

VII-D Reductive Activation of Carbon Dioxide and Oxidative Activation of Water Aiming at Reversible Conversion between CO₂ and Organic Molecules

Multi-electron reduction of CO₂ aiming at smooth conversion to organics is highly desired in the viewpoints of not only the utilization of C1 resources but also the decrease of the concentration in the air. Carbon dioxide easily reacts with coordinatively unsaturated low-valent metal complexes to form η^1 - or η^2 -CO₂ adducts, the former of which are easily converted to metal-CO complexes in protic media. Accumulation of much electrons on metal centers usually accelerates not only reduction of CO₂ but also metal-CO bond cleavages. As a result, CO is the main product in photo- and electro-chemical reduction of CO₂ catalyzed by metal complexes. It is, therefore, highly desired to develop new methodologies that can supply electrons to the carbonyl ligand of metal-CO complexes derived from CO₂ without accumulation of electrons at the central metals. Along the line, we are designing new types of metal complexes that have an ability to provide electrons to carbonyl carbon through metallacycle rings involving the CO groups aiming at catalytic generation higher organic molecules by the electro- and photochemical reduction of CO₂.

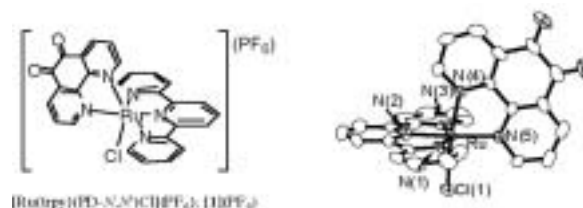
Oxygenations and oxidations of organic molecules by high valent metal-oxo complexes are of current interest from the viewpoints of the enzymatic activities of P-450. Mechanistic understandings of the reactivity of metal-oxo species derived from O₂, however, have been limited because of the difficulty of selective cleavage of the O–O bond of M–O₂ frameworks in artificial systems. Alternatively, high valent Ru=O complexes can be obtained by sequential electron and proton loss of the Ru–OH₂ frameworks, and some of Ru=O complexes have proven to work as oxidants of organic molecules. Introduction of quinone molecules, which are reduced to semiquinone and catecholates in a wide range of potentials, into M–OH₂ frameworks also induces sequential electron and proton loss of the Ru–OH₂ ones without addition of oxidizing agents. Such acid-base equilibria of the aqua ligands by taking advantages of smooth redox reactions of quinone ligands can be applied for energy conversion from pH gradients to electronic energy.

VII-D-1 Coordination Ability of 1,10-Phenanthroline-5,6-Dione: Syntheses and Redox Behavior of a Ru(II) Complex with an o-Quinoid Moiety and of Bridged Ru(II)-M(II) Complexes (M = Pd, Pt)

FUJIHARA, Tetsuaki¹; OKAMURA, Rei¹; WADA, Tohru; TANAKA, Koji
(¹IMS, CREST/JST)

[*Dalton Trans.* 3221–3226 (2003)]

The synthesis and electrochemical properties of Ru(II) complexes having 1,10-phenanthroline-5,6-dione (PD), [Ru(trpy)(PD-N,N')Cl](PF₆) (**1**)(PF₆), mixed-metal complexes [(PPh₃)₂Pd(O,O'-PD-N,N')Ru(trpy)Cl](PF₆) (**2**)(PF₆), and [(PPh₃)₂Pt(O,O'-PD-N,N')Ru(trpy)Cl](PF₆) (**3**)(PF₆) (trpy = 2,2':6',2''-terpyridine) are presented. The PD ligand of **1**⁺, which was prepared by the reaction of Ru(trpy)(DMSO)Cl₂ with PD in hot ethanol, existed as the quinoid form and underwent two reversible ligand-based redox reactions. The quinoid group of **1**⁺ did not show any interactions with Pd(II) and Pt(II), whereas the ligand was endowed with coordination ability to metals by one- and two-electron reduction of the ligand-based redox reaction. Indeed, the mixed-metal complexes of **2**⁺ and **3**⁺ prepared by the reactions of **1**⁺ with M(PPh₃)₄ (M = Pd, Pt) have the **1**⁻ core bearing the two-electron reduced form of PD (catecolato form) and M(II) frameworks.



VII-D-2 Characterization of a Stable Ruthenium Complex with an Oxyl Radical

KOBAYASHI, Katsuaki¹; OHTSU, Hideki¹; WADA, Tohru; KATO, Tatsuhisa; TANAKA, Koji
(¹IMS, CREST/JST)

[*J. Am. Chem. Soc.* **125**, 6729–6739 (2003)]

The ruthenium oxyl radical complex, [Ru^{II}(trpy)(Bu₂SQ)O⁻] (trpy = 2,2':6',2''-terpyridine, Bu₂SQ = 3,5-di-tert-butyl-1,2-benzosemiquinone) was prepared for the first time by the double deprotonation of the aqua ligand of [Ru^{III}(trpy)(Bu₂SQ)(OH₂)](ClO₄)₂. [Ru^{III}(trpy)(Bu₂SQ)(OH₂)](ClO₄)₂ is reversibly converted to [Ru^{III}(trpy)(Bu₂SQ)(OH⁻)]⁺ upon dissociation of the aqua proton (pK_a 5.5). Deprotonation of the hydroxo proton gave rise to intramolecular electron transfer from the resultant O²⁻ to the Ru-dioxolene framework. The resultant [Ru^{II}(trpy)(Bu₂SQ)O⁻] showed antiferromagnetic behavior with a Ru^{II}-semiquinone moiety and oxyl radical, the latter of which was characterized by a spin trapping technique. The most characteristic structural feature of [Ru^{II}(trpy)(Bu₂SQ)O⁻] is a long Ru–O bond length (2.042(6) Å) as the first terminal metal–O bond with a single bond length. To elucidate

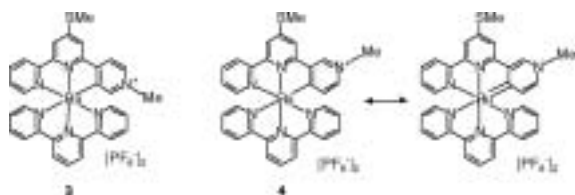
the substituent effect of a quinone ligand, we prepared $[\text{Ru}^{\text{III}}(\text{trpy})(4\text{ClSQ})(\text{OH}_2)](\text{ClO}_4)_2$ (4ClSQ = 4-chloro-1,2-benzoquinone) and compared the deprotonation behavior of the aqua ligand with that of $[\text{Ru}^{\text{III}}(\text{trpy})(\text{Bu}_2\text{SQ})(\text{OH}_2)](\text{ClO}_4)_2$. Deprotonation of the aqua ligand of $[\text{Ru}^{\text{III}}(\text{trpy})(4\text{ClSQ})(\text{OH}_2)](\text{ClO}_4)_2$ induced intramolecular electron transfer from OH^- to the $[\text{Ru}^{\text{III}}(4\text{ClSQ})]$ moiety affording $[\text{Ru}^{\text{II}}(\text{trpy})(4\text{ClSQ})(\text{OH})]^+$, which then probably changed to $[\text{Ru}^{\text{II}}(\text{trpy})(4\text{ClSQ})\text{O}^-]$. The antiferromagnetic interactions (J values) between Ru^{II} -semiquinone and the oxyl radical for $[\text{Ru}^{\text{II}}(\text{trpy})(\text{Bu}_2\text{SQ})\text{O}^-]$ and for $[\text{Ru}^{\text{II}}(\text{trpy})(4\text{ClSQ})\text{O}^-]$ were $2J = -0.67 \text{ cm}^{-1}$ and -1.97 cm^{-1} , respectively.

VII-D-3 Terpyridine-Analogous (N,N,C)-Tridentate Ligands: Synthesis, Structures, and Electrochemical Properties of Ruthenium(II) Complexes Bearing Tridentate Pyridinium and Pyridinylidene Ligands

KOIZUMI, Take-aki¹; TOMON, Takashi¹;
TANAKA, Koji
(¹IMS, CREST/JST)

[*Organometallics* **22**, 970–975 (2003)]

The cyclometalated complexes $[\text{RuL}(\text{terpy})][\text{PF}_6]_2$ (**3**, L = N^{''}-methyl-4'-methylthio-2,2':6',4''-terpyridinium; **4**, L = N^{''}-methyl-4'-methylthio-2,2':6',3''-terpyridinium) with a (N,N,N)(N,N,C)-coordination mode were synthesized in good yields and fully characterized by x-ray crystallographic, spectroscopic, and electrochemical measurements. ¹³C{¹H} NMR and electronic spectra revealed that the Ru–C bond of complex **4**, which has a quaternized N–Me unit at the para-position of the carbon atom bonding to the metal center in the terminal ring of the tridentate ligand, involves carbenic (Ru=C) character in solutions.



VII-D-4 Syntheses of a 6-(2-pyrrolyl)-2,2'-Bipyridine Derivative and its Ruthenium Complex

NAGATA, Toshi; TANAKA, Koji

[*Bull. Chem. Soc. Jpn.* **75**, 2469–2470 (2002)]

Syntheses of a new planar terdentate ligand, 6-(3,5-diphenyl-2-pyrrolyl)-2,2'-bipyridine (L^1H) and its Ru(II) complex ($[\text{Ru}(\text{L}^1)_2]$) are reported. The x-ray structure of $[\text{Ru}(\text{L}^1)_2]$ showed the distorted octahedral Ru(II) center similar to the structures of terpyridine complexes. The cyclic voltammograms revealed that $[\text{Ru}(\text{L}^1)_2]$ was more easily oxidized than $[\text{Ru}(\text{terpy})_2]^{2+}$ by 1.10 V.

VII-D-5 Acid-Base Equilibrium of Aqua-Chromium-Dioxolene Complexes Aimed at Formation of Oxo-Chromium Complexes

SHIREN, Kazushi¹; TANAKA, Koji
(¹IMS, CREST/JST)

[*Inorg. Chem.* **41**, 5912–5919 (2002)]

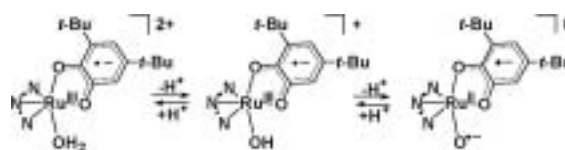
A series of aqua-Cr(III)-dioxolene complexes, $[\text{Cr}(\text{OH}_2)(3,5\text{-Bu}_2\text{SQ})(\text{trpy})](\text{ClO}_4)_2$ (**1s**), $[\text{Cr}(\text{OH}_2)(3,5\text{-Bu}_2\text{Cat})(\text{trpy})]\text{ClO}_4$ (**1c**), $[\text{Cr}(\text{OH}_2)(3,6\text{-Bu}_2\text{SQ})(\text{trpy})](\text{ClO}_4)_2$ (**2**), $[\text{Cr}(\text{OH}_2)(\text{Cat})(\text{trpy})]\text{ClO}_4$ (**3**), $[\text{Cr}(\text{OH}_2)(\text{Cl}_4\text{Cat})(\text{trpy})]\text{ClO}_4$ (**4**), $[\text{Cr}(\text{OH}_2)(3,5\text{-Bu}_2\text{SQ})(\text{Me}_3\text{-tacn})](\text{ClO}_4)_2$ (**5**), $[\text{Cr}(\text{OH}_2)(\text{Cat})(\text{Me}_3\text{-tacn})]\text{ClO}_4$ (**6**), and $[\text{Cr}(\text{OH}_2)(\text{Cl}_4\text{Cat})(\text{Me}_3\text{-tacn})]\text{ClO}_4$ (**7**) (Bu_2SQ = di-*tert*-butyl-*o*-benzoquinone anion, Bu_2Cat = di-*tert*-butylcatecholate dianion, Cat = catecholate dianion, Cl_4Cat = tetrachlorocatecholate dianion, trpy = 2,2':6',2''-terpyridine, and $\text{Me}_3\text{-tacn}$ = 1,4,7-trimethyl-1,4,7-triazacyclononane), were prepared. On the basis of the crystal structures, redox behavior, and elemental analyses of these complexes, dioxolene in **1c**, **3**, **4**, **6**, and **7** coordinated to Cr(III) as the catechol form, and the ligand in **1s**, **2**, and **5** was linked to Cr(III) with the semiquinone form. All the aqua-Cr(III) complexes reversibly changed to the hydroxo-Cr(III) ones upon dissociation of the aqua proton, and the pK_a value of the aqua-Cr(III) complexes increased in the order **6** > **3** ≈ **1c** > **7** > **5** ≈ **4** > **1s**. Hydroxo-Cr(III)-catechol complexes derived from **1c**, **3**, **4**, **6**, and **7** did not show any signs of dissociation of their hydroxy proton. On the other hand, hydroxo-Cr(III)-semiquinone complexes were reduced to hydroxo-Cr(III)-catechol in $\text{H}_2\text{O}/\text{THF}$ at pH 11 under illumination of visible light.

VII-D-6 Ruthenium Oxyl Radical Complex Containing *o*-Quinone Ligand Detected by ESR Measurements of Spin Trapping Technique

KOBAYASHI, Katsuaki¹; OHTSU, Hideki¹;
WADA, Tohru; TANAKA, Koji
(¹IMS, CREST/JST)

[*Chem. Lett.* 868–869 (2002)]

Ru-quinone complex containing an aqua ligand, $[\text{Ru}(\text{II})(\text{trpy})(35\text{tBu}_2\text{Q})(\text{OH}_2)](\text{ClO}_4)_2$ (trpy = 2,2':6',2''-terpyridine, $35\text{tBu}_2\text{Q}$ = 3,5-di-*tert*-butyl-1,2-benzoquinone) underwent deprotonation of an aqua ligand accompanied with intramolecular electron transfer from O^{2-} ligand to quinone ligand generating O^- ligand.



VII-D-7 Multi-Electron Reduction of CO₂ via Ru-CO₂, -C(O)OH, -CO, -CHO, and -CH₂OH Species

TANAKA, Koji; OYAMA, Dai¹
(¹Fukushima Univ., CREST/JST)

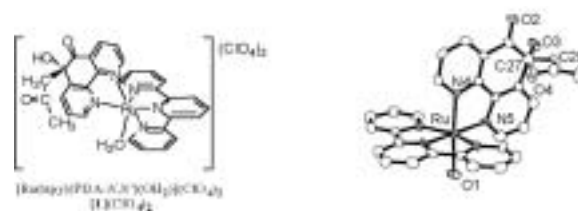
[*Coord. Chem. Rev.* **226**, 211–218 (2002)]

A review about preparations and the molecular structures determined by x-ray analyses of $[\text{Ru}(\text{bpy})_2(\text{CO})\text{L}]^{n+}$ ($\text{L} = \text{CO}_2$, $\text{C}(\text{O})\text{OH}$, CO , CHO , CH_2OH , CH_3 , and $\text{C}(\text{O})\text{CH}_3$; $n = 0, 1, 2$) were presented. 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 . Thermodynamically, 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 $[\text{Ru}(\text{bpy})_2(\text{CO})\text{L}]^{n+}$ were assessed by the $\nu(\text{Ru}-\text{L})$ 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–C bond strength of each intermediate. The Ru–C bond distance of $[\text{Ru}(\text{bpy})_2(\text{CO})\text{L}]^{n+}$ largely depends on the hybrid orbital of the C atom bonded to Ru and lengthens in the order $\text{Ru}-\text{C}sp < \text{Ru}-\text{C}sp_2 < \text{Ru}-\text{C}sp_3$. An unusual shift of the $\nu(\text{Ru}-\text{L})$ bands to higher wavenumber with decrease of the Ru–L bond distances is discussed in terms of σ - and π -character of the Ru–C bonds.

VII-D-8 Acid-Base Equilibria of Various Oxidation States of Aqua-Ruthenium Complexes with 1,10-Phenanthroline-5,6-Dione in Aqueous Media

FUJIHARA, Tetsuaki¹; WADA, Tohru; TANAKA, Koji
(¹IMS, CREST/JST)

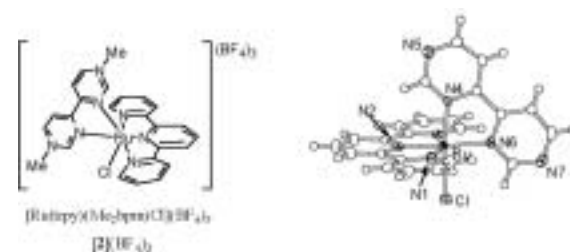
Synthesis and electrochemical behavior of aqua-ruthenium(II) complexes, $[\text{Ru}(\text{trpy})(\text{PDA}-N,N')(\text{OH}_2)](\text{ClO}_4)_2$ (**[1]**)(ClO_4)₂ and $[\text{Ru}(\text{trpy})(\text{PD}-N,N')(\text{OH}_2)](\text{ClO}_4)_2$ (**[2]**)(ClO_4)₂ ($\text{trpy} = 2,2':6',2''$ -terpyridine, PDA = 6-acetyl-6-hydroxy-5-oxo-1,10-phenanthroline, PD = 1,10-phenanthroline-5,6-dione) are presented. Treatment of $[\text{Ru}(\text{trpy})(\text{PD}-N,N')\text{Cl}](\text{PF}_6)$ with AgClO_4 in a mixed solvent of acetone and H_2O selectively produced the acetylonyl-PD complex **[1]**(ClO_4)₂, and the similar treatment in a mixed solvent of 2-methoxyethanol and H_2O gave the PD complex **[2]**(ClO_4)₂. The molecular structures of both complexes were determined by X-ray structural analysis. Simulation of pH dependent redox potentials ($E_{1/2}$) of **[1]**²⁺ and **[2]**²⁺ in H_2O revealed that the acetylonyl-PD complex **[1]**²⁺ underwent closely successive Ru(II)/Ru(III) and Ru(III)/Ru(IV) redox reactions. In addition to the similar successive Ru(II)/Ru(III) and Ru(III)/Ru(IV) redox reactions, the aqua complex **[2]**²⁺ showed simultaneous two-electron quinone/catechol redox couple of the PD ligand.



VII-D-9 Syntheses and Electrochemical Properties of Ruthenium(II) Polypyridyl Complexes with 4,4'-Bipyrimidine and Quaternized 4,4'-Bipyrimidinium Ligands

FUJIHARA, Tetsuaki¹; WADA, Tohru; TANAKA, Koji
(¹IMS, CREST/JST)

The synthesis and electrochemical properties of novel ruthenium(II) polypyridyl complexes with 4,4'-bipyrimidine, $[\text{Ru}(\text{trpy})(\text{bpm})\text{Cl}](\text{X})$ (**[1]**)(X ; $\text{X} = \text{PF}_6^-$, BF_4^-), and with a quaternized bipyrimidinium ligand, $[\text{Ru}(\text{trpy})(\text{Me}_2\text{bpm})\text{Cl}](\text{BF}_4)_3$ (**[2]**)(BF_4)₃ ($\text{trpy} = 2,2':6',2''$ -terpyridine, bpm = 4,4'-bipyrimidine, $\text{Me}_2\text{bpm} = 1,1'$ -dimethyl-4,4'-bipyrimidinium) are presented. The bpm complex of **[1]**⁺ was prepared by the reaction of $\text{Ru}(\text{trpy})\text{Cl}_3$ with 4,4'-bipyrimidine in $\text{EtOH}/\text{H}_2\text{O}$. The structural characterization of **[1]**⁺ revealed that the bpm ligand was coordinated to the ruthenium atom with the bidentate fashion. Diquaternization of the non-coordinating nitrogen atoms on bpm of **[1]**⁺ by $(\text{CH}_3)_3\text{OBF}_4$ in CH_3CN gave **[2]**(BF_4)₃. The electrochemical and spectroelectrochemical properties of the complexes are described.

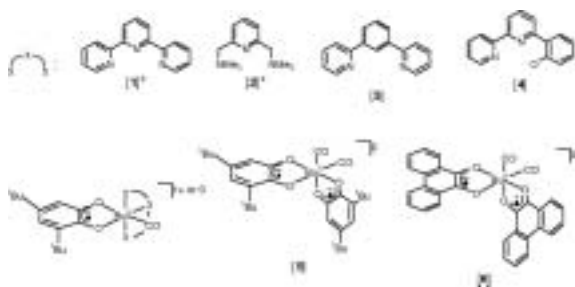


VII-D-10 Strong Interaction between Carbonyl and Dioxolene Ligands through Charge Distribution of Mono- and Dicarbonyl Ruthenium Complexes with Semiquinone

WADA, Tohru; FUJIHARA, Tetsuaki¹; TOMORI, Mizuno²; OYAMA, Dai²; TANAKA, Koji
(¹IMS, CREST/JST; ²Fukushima Univ., CREST/JST)

Monocarbonyl Ru(II) Complexes with semiquinone, $([\text{Ru}(\text{CO})(\text{sq})(\text{L})]^n)$ ($\text{sq} = 3,5$ -di-*tert*-butyl-1,2-benzo-semiquinone, $\text{L} = \text{terpyridine}$ (**[1]**⁺), 2,6-bis(*N,N*-dimethylaminomethyl)-pyridine (**[2]**⁺), 2,6-dipyrid-2-ylphenyl (**[3]**⁰), 2-(2,2'-bipyrid-6-yl)phenolato (**[4]**⁰), $n = 1+$ or 0), and dicarbonyl Ru(II) complexes with two semiquinones, $[\text{Ru}(\text{CO})_2(\text{sq})_2]$ (**[5]**⁰) and $[\text{Ru}(\text{CO})_2(\text{phsq})_2]$ ($\text{phsq} = 9,10$ -phenanthrasemiquinone, **[6]**⁰), were synthesized. Red shift of $\nu(\text{CO})$ bands caused by one-electron reduction of semiquinone is in a range of -41 to -56 cm^{-1} . Unusual large red shift of $\nu(\text{CO})$ bands

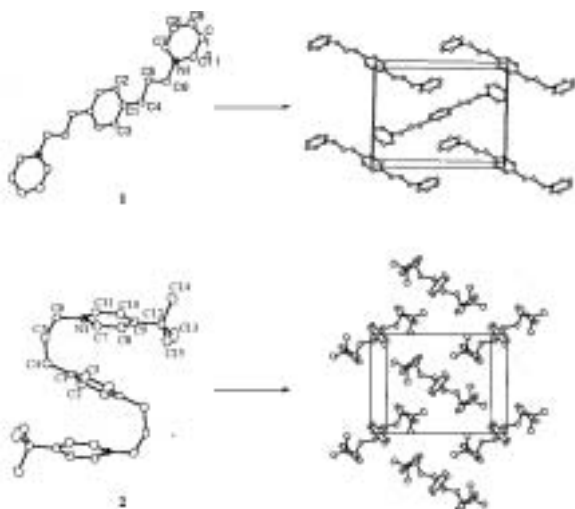
compared with analogous Ru(II)–polypyridyl results from the strong interaction between carbonyl and dioxolene across Ru(II).



VII-D-11 Regulation of Inter- and Intra-Molecular A–D–A π - π Stacking. Solid State Structures of Bis(pyridinium) Compounds

KOIZUMI, Take-aki; TSUTSUI, Kanako; WADA, Tohru; TANAKA, Koji

The synthesis and molecular structures of bis(pyridinium) compounds, [1,4-(4-R-C₅H₄N⁺CH₂-CH₂CH₂)₂C₆H₄][X⁻]₂ (**1**, R = H, X = I; **2**, R = t-Bu, X = Br) are investigated. The compound **1** is a linear structure in the solid state and the crystal packing geometry of **1** is defined as isolated triplets formed by the phenylene ring of a molecule and two pyridinium rings of two neighboring molecules. On the other hand, compound **2** has an S-shaped arrangement, and an intramolecular acceptor-donor-acceptor triplet is formed among the central phenylene ring and two terminal pyridinium rings in the same molecule. Such a distinct difference in the crystal structures of **1** and **2** is ascribed to the substituent in the pyridinium unit. The steric repulsion of the bulky tert-butyl group hinders intermolecular A–D–A π - π stacking.

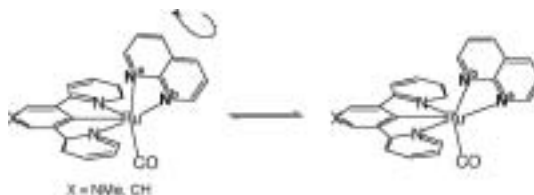


VII-D-12 Synthesis, Structures and Fluxional Behavior of Ruthenium(II) Complexes Bearing a Bidentate 1,8-Naphthyridine Ligand

KOIZUMI, Take-aki¹; TOMON, Takashi¹; TANAKA, Koji

(¹IMS, CREST/JST)

The ruthenium complexes bearing 1,8-naphthyridine (napy) and terpyridine analogous (N,C,N)-tridentate ligands were synthesized and characterized. Reaction of RuCl₂(η^2 -napy)(DMSO)₂ with 2 equiv of AgPF₆ and subsequent addition of LH and CO gave [RuL(η^2 -napy)(CO)](PF₆)_n (**6a**: L = N-methyl-3,5-di(2-pyridyl)-4-pyridyl, *n* = 2; **6b**: L = 2,6-di(2-pyridyl)phenyl, *n* = 1) via the formation of [RuL(η^2 -napy)(DMSO)](PF₆)_n (**5a**: L = N-methyl-3,5-di(2-pyridyl)-4-pyridyl, *n* = 2; **5b**: L = 2,6-di(2-pyridyl)phenyl, *n* = 1). The crystal structures of **5a** and **6a** show that these complexes have distorted octahedral coordination with the tridentate (N,C,N)-ligand as mer-fashion, two nitrogen of bidentate napy and sulfur of DMSO (**5a**) or carbon of the CO (**6a**) ligand. Detailed irradiation and variable-temperature ¹H-NMR studies reveal fluxional process of the chelated napy ligand in solution.



VII-D-13 Acid-Base Equilibrium of 6-Hydroxy-2,2'-Bipyridine Ligated on Ruthenium-Carbonyl Complexes and Cyclometalation Driven by Ligand Based Redox Reaction

TOMON, Takashi¹; KOIZUMI, Take-aki¹; TANAKA, Koji
(¹IMS, CREST/JST)

Two isomers of [Ru(trpy)(bpy-O)(CO)](PF₆) (**[1]**⁺ and **[2]**⁺) (trpy = terpyridine, bpy-O = 2-(2'-pyridyl)-6-pyridonato; pyridonato in bpy-O of **[1]**⁺ and **[2]**⁺ is located in a position *trans* and *cis* to CO. Treatments of **[1]**⁺ and **[2]**⁺ with HPF₆ produced **[1H]**²⁺ and **[2H]**²⁺ with bpy-OH (bpy-OH = 6-hydroxy-2, 2'-bipyridine), and the reactions of **[1H]**²⁺ and **[2H]**²⁺ with Et₃N regenerated **[1]**⁺ and **[2]**⁺. The molecular structures of **[1]**(PF₆), **[2]**(PF₆)·H₂O and **[2H]**(PF₆)₂·2H₂O were determined by X-ray analysis. The cyclic voltammograms of **[1]**⁺ and **[2]**⁺ displayed one nearly reversible redox couple at *E*_{1/2} = -1.65 V and -1.51 V, and one irreversible cathodic wave at *E*_{p,c} = -1.97 and *E*_{p,c} = -2.15 V, respectively. The complex of **[1]**⁺ showed the ν (C≡O) band at 1979 cm⁻¹, which shifted to 1932 and 1853 cm⁻¹ upon one- and two-electron reduction of **[1]**⁺, respectively, and the intensity of the 1853 cm⁻¹ band became weak compared with those of the 1979 and 1932 cm⁻¹ bands due to loss of CO from **[1]**⁻. **[2]**⁺ and **[2]**⁰ also displayed the ν (C≡O) band at 1997 and 1953 cm⁻¹, the latter of which moved to 1587 cm⁻¹ upon one electron reduction of **[2]**⁰. Reoxidation of **[2]**⁻ at 0 V almost fully regenerated the IR spectra of **[2]**⁺. Unusual large red shift of the ν (C≡O) band between **[2]**⁰ and **[2]**⁻ ($\Delta\nu$ = 345 cm⁻¹) is ascribed to a cyclometalation resulting from an attack of pyridonato oxygen to carbonyl carbon of **[2]**⁻.