 mol L⁻¹) under N₂ shows an irreversible cathodic wave at -1.40 V (all potentionals are given versus that of Ag/Ag⁺) and three (quasi-)reversible redox couples at $E_{pc} = -1.63$, -1.80, and -2.02 V with peak separations (ΔE_{p-p}) of 60, 80 and 94 mV, respectively (Figure 2). The bis-napy complex **2** displays two irreversible



Figure 2. Cyclic voltammograms of **1** and **2** in the presence of $(CH_3)_4NBF_4$ under N₂ (----) and CO₂ (----) in DMSO. The potential *E* is given in V versus Ag/Ag⁺.

cathodic waves at $E_{\rm pc} = -0.76$ and -0.98 V as well as three quasi-reversible couples at $E_{\rm pc} = -1.44$, -1.58, and -1.94 V with $\Delta E_{\rm p-p} = 80$ mV under the same conditions. One irreversible cathodic wave of **1** ($E_{\rm pc} = -1.42$ V) and two irreversible waves of **2** ($E_{\rm pc} = -0.76$ and -0.98 V) result from reduction of the napy ligands followed by formation of the Ru-C(O)-N-N ring [Eq. (3)]. Introduction of CO₂ to the solutions of **1** and **2** in DMSO causes strong catalytic currents due to the reduction of CO₂ (Figure 2), since electrochemical reduction of CO₂ takes place at potentials more negative than -2.4 V in the absence of these complexes. It is noteworthy that the reduction of CO₂ by **2** occurs at potentials more negative than -1.4 V, while the threshold potential of the CO₂ reduction by **1** is close to -2.0 V.

In agreement with Equation (1), only CO and Li_2CO_3 were produced in the controlled potential electrolysis of **2**

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 $(0.6 \text{ mmol L}^{-1})$ at -1.65 V with a glassy carbon (GC) electrode (4 cm²) in CO₂-saturated DMSO (30 mL)^[5] containing LiBF₄ (0.1 mol L⁻¹) as electrolyte. On the other hand, when (CH₃)₄NBF₄ was used as an electrolyte under otherwise similar conditions, acetone was selectively generated with a traces of CO. The amounts of these products increased with the electricity, as shown in Figure 3. Besides acetone and CO,



Figure 3. The amounts x of acetone (•) and CO (\odot) generated in the electrochemical reduction of CO₂ catalyzed by **2** in the presence of (CH₃)₄NBF₄ in DMSO at -1.60 V. The dashed line represents the theroretical amount of acetone expected based on Equation (4).

 $(CH_3)_3N$ and $\{(CH_3)_4N\}_2CO_3$ were the only other products detected in the solution. Thus, $(CH_3)_4N^+$ works not only as an electrolyte, but also as a methylation reagent for the catalytic generation of acetone in the electrochemical reduction of CO_2 catalyzed by **2** [Eq. (4)].

$$2 \text{CO}_2 + 4e^- + 2(\text{CH}_3)_4 \text{N}^+ \longrightarrow \text{CH}_3\text{C}(\text{O})\text{CH}_3 + \text{CO}_3^{2-} + 2(\text{CH}_3)_3 \text{N}$$
 (4)

Based on the stoichiometry of Equation (4), the current efficiency of acetone was 70% at 100°C (turnover number 8.5) and that of CO was less than 1%. This first selective formation of acetone in the electrochemical reduction of CO₂ [Eq. (4)] is associated with the suppression of reductive cleavage of the Ru-CO bond [Eq. (1)] by the metallacyclization shown in Equation (3).^[6] Indeed, the current densities of the GC electrodes in the reduction of CO₂ catalyzed by 2 were 5 and 0.25 mA cm⁻² in the presence of (CH₃)₄NBF₄ [Eq. (4)]^[7] and LiBF₄ [Eq. (1)], respectively. Moreover, the electrolysis potential is of fundamental importance for the catalytic generation of acetone, since acetone undergoes irreversible reduction at potentials of -2.0 V on GC electrodes in DMSO. Therefore, from the viewpoints of the threshold potential for the reduction of CO_2 (Figure 2), **1** is not a suitable catalyst for the reduction shown in Equation (4) even though CO evolution is depressed by the metallacyclization reaction of Equation (3).^[8]

Experimental Section

To a solution of $RuCl_3 \cdot 3H_2O(1 \text{ mmol})$ in ethanol (50 mL) was added bpy (1 mmol), and the solution was heated under reflux for 2 h. Then $Et_3N(0.5 \text{ mL})$ and napy (3 mmol) were added, and the solution was heated under reflux for 2 h. The reaction mixture was concentrated to about 5 mL. Addition of NaBF₄ (2 mmol) in H₂O resulted in precipitation of purple [Ru(bpy)(napy)₂Cl]BF₄ in 80% yield. A suspension of [Ru(bpy)-

 $(napy)_2Cl]BF_4$ in ethanol was heated at 60 °C under CO (40 atm) for 15 h. Concentration of the solution and treatment with an aqueous solution of NaBF₄ gave [Ru(bpy)(napy)₂(CO)₂](BF₄)₂ as a yellow powder in 70% yield. Elemental analysis calcd for $C_{28}H_{20}N_6B_2F_8Ru$: C 44.98, H 2.68, N 11.24; found: C 44.83, H 2.39, N 11.24; IR: $\tilde{\nu} = 2077$, 2027 cm⁻¹ (CO).

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- [4] a) Crystal data for 1: monoclinic, $P2_1/n$, a = 10.696(2), b = 14.989(3), c = 18.395(2) Å, $\beta = 99.58(1)^\circ$, V = 2907.7(8) Å³, Z = 4, $\rho_{calcd} =$ 1.707 g cm⁻³, $20.2 < 2\theta < 23.6^\circ$, Mo_{Ka} ($\lambda = 0.71069$ Å); of 7296 reflections observed, 6936 were independent. The structure was solved by direct methods (SAPI91) and refined against |F| with 2230 reflections $(I > 3.0\sigma(I))$ and 234 parameters; R = 0.071 and $R_w = 0.060$. b) Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-101753. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
- [5] The concentration of residual water in the DMSO was 21 µmolL⁻¹.
- [6] The electrochemical reduction of CO_2 also took place in CH₃CN, though in this case CO_3^{2-} is likely to deposit on the electrode. An orange solution obtained upon concentration of the electrolyzed solution of **2** in CH₃CN became yellow after exposure to air. Appearance of the two ν (CO) bands typical of **2** in the IR spectra of the resultant yellow solution strongly indicates that the reduced form of **2** is the stable catalyst in the formation of acetone.
- [7] An initial current density of 5 mA cm^{-2} dropped to about one-third at 100 C due to consumption of (CH₃)₄NBF₄. Renewed addition of electrolyte to the solution resulted in almost complete recovery of the initial current density.
- [8] Only a small amount of isopropyl alcohol was detected (current efficiency of about 10%) in the electrochemical reduction of CO_2 catalyzed by **1** at -2.00 V in DMSO in the presence of $(CH_3)_4NBF_4$.

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