Redox Chemistry

Electrochemical Hydrogenation of $[Ru(bpy)_2(napy\text{-}\kappa N)(CO)]^{2+}$: Inhibition of Reductive Ru–CO Bond Cleavage by a Ruthenacycle**

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Multielectron reduction of CO_2 and CO to afford highly reduced organic molecules has a fundamental importance in the utilization of C_1 resources. A number of metal complexes have been proven to work as catalyst precursors in photo-[1] and electrochemical[2] reduction of CO_2, although the reduction products are limited to CO and HCOOH as two-electron-reduced products. The generation of CO occurs by reductive cleavage of metal–CO bonds derived from M-η^1-CO_2 and M-η^1-CO(O)H complexes in protic media. The

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[**] bpy = 2,2′-bipyridine, napy = 1,8-naphthyridine.

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requisites for multielectron reduction of CO_2 and CO catalyzed by metal complexes, therefore, are electrochemical hydrogenation of CO in aqueous media without accompanying reductive cleavage of the M–CO bonds. We have been studying electro- and photochemical reduction of CO_2 using polypyridyl ruthenium carbonyl complexes,[3] in which ligand-based redox reactions supply the electrons required for the reduction of CO_2. A Ru–CO complex with monodentate 1,8-naphthyridine (napy) appears to be a suitable candidate to satisfy the contradicting requisites for suppression of the reductive cleavage of Ru–CO bonds and reductive activation of the carbonyl ligands in aqueous media, since the napy-localized redox reaction that enhances the nucleophilicity of the nonbonded nitrogen atom may trigger an intramolecular attack at the α-carbon atom of a neighboring ligand to form a metallacycle.[4] Therefore, we examined the possibility of metallacyclization of $[Ru(bpy)_2(napy\text{-}\kappa N)(CO)]^{2+}$ ($\mathbf{1}^{2+}$; napy = 1,8-naphthylidine) driven by the napy-based redox reaction with the aim of inhibiting the reductive cleavage of the Ru–CO bond and reductive activation of the carbonyl group in H_2O.

The cyclic voltammogram (CV) of the monocarbonylruthenium(II) complex $\mathbf{1}(BF_4)_2$ exhibits one irreversible cathodic wave at $E_{p,c} = -1.40$ V and two reversible redox couples at $E_{1/2} = -1.85$ and -2.09 V (versus Ag/Ag^+ in CH_3CN; Figure 1). The former and the latter two couples can be assigned to the napy- and bpy-localized reductions, respectively, based on the redox potentials of $[Ru(bpy)_2(napy\text{-}\kappa N)(CH_3CN)]^{2+}$.[5] The exhaustive electrolysis of $\mathbf{1}(BF_4)_2$ at -1.40 V in CD_3CN consumed just 1.0 $F\,mol^{-1}$ of electricity. The IR spectrum of $\mathbf{1}(BF_4)_2$ shows a strong ν(CO) band at $\tilde{\nu} = 2000\,cm^{-1}$ in CD_3CN. Electrochemical reduction of $\mathbf{1}^{2+}$ at -1.40 V resulted in complete disappearance of the bands between 2000 and 1700 cm^{-1}, and a new band emerged at 1587 cm^{-1}.[4b] The original IR spectrum of $\mathbf{1}^{2+}$ in CD_3CN could be regenerated by electrochemical oxidation of the resulting solution at 0 V. Attempts to isolate the one-electron-reduced form of $\mathbf{1}^{2+}$ were unsuccessful; however, exposure of the solution of the reduced complex $\mathbf{2}^{+}$ in CH_3CN to air regenerated $\mathbf{1}^{2+}$. The unusually large shift of the ν(CO) band ($|\Delta\tilde{\nu}| = 413\,cm^{-1}$) of $\mathbf{1}^{2+}$ during the one-electron reduction/oxidation cycle in CH_3CN can be reasonably explained by a nucleophilic attack of the free nitrogen atom of napy at the carbonyl carbon [Eq. (1)].

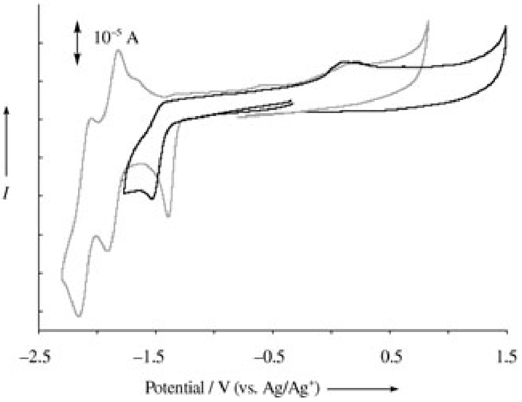
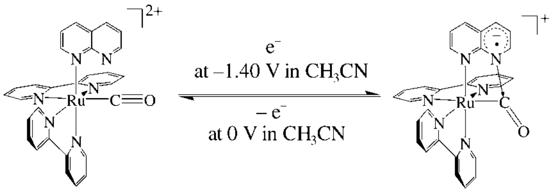


Figure 1. Cyclic voltammograms of $\mathbf{1}(BF_4)_2 \cdot H_2O$ in CH_3CN (light gray) and H_2O (dark gray).



$\mathbf{1}^{2+}$ $\mathbf{2}^{+}$ (1)

In H_2O, $\mathbf{1}^{2+}$ also displays one irreversible cathodic wave for the napy-based reduction, at -1.54 V. The bpy-localized redox couples were not detected as a consequence of the strong irreversible cathodic currents arising from the reduction of protons on a glassy carbon electrode at potentials more negative than -1.60 V in H_2O (Figure 1). In sharp contrast with the electrolysis of $\mathbf{1}(BF_4)_2$ at -1.40 V in CH_3CN, 2.0 $F\,mol^{-1}$ of electricity flowed during the exhaustive electrolysis of the complex in H_2O under otherwise similar electrolysis conditions. Addition of a large excess of NH_4PF_6 to the resulting electrolyte solution precipitated $\mathbf{3}(PF_6)$ as a red powder. Diffusion of diethyl ether vapor into a solution of the crude products in CH_3CN afforded single crystals of $\mathbf{3}(PF_6)$.

The molecular structures of $\mathbf{1}^{2+}$ and $\mathbf{3}^{+}$ determined by X-ray crystallography[6] are shown in Figures 2 and 3, respectively. The ruthenium centers of $\mathbf{1}^{2+}$ and $\mathbf{3}^{+}$ have a distorted octahedral N_5C coordination sphere consisting of four nitrogens of two bpy ligands, one nitrogen of napy, and one carbon of CO. The Ru1–C29 and C29–O1 bond lengths in $\mathbf{1}^{2+}$ are 1.870(5) and 1.143(7) Å, respectively, and are similar to those of $[Ru(bpy)_2(X)(CO)]^{n+}$ (Ru–C = 1.861 Å for X = Cl,[7] and 1.865 and 1.906 Å for X = CO;[8] C–O = 1.122 Å for X = Cl

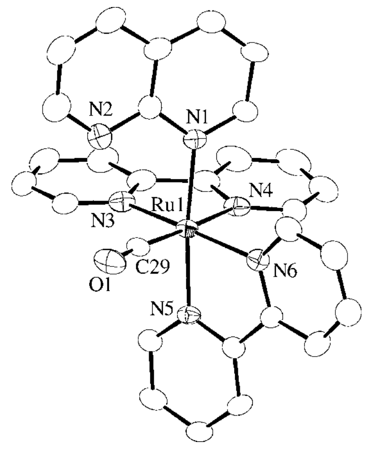


Figure 2. An ORTEP view of $\mathbf{1}^{2+}$. The hydrogen atoms have been omitted. Selected bond lengths [Å] and angles [°]: Ru1-N1 2.139(4), Ru1-N3 2.096(5), Ru1-N4 2.136(4), Ru1-N5 2.071(4), Ru1-6 2.077(4), Ru1-C29 1870(5), O1-C29 1.143(7); N1-Ru1-C29, 93.2(2), N3-Ru1-N4 78.3(2), N5-Ru1-N6 78.5(2), Ru1-C29-O1 175.6(5).

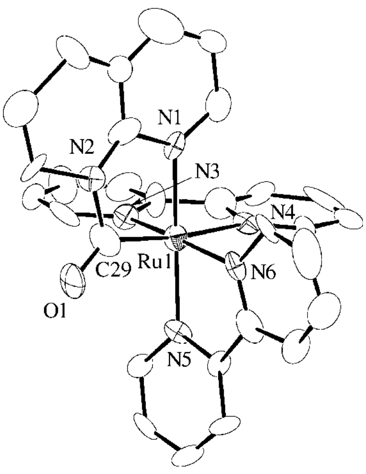
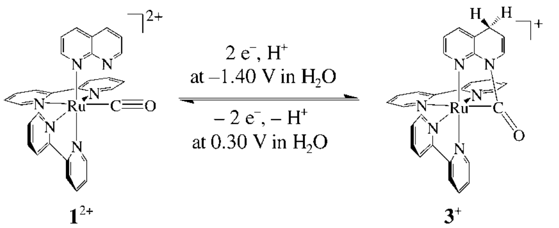


Figure 3. An ORTEP view of $\mathbf{3}^+$. The hydrogen atoms have been omitted.

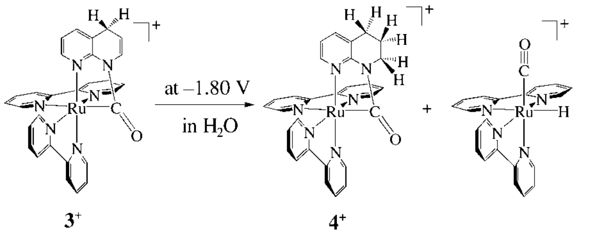
and 1.144 and 1.125 Å for X = CO). The N1-Ru1-C29 and Ru1-C29-O1 bond angles are 93.2(2)° and 175.6(5)°, respectively. The aromatic ring of the napy ligand of $\mathbf{1}^{2+}$ is located above the CO ligand with a torsion angle C7-N1-Ru1-C29 of 35.6(4)°. However, the atomic distance between N2 and C29 of $\mathbf{1}^{2+}$ (2.765(7) Å) is apparently too long for a dative bond to form between the uncoordinated nitrogen atom of napy and the carbonyl carbon atom of $\mathbf{1}^{2+}$. The Ru1–N1 bond length (2.139(4) Å) is close to that in the analogous complex $[\mathrm{Ru(bpy)_2(napy\text{-}\kappa \mathit{N})(CH_3CN)}]^{2+}$ (2.137 Å),[5] although the napy plane of the latter is located on the opposite side to the CH_3CN ligand, and is situated in the space between the two bpy ligands of the axial and equatorial planes. Although the quality of the crystals of $\mathbf{3}(\mathrm{PF_6})\cdot 2\,\mathrm{CH_3CN}$ was not good enough for a detailed analysis of the bond angles and lengths ($R_1 = 0.17$, $R_w = 0.226$), it is clear that $\mathbf{3}^+$ has a ruthenacycle structure which results from bond formation between the free nitrogen atom of napy and the carbonyl carbon atom of $\mathbf{1}^{2+}$. The almost planar napy ring of $\mathbf{3}^+$ is coplanar with the C29-Ru1-N4 axis and the C29-Ru1-N5 plane. Moreover, the O1-C29-Ru1 angle deviates significantly from the 180° expected for the sp-hybridized C29.

The ESI mass spectra of a CH_3CN solution of $\mathbf{3}(\mathrm{PF_6})$ prepared in H_2O and D_2O exhibit signals at m/z 573 and m/z 574, respectively, for the monocationic parent complexes thus indicating that $\mathbf{3}^+$ is produced by a proton-coupled one-electron reduction of $\mathbf{2}^+$. The ^{1}H NMR spectrum of $\mathbf{3}(\mathrm{PF_6})$ prepared in H_2O shows a new multiplet signal at $\delta = 3.66$ ppm with an intensity of two protons. The NOE spectrum indicates that this new CH_2 signal arises from the addition of a proton at the 4-position of napy [Eq. (2)]; the chemical shift of the signal is very close to that of the CH_2 group of 4-dihydro-*N*-methyl quinoline ($\delta = 3.52$ ppm). [9] Furthermore, electrochemical oxidation of $\mathbf{3}^+$ at +0.4 V in H_2O and treatment of $\mathbf{3}^+$ with an equivalent amount of chloranil in CH_3CN regenerates $\mathbf{1}^{2+}$ almost quantitatively.[10] Such an unprecedented reversible ring-closing and -opening coupled with hydrogenation and dehydrogenation of napy can be explained as follows: the napy-localized reduction of $\mathbf{1}^{2+}$ at −1.40 V results in a substantial increase in the basicity of the uncoordinated nitrogen atom, which leads to a nucleophilic attack of this atom at the carbonyl carbon atom to give the metallacyclic complex $\mathbf{2}^+$. Protonation of the 4-position of napy in $\mathbf{2}^+$ in H_2O induces a further one-electron reduction of the ligand, which changes the dative C–N in $\mathbf{2}^+$ to the covalent one in $\mathbf{3}^+$.



(2)

Further electrolysis of $\mathbf{3}^+$ at −1.80 V at an Hg electrode in H_2O caused the disappearance of the parent peak of $\mathbf{3}^+$ (m/z 573) and the emergence of two peaks at m/z 443 and 575 for monocationic species in the electrospray mass spectra of the electrolyte solution. Addition of NH_4PF_6 to the electrolyte solution precipitated a mixture of orange and red powders (ca. 3:1 based on ^{1}H NMR analysis). The ^{1}H NMR spectrum of the orange powder ($m/z = 443$) in CD_3CN is consistent with $[\mathrm{Ru(bpy)_2(CO)H}](\mathrm{PF_6})$ (δ(Ru–H) = −11.45 ppm). The ^{1}H NMR spectrum of the red powder ($\mathbf{4}^+$: $m/z = 575$) shows three methylene proton signals at $\delta = 1.88$, 2.83, and 3.82 ppm, while the ^{13}C NMR spectrum shows a signal corresponding to a carbamoyl group $\delta = 222$ ppm. The fact that these chemical shifts are similar to those of *N*-alkyl-1,2,3,4-tetrahydroquinoline derivatives[11] indicates that the carbamoyl moiety of $\mathbf{3}^+$ is not reduced even at −1.80 V in H_2O. Instead, the 2- and 3-positions of the napy moiety are hydrogenated, and about 75% of $\mathbf{3}^+$ is converted into $[\mathrm{Ru(bpy)_2(CO)H}]^+$ [Eq. (3)].



(3)

The present study reveals that the napy-localized reduction of $[\mathrm{Ru(bpy)_2(napy\text{-}\kappa \mathit{N})(CO)}]^{2+}$ ($\mathbf{1}^{2+}$) forms a metallacycle. Electrochemical reduction of $\mathbf{1}^{2+}$ in H_2O at −1.40 V causes an attack of the free nitrogen atom of napy at the carbonyl carbon atom, followed by hydrogenation at the 4-position of napy to produce the ruthenacyclic complex $\mathbf{3}^+$. The resultant metallacycle ring effectively inhibits reductive cleavage of the Ru–CO bond, and hydrogenation takes place on the napy ligand rather than on the CO group ($\mathbf{3}^+$) in H_2O. Both electrochemical oxidation of $\mathbf{3}^+$ in H_2O and treatment of the complex with chloranil in CH_3CN can be used to regenerate $\mathbf{1}^{2+}$ almost quantitatively. Such an unprecedented intramolecular reversible formation and cleavage of a C–N bondcoupled with hydrogenation and dehydrogenation of napy is ascribed to the drastic change of nucleophilicity of the nonbonded nitrogen atom of monodentate napy in a ligand-localized redox reaction.

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[6] Crystal data for **1**$(BF_4)_2\cdot H_2O$: $C_{29}H_{24}B_2F_8N_6O_2Ru$, $M_r = 763.22$, orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 12.6480(8)$, $b = 12.8137(7)$, $c = 18.815(1)$ Å, $V = 3049.2(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.662\ \mathrm{g\,cm^{-3}}$, $\mu = 0.603\ \mathrm{mm^{-1}}$, $F(000) = 1528.00$, 3865 unique reflections, 3865 independent reflections, ($R_{int} = 0.033$), $R1 = 0.047$, $wR2 = 0.123$ (all data); **3**$(PF_6)\cdot$MeCN: $C_{31}H_{26}F_6N_7OPRu$, $M_r = 758.63$, monoclinic, space group $P2_1/c$ (no. 14), $a = 13.342(8)$, $b = 15.718(9)$, $c = 29.49(2)$ Å, $V = 6020(6)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.674\ \mathrm{g\,cm^{-3}}$, $\mu = 0.615\ \mathrm{mm^{-1}}$, $F(000) = 3056.00$, 14164 unique reflections, 6898 reflections with $I > 3.00\sigma(I)$, $R1 = 0.169$, $wR2 = 0.226$ (all data). Crystals for X-ray analyses of the complexes were obtained as described in the text for **1**-$(BF_4)_2\cdot H_2O$ and by vapor diffusion of diethyl ether into a CH_3CN solution for **3**$(PF_6)\cdot CH_3CN$. A suitable single crystal for the measurement was mounted on a glass fiber for **1**$(BF_4)_2\cdot H_2O$ and in a capillary for **3**$(PF_6)\cdot CH_3CN$. Data were collected at −100 °C on a Rigaku/MSC Mercury CCD diffractometer equipped with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71070$ Å). All data were collected and processed using the Crystal Clear program (Rigaku). All the calculations were carried out with the teXsan software package.[12] All structures were solved by direct methods and expanded using Fourier techniques. Refinements were performed anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. Hydrogen atoms were placed at their calculated positions and were included in the structure calculation without further refinement of the parameters. CCDC-254155 (**1**$(BF_4)_2\cdot H_2O$) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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