VII-H Multi-Electron Reduction of Carbon Dioxide through Metal-Carbonyl and Oxidative Activation of Water *via* Metal-Oxo Complexes

An electrophilic attack of CO_2 to coordinatively unsaturated low valent metal complexes affords M-η^1-CO_2 complexes, which are smoothly converted to M-CO ones in protic and aprotic media. Organic synthesis through M-CO complexes derived from CO_2, therefore, is highly desired in the viewpoint of C1 chemistry. A major problem to make multi-electron reduction of CO_2 is reductive cleavages of M–CO bonds (CO evolution). This problem may be overcome by the construction of a catalytic system, which can supply electrons to carbonyl group of M–CO bonds with depressing of an increase in the electron density at the central metal. Such requirements would be fulfilled by the metal complexes with a structurally flexible ligand having an ability to not only open and close a chelate ring for CO_2 binding but also to form a metallacycle including metal and carbon atoms of M–CO bonds for inhibition of the bond cleavage.

High valent metal-oxo complexes are feasible candidates for oxidation and hydroxylation of non-activated hydrocarbons from the viewpoints of the enzymatic activity of P-450 enzymes. Mechanistic understandings of the reactivity of high-valent metal-oxo complexes have, however, been limited because no reasonable synthetic route for metal-oxo complex from dioxygen has been proposed so far in artificial systems. On the other hand, Ru–OH_2 complexes are smoothly converted to high-valent Ru=O ones by sequential electron and proton loss, and the latter has attracted much attention in the viepoint of the elucidation of reactivity of metal-oxo frameworks. Taking into account that quinone undergoes stepwise reduction to yield semiquinone and catecholate, introduction of quinone ligands into the Ru–OH_2 framework would assist smooth conversion from aqua to oxo ligands without changing of the oxidation states of the central Ru.

VII-H-1 Syntheses of New Ruthenium Carbonyl Terpyridine *o*-Phenylene Complexes: Strong Interaction between Carbonyl and *o*-Phenylene Ligands

SUGIMOTO, Hideki[1]; TANAKA, Koji
(*[1]Osaka City Univ.*)

Ruthenium carbonyl *o*-phenylene complexes, Ru(CO)(3,6-Bu$_2$seq)(trpy)]PF$_6$ ([**1**]PF$_6$) and [Ru(CO)(*o*-monothiocat)(trpy)] (**2**) were prepared by the reaction of [Ru(CO)C1$_2$(trpy)] with the corresponding *o*-phenylenes in 2-methoxyethanol. X-ray crystallographic study of [**1**]BF$_4$ indicated that the ruthenium center is coordinated by carbonyl, three nitrogens of trpy and two oxygens of 3,6-Bu$_2$seq. ESR of [**1**]PF$_6$ and **2** indicated that the electronic structures of ruthenium-*o*-phenylene unit of the complexes have Ru(II)-3,6-Bu$_2$seq and Ru(II)-*o*-monothiocat forms, respectively. Significant differences in the redox behavior and the spectroscopical properties between [**1**]PF$_6$ and **2** and [RuCl(3,5-Bu$_2$seq)(trpy)] were ascribed to the strong interaction between *o*-phenylene and carbonyl ligands through Ru(II).
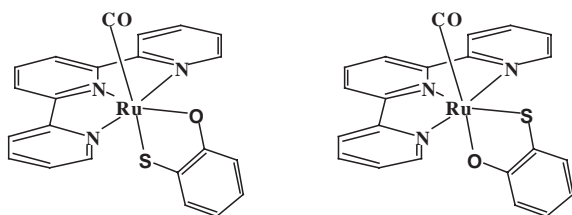

**Figure 1.** Two isomers of **2**.

VII-H-2 Synthesis and Redox Properties of Bis(ruthenium-hydroxo)complexes with Quinone and Bipyridine Ligand as a Water-Oxidation Catalysts

WADA, Tohru; TSUGE, Kiyoshi; TANAKA, Koji

The novel bridging ligand 1,8-bis(2,2':6',2"-terpyridyl)anthracene (btpyan) is synthesized by three reactions from 1,8-diformylanthracene to connect two [Ru(L)(OH)]$^+$ units (L = 3,6-*di-tert*-butyl-1,2-benzo-quinone (3,6-*t*Bu$_2$qui) and 2,2'-bipyridine (bpy)). An addition of *t*BuOK (2.0 equiv) to a methanolic solution of [Ru$^{II}_2$(OH)$_2$(3,6-*t*Bu$_2$qui)$_2$(btpyan)](SbF$_6$)$_2$ ([**1**](SbF$_6$)$_2$) results in the generation of [Ru$^{II}_2$(O)$_2$(3,6-*t*Bu$_2$sq)$_2$(btpyan)]^0 (3,6-*t*Bu$_2$sq = 3,6-*di-tert*-butyl-1,2-semiquinone) due to the reduction of quinone coupled with the dissociation of the hydroxo protons. The resultant complex [Ru$^{II}_2$(O)$_2$(3,6-*t*Bu$_2$sq)$_2$(btpyan)]^0 undergoes ligand-localized oxidation at $E_{1/2}$ = +0.40 V (*vs* Ag/AgCl) to give [Ru$^{II}_2$(O)$_2$(3,6-*t*Bu$_2$qui)$_2$-(btpyan)]$^{2+}$ in MeOH solution. Furthermore, metal-localized oxidation of [Ru$^{II}_2$(O)$_2$(3,6-*t*Bu$_2$qui)$_2$-(btpyan)]$^{2+}$ at E_p = +1.2 V in CF$_3$CH$_2$OH/ether or water gives [Ru$^{III}_2$(O)$_2$(3,6-*t*Bu$_2$qui)$_2$(btpyan)]$^{4+}$, which catalyzes water oxidation. Controlled-potential electrolysis of [**1**](SbF$_6$)$_2$ at +1.70 V in the presence of H_2O in CF$_3$CH$_2$OH evolves dioxygen with a current efficiency of 91% (21 turnovers). The turnover number of O_2 evolution increases to 33 500 when the electrolysis is conducted in water (pH 4.0) by using a [**1**](SbF$_6$)$_2$-modified ITO electrode. On the other hand, the analogous complex [Ru$^{II}_2$(OH)$_2$(bpy)$_2$(btpyan)](SbF$_6$)$_2$ ([**2**](SbF$_6$)$_2$) shows neither dissociation of the hydroxo protons, even in the presence of a large excess of *t*Bu-

OK, nor activity for the oxidation of H_2O under similar conditions.
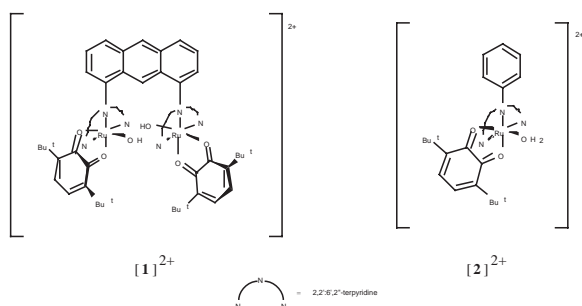
VII-H-3 Ruthenium Terpyridine Complexes with Mono- and Bi-Dentate Dithiolene Ligands

SUGIMOTO, Hideki[1]; TSUGE, Kiyoshi; TANAKA, Koji
(*[1]Osaka City Univ.*)

The reaction of $[Ru(CO)_2Cl(terpy)]PF_6$ (terpy = 2,2':6':2''-terpyridine) with Na_2mnt (mnt = $S_2C_2(CN)_2$) initially produced $[Ru(CO)_2(mnt)(terpy-\kappa^3NN'N'')]$ **1a**, which rearranged to $[Ru(CO)_2(mnt-\kappa^2SS')(terpy-\kappa^2NN')]$ **1b** in solution. The molecular structures of **1a** and **1b** indicate that the rearrangement proceeds *via* a five-coordinated complex with monodentate mnt and bidentate terpy. The reaction of $[Ru(CO)_2Cl(terpy)]PF_6$ with 3,4-toluenedithiol (H_2tdt) gave $[Ru(CO)_2(tdt-\kappa^2SS')(terpy-\kappa^2NN')]$ **2b** but $[Ru(CO)_2(tdt-\kappa S)(terpy-\kappa^3NN'N'')]$ **2a** was not identified. Thus, ruthenium complexes with bidentate dithiolene and bidentate terpyridine seem to be more stable than those with monodentate dithiolene and tridentate terpyridine. Neither $[Ru(CO)_2(pdt-\kappa S)(terpy-\kappa^3NN'N'')]$ **3a** nor $[Ru(CO)_2(pdt-\kappa^2S)(terpy-\kappa^2NN')]$ **3b** (pdt = PhC(S)-C(S)Ph) was obtained in the reaction of $[Ru(CO)_2Cl-(terpy)]PF_6$ with the Cs^+ salt of pdt^{2-} in CH_3OH under N_2. The same reaction conducted under aerobic conditions afforded $[Ru(CO)(C(O)OCH_3)(SC(Ph)C(Ph)-SC(O)OMe)(terpy-\kappa^3NN'N'')]$ **3a** resulting from double addition of CO_2 and CH_3OH to the terminal sulfur of pdt and a carbonyl carbon of **3a**, respectively, followed by esterification of the resultant $[Ru(CO)(C(O)OCH_3)-(SC(Ph)C(Ph)SC(O)OH)(terpy-\kappa^3NN'N'')]$ in CH_3OH. The addition of CO_2 to the sulfur of **3a** is ascribed to the strong basicity and weak chelating ability of pdt compared with those of mnt and tdt. A series of $[RuX-(dithiolene)(terpy)]^{n+}$ (X = dmso, Cl or OSO_2CF_3; n =0 or 1) were also prepared.
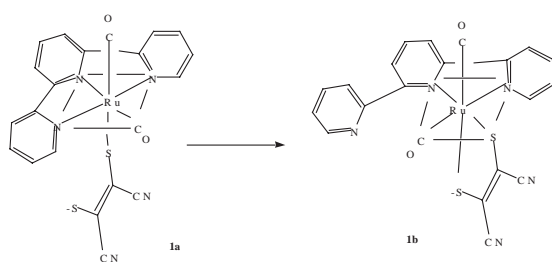

VII-H-4 A Ru-Carbene Complex with a Metallacycle Involving a 1,8-Naphthylidine Framework

TOMON, Takashi; OOYAMA, Dai[1]; WADA, Tohru; SHIREN, Kazushi; TANAKA, Koji
(*[1]Fukushima Univ.*)

A CH_3OH/H_2O solution containing $[\mathbf{1}](PF_6)_2$ and HCCC(O)OH was refluxed for 2 h, and $[\mathbf{2a}](PF_6)_2$ was obtained from the solution. Recrystallization of the crude product from CH_3CN/CH_3OH gave single crystals of $[\mathbf{2a}](PF_6)_2 \cdot CH_3CN$ in 64% yield. The similar reaction between $[\mathbf{1}](SbF_6)_2$ and HCCC(O)OH in C_2H_5-OH/H_2O under similar reaction conditions afforded $[\mathbf{2b}](SbF_6)_2$ in 56% yield. The ruthenium atom of $\mathbf{2a}^{2+}$ has octahedral geometry with four nitrogen atoms of two bpy ligands, one nitrogen from napy and one carbon of the CCH_3 group. The characteristic features of $\mathbf{2a}^{2+}$ are the C–N bond formation between the CCH_3 group and one nitrogen of napy, and the attachment of the CH_3O group to the 2-position of the napy moiety. The resultant five-membered metallacycle consisting of Ru, N(1), C(11), N(2), and C(2) atoms in an almost planar structure, and the sum of the bond angles around the five-membered ring is almost 360. Despite the attachment of CH_3O to the 2-positon of the napy moiety, the resultant ligand still maintains the planar structure in $\mathbf{2a}^{2+}$. As a result, the napy moiety and the five-membered metallacycle are co-planar. The Ru–N(4) (2.156(9) Å) bond trans to Ru–C(2) is substantially longer than the other Ru–N bonds of $\mathbf{2a}^{2+}$ (2.03(1)–2.08(1) Å), suggesting a strong trans effect of the carbene ligand. The Ru–C(2) bond distance (1.93(1) Å) is in the expected range of hexa-coordinated ruthenium carbene bonds (1.941–1.98 Å), and the bond length is longer than those expected for penta-coordinated ruthenium carbene complexes (1.810–1.861 Å). The ^{13}C NMR spectrum of $\mathbf{2a}^{2+}$ also showed the carbon signal of the Ru–CCH_3 group at 293 ppm as a singlet, similar to most Ru carbene complexes.
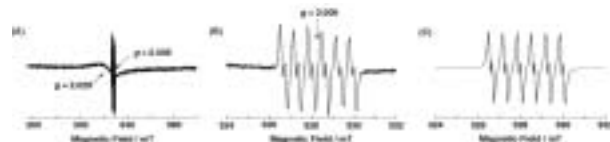

Scheme
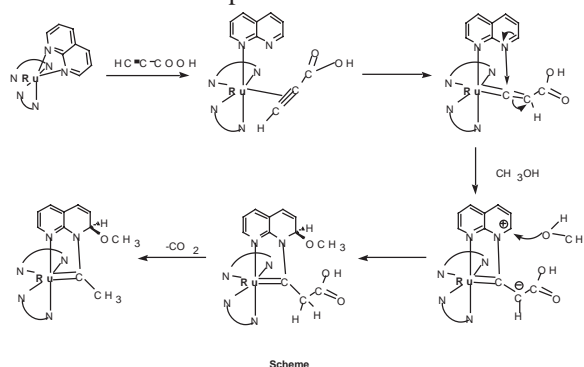
VII-H-5 Ruthenium Oxyl Radical Complex Containing *o*-Quinone Ligand Detected by ESR Measurements of Spin Trapping Technique

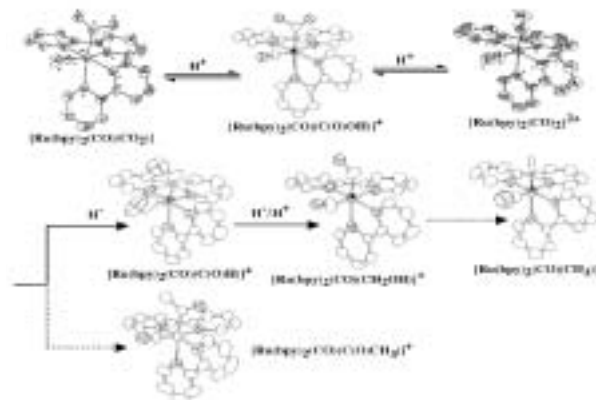KOBAYASHI, Katsuaki; OHTSU, Hideki; WADA, Tohru; TANAKA, Koji

The ESR spectrum obtained upon an addition of a 3 equiv of *t*BuOK and DMPO to a CH_2Cl_2 solution of $[Ru(trpy)(3,5\text{-}dbQ)(OH_2)]^{2+}$ at 193 K is depicted in Figure 1A and 1B, which shows an isotropic broad signal without hyperfine structure ($g = 2.029$, $\Delta H_{msl} = 7.3$ mT) together with 12-line sharp signal centered at $g = 2.006$ (Figure 1B). The pattern of ESR spectrum was not perturbed by a change of modulation amplitude within 0.14 mT. The hyperfine coupling constants values of the characteristic 12-line sharp signal ($g = 2.006$, $a_N^\alpha = 1.32$, $a_H^\beta = 0.63$ and $a_H^\gamma = 0.20$ mT) are determined by the computer simulation. The ESR signal centered at $g = 2.029$ is very close to those of the Ru^{II}-semiquinone complex, $[Ru^{II}(trpy)(35tBu_2SQ)AcO^-]$ ($g = 2.030$, $\Delta H_{msl} = 8.0$ mT), thus, the isotropic broad signal ($g = 2.029$) can be assigned to the Ru^{II}-SQ moiety. The signal intensity resulted from the Ru^{II}-SQ moiety linearly increased with increasing amounts of *t*BuOK, when more than 1 eq of *t*BuOK was added to the solution. The other ESR signal centered at $g = 2.006$ can be assigned to the DMPO spin adduct, $[Ru^{II}(trpy)\text{-}(35tBu_2SQ)(O)(DMPO)]l^0$.

Formation of the DMPO spin adduct is further confirmed by ESI mass spectrum which exhibited a signal at *m/z* 684. The observed mass and isotope patterns corresponded to $[Ru^{II}(trpy)(35tBu_2SQ)(^{16}O)\text{-}(DMPO)]^+$. The labeling experiment using $H_2^{18}O$ showed an expected signal at *m/z* 686 corresponding to $[Ru^{II}(trpy)(35tBu_2SQ)(^{18}O)(DMPO)]^+$ suggesting that an oxyl radical ligand was generated by the deprotonation of an aqua ligand. Thus, oxyl radical is induced by the acid-base equilibrium of the aqua ligand coupled with the reduction of the quinone ligand.

VII-H-6 Multi-Electron Reduction of CO_2 *via* Ru-CO_2 -C(O)OH, -CO, -CHO, and -CH_2OH Species

TANAKA, Koji; OOYAMA, Dai

A series of $[Ru(bpy)_2(CO)L]^{n+}$ ($L = CO_2$, C(O)OH, CO, CHO, CH_2OH, CH_3, and $C(O)CH_3$; $n = 0, 1, 2$) were prepared and their molecular structures were determined by X-ray analyses. These complexes are reasonable models of reaction intermediates in the multi-electron reduction of CO_2 catalyzed by metal complexes, since reductive cleavage of the Ru–*L* bonds of the complexes in protic media affords HCOOH, CO, HCHO, CH_3OH, and CH_4 as two-, four-, six- and eight-electron reduction products of CO_2. The free energy required in the reduction of CO_2 progressively decreases with an increase of the number of electrons participating in the reduction of CO_2. The Ru–*L* bond character of the series of $[Ru(bpy)_2(CO)L]^{n+}$ was assessed by the ν(Ru–L) bands and the Ru–L bond distances from the viewpoint of elucidation of a correlation between free energy changes in the multi-electron reduction of CO_2

catalyzed by metal complexes and the metal–carbon bond strength of each intermediate. The ruthenium–carbon bond distance of $[Ru(bpy)_2(CO)L]^{n+}$ largely depends on the hybrid orbital of the carbon atom bonded to ruthenium and lengthens in the order Ru–C_{sp} < Ru–C_{sp2} < Ru–C_{sp3}. An unusual shift of the ν(Ru–L) bands to higher wavenumber with decrease of the Ru–L bond distances was discussed in terms of σ- and π-character of the ruthenium–carbon bonds.