Novel Reversible Metallacyclization in $[Ru(bpy)_2(\eta^1\text{-napy})(CO)]^{2+}$ (bpy = 2,2-bipyridine, napy = 1,8-naphthyridine) by Intramolecular Attack of Non-Bonded Nitrogen of napy to Carbonyl Carbon

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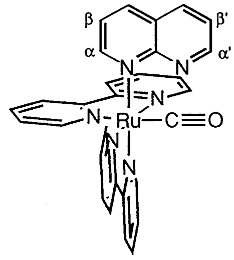
One-electron reduction of $[Ru(bpy)_2(\eta^1\text{-napy})(CO)]^{2+}$ (bpy = 2,2-bipyridine, napy = 1,8-naphthyridine) induces a reversible attack of non-bonded nitrogen of napy to carbonyl carbon producing a five-membered metallacyclic Ru-C(O)-N-C-N moiety.

Photo- and electrochemical CO_2 reduction mediated by metal complexes are extensively studied.[1] Metal-carbonyl species ($[M\text{-}CO]^{n+}$) which result from either an acid-base equilibrium among $[M\text{-}CO_2]^{(n-2)+}$ and $[M\text{-}COOH]^{(n-1)+}$ in protic media[2] or oxide transfer from $[M\text{-}CO_2]^{(n-2)+}$ to CO_2 in aprotic media[3,4] are considered as precursors for CO generation. The evolution of CO caused by the reduction of $[M\text{-}CO]^{n+}$ is, however, a major problem for the conversion of CO_2 to highly reduced organic compounds on metals. We have demonstrated that ligands based redox reactions of $[Ru(bpy)(trpy)(CO)]^{2+}$ (bpy = 2,2'-bipyridine, trpy = 2,2':6'2''-terpyridine) and $[Ru(bpy)_2(quinoline)(CO)]^{2+}$ effectively depress the unfavorable CO dissociation and enable to catalyze the first multi-electron reduction of CO_2.[4,5] Accordingly, direct interaction of a reduced ligand with a carbonyl moiety would lead to another methodology for the activation of the carbonyl ligand without the metal-carbonyl cleavage. This paper reports the first reversible metallacyclization in $[Ru(bpy)_2(napy)(CO)](PF_6)_2$ (napy = 1,8-naphthyridine) (**1**) forming a five-membered carbamoyl ring by an attack of non-bonded nitrogen of one-electron reduced napy to the carbonyl carbon.

Figure 1 shows the ^1H-NMR (270 MHz) spectrum of $[\mathbf{1}](PF_6)_2$[6] in CD_2Cl_2 at 25 °C. The assignment of signals was accomplished by the ^1H-^1H COSY spectrum. The β, β' and γ protons of napy (structure 1) are overlapped with aromatic protons of bpy ligands. Three doublets at $\delta = 9.91$, 9.35, and 8.79 were assigned to the α, α', and γ protons, respectively, in which determination of the α and α' protons was based on the deduction that the former undergoes stronger deshielding of the magnetic field than the latter due to the ring-current of bpy. The close chemical shift of α' proton to that of an orth-proton of free naphthyridine ($\delta = 9.20$) suggests that the ring-current of bpy has little effect on the α' proton. Some of η^1-napy metal complexes show fluctuation of ring proton signals in NMR spectra on raising temperature due to a site exchange isomerization between the two nitrogen atoms.[7] The essentially same NMR spectrum of $[\mathbf{1}]^{2+}$ in DMSO as that in CH_2Cl_2, however, almost unchanged up to 80 °C. Assuming the site exchange of napy in $[\mathbf{1}]^{2+}$, the ring-current effect of bpy would be induced on the α' proton resulting in a lower field shift of its signal. No change of the signal on raising temperature, therefore, implies rigidity of the conformation of $[\mathbf{1}]^{2+}$ with η^1-napy.



Structure 1.

The cyclic voltammogram of $[\mathbf{1}](PF_6)_2$ in CH_3CN containing Me_4NBF_4 (0.05 $mol\cdot dm^{-3}$) showed one irreversible

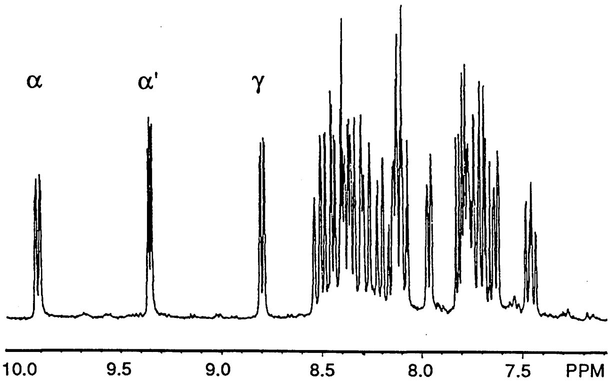


Figure 1. ^1H-NMR spectrum of $[\mathbf{1}](PF_6)_2$ in CD_2Cl_2 at 20 °C. Assignment of the protons are performed by ^1H - ^1H COSY spectrum.

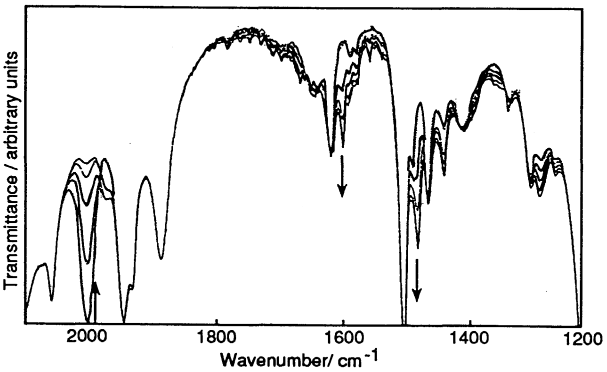
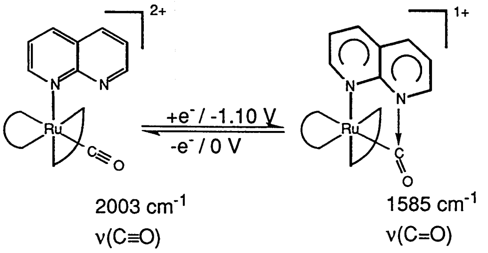


Figure 2. Solution IR spectra of $[\mathbf{1}](PF_6)_2$ (10 $mmol\cdot dm^{-3}$) in CD_3CN containing $(CH_3)_4NBF_4$ (50 $mmol\cdot dm^{-3}$) under electrolysis condition at -1.10 V (*vs.* Ag|AgCl).

cathodic wave at $E_{p,c}$ = -1.03 V (*vs.* Ag|AgCl) and successive two reversible couples at $E_{1/2}$ = -1.50 and -1.74 V. Taking into account that analogous $[Ru(bpy)_2(quinoline)(CO)]^{2+}$ undergoes three reversible redox process (2+/1+/0/1-) at -1.11, -1.37 and -1.65 V in CH_3CN,[4] the first irreversible and two reversible redox couples of $[\mathbf{1}]^{2+}$ are associated with the napy and two bpy ligands based reduction process, respectively. To elucidate the irreversible cathodic process of $[\mathbf{1}]^{2+}$ at -1.03 V, solution IR spectra of $[\mathbf{1}]^{2+}$ were measured under the electrolysis conditions (Figure 2); the controlled potential electrolysis of $[\mathbf{1}](PF_6)_2$ at -1.1 V in CD_3CN containing Me_4NBF_4 (0.05 mol·dm^{-3}) results in a gradual disappearance of the strong ν(C≡O) band at 2003 cm^{-1} of $[\mathbf{1}]^{2+}$ and emergence of a new band at 1585 cm^{-1} accompanying some changes in ν(C=C) bands region of bpy and napy rings between 1400 and 1500 cm^{-1}. Similarly, electrochemical one-electron reduction of $[Ru(bpy)_2(napy)(^{13}CO)](PF_6)_2$ in CD_3CN under the same electrolysis conditions also caused an appearance of a new band at 1543 cm^{-1} with the sacrifice of the strong ν(^{13}C≡O) band at 1958 cm^{-1}. A dark red precipitate obtained by concentration of the electrolyzed CH_3CN solution of $[\mathbf{1}](PF_6)_2$ and subsequent extraction with CH_2Cl_2 also showed a strong band at 1565 cm^{-1} in the solid state, and gave a parent peak at m/z = 572 (M) in the FAB-mass spectrum.[8] Furthermore, one-electron reduction of $[\mathbf{1}](PF_6)_2$ at -1.10 V in CH_3CN and the subsequent oxidation of the solution by air afforded the starting complex within 2 hr in an almost quantitative yield.[9] These results clearly indicate that neither degradation of nor solvation to $[\mathbf{1}]^{+}$ is involved in the irreversible one-electron reduction.

It is worthy of note that one- and two-electron reduction of homologous $[Ru(bpy)_2(quinoline)(CO)]^{2+}$ caused red shift in the ν(C≡O) band from 2015 cm^{-1} to 1980 and 1939 cm^{-1}, successively.[4] The tremendous red shift for the ν(C≡O) band of $[\mathbf{1}]^{2+}$ by 418 cm^{-1} upon a one-electron reduction, therefore, is reasonably explained by an intramolecular nucleophilic attack of the non-bonded nitrogen of η^1-napy to the carbonyl carbon resulting in the five-membered carbamoyl ring (scheme 1).



Scheme 1.

Metallacyclization in scheme 1 was also confirmed by ^{13}C NMR spectra. One-electron reduction of $[Ru(bpy)_2(napy)(^{13}CO)](PF_6)_2$ under the electrolysis in CD_3CN resulted in a disappearance of the carbonyl carbon signal of $[\mathbf{1}]^{2+}$ at δ = 199.5 ppm accompanying with the broadening of aromatic carbon signals in a region from 120 to 160 ppm due to the paramagnetism of the introduced electron in napy. However, the solution clearly showed a strong signal at δ = 219.5 ppm assignable to the carbamoyl carbon[10] of the five membered metallacyclic $\overline{\text{Ru-C(O)-N-C-N}}$ moiety (scheme 1). Thus, metallacyclization (scheme 1) by taking advantage of the napy based redox process, enables reversible conversion between carbonyl and carbamoyl moieties with no Ru-CO bond cleavage.

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References and Notes

1 P. A. Lay, A. F. Masters, C. D. Wasiowych, *Aust. J. Chem.*, **48**, 835 (1995); K. -M. Lam, K. -Y. Wong, S. -M. Yang, and C. -M. Che, *J. Chem. Soc., Dalton Trans.*, **1995**, 1103; A. M. Herring, B. D. Steffey, A. Miedaner, S. A. Wander, and D. L. DuBois, *Inorg. Chem.*, **34**, 1100 (1995); Steffey, Bryan D.; Miedaner, Alex; Maciejewski-Farmer, Mary L.; P. R. Bernatis, A. M. Herring, V. S. Allured, V. Carperos, D. L. DuBois, *Organometallics*, **13**, 4844 (1994); E. Fujita, J. Haff, R. Sanzenbacher, and H. Elias, *Inorg. Chem.*, **33**, 4627 (1994); O. Ishitani, M. W. George, T. Ibusuki, F. P. A. Johnson, K. Koike, K. Nozaki, C. Pac, J. J. Turner, and J. R. Westwell, *Inorg. Chem.*, **33**, 4712 (1994); E. Kimura, S. Wada, M. Shionoya, and Y. Okazaki, *Inorg. Chem.*, **33**, 770 (1994); B. P. Sullivan, *Electromchemical and Electrocatalytic Reaction of Carbon Dioxide*, Elsevier, Amsterdam (1993), and references are therein.

2 H. Ishida, K. Tanaka, and T. Tanaka, *Chem. Lett.*, **1985**, 405.; H. Tanaka, B. -C. Tzeng, H. Nagao, S. -M. Peng, and K. Tanaka, *Inorg. Chem.*, **32**, 1508 (1993).

3 G. R. Lee, J. H. Maher, and N. J. Cooper, *J. Am. Chem. Soc.*, **109**, 2956 (1987); G. R. Lee and N. J. Cooper, *Organometallics*, **4**, 794 (1985).

4 H. Nakajima, T. Mizukawa, H. Nagao, and K. Tanaka, *Chem. Lett.*, **1995**, 251.

5 H. Nagao, T. Mizukawa, and K. Tanaka, *Inorg. Chem.*, **33**, 3415 (1994).

6 Anal. Calced (%) for $C_{29}H_{22}N_6OP_2F_{12}Ru$: C, 40.43; H, 2.58; N, 9.75 Found (%) : C, 40.09; H, 2.86; N, 9.47. IR(KBr): ν(C≡O) = 1996 cm^{-1}. FAB-Mass (m/z) = 717 ($M-PF_6$).

7 M. -J. Bermejo, J. -I. Ruiz, X. Solans, and J. Vinaixa, J. Organomet. Chem., **463**, 143 (1993); M. -J. Bermejo, J. -I. Ruiz, X. Solans, and J. Vinaixa, *Inorg. Chem.*, **27**, 4385 (1988).

8 Attempts of complete separation of $[\mathbf{1}](BF_4)$ from the electrolyte (Me_4NBF_4) by recrystalization is now in progress.

9 The controlled potential electrolysis of $[\mathbf{1}]^{+}$ at 0 V also generated $[\mathbf{1}]^{2+}$ although the cyclic voltammogram of $[\mathbf{1}]^{2+}$ did not show an anodic wave coupled with the first cathodic wave at -1.03 V. This fact suggests a slow electron transfer from $[\mathbf{1}]^{+}$ to a working electrode probably due to a large configurational barrier from the metallacyclo structure of $[\mathbf{1}]^{+}$ to η^1-napy ligated $[\mathbf{1}]^{2+}$.

10 F. Ozawa, S. Chikaoka, X. Cao, A. Yamamoto, *J. Organomet. Chem.*, **424**, 173 (1992); M. Nonoyama, *Inorg. Chim. Acta*, **115**, 169 (1986).