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 organic 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 η¹- or η²-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.

Oxidations and oxidations of organic molecules by high valent metal-oxo complexes are of current interest from the viewpoints of the enzymatic activities of P₄₅₀. 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 catecholate 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)

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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), mixed-metal complexes [(PPh₃)₂Pd(O,O'-PD-N,N')Ru(trpy)-Cl](PF₆) (²), and [(PPh₃)₂Pt(O,O'-PD-N,N')Ru(trpy)-Cl](PF₆) (³) (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

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The ruthenium oxyl radical complex, [Ru(II)(trpy)-(Bu₂SQ)O.–.] (trpy = 2,2':6',2"-terpyridine, Bu₂SQ = 3,5-di-tert-butyl-1,2-benzoquinone) was prepare 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 (pKₐ 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=O complex was converted to the Ru(III)-semiquinone moiety and oxyl radical, the latter of which was characterized by a spin trapping technique. The most characteristic structural feature of [Ru(III)(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}^{III}\text{(trpy)}(4\text{ClISO})(\text{OH}_2)](\text{ClO}_4)_2 (4\text{ClISO} = 4\text{-chloro-}
1,2\text{-benzosemiquinone}) and compared the deprotonation
behavior of the aqua ligand with that of [\text{Ru}^{III}\text{(trpy)}-
(\text{Bu}_2\text{SQ})(\text{OH}_2)](\text{ClO}_4)_2. Deprotonation of the aqua
ligand of [\text{Ru}^{III}\text{(trpy)}(4\text{ClISO})(\text{OH}_2)](\text{ClO}_4)_2 induced
intramolecular electron transfer from \text{OH}^{-} to the
[\text{Ru}^{III}(4\text{ClISO})] moiety affording [\text{Ru}^{III}\text{(trpy)}(4\text{ClISO})-
(OH)]^{2+}, which then probably changed to [\text{Ru}^{III}\text{(trpy)}-
(4\text{ClISO})O^{-}]. The antiferromagnetic interactions (J values)
between \text{Ru}^{II}, \text{Ru}-\text{semiquinone} and the oxyl radical
for [\text{Ru}^{III}\text{(trpy)}(\text{Bu}_2\text{SO})O^{-}] and for [\text{Ru}^{III}\text{(trpy)}(4\text{ClISO})-
(OH)]^{2+} were 2J = -0.67 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
Pyridylidene Ligands

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[Organometallics 22, 970–975 (2003)]

The cyclometalated complexes [\text{RuL(terpy)}][\text{PF}_6]_2
(3, \text{L} = \text{N}^\text{N}-\text{methyl-4'-methylthio-2',6',4'-terpyridinium}; 4, \text{L} = \text{N}^\text{N}-\text{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 charac-
terized by x-ray crystallographic, spectroscopic, and
electrochemical measurements. \textsuperscript{13}C{\textsuperscript{1}H} 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


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

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

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[Inorg. Chem. 41, 5912–5919 (2002)]

A series of aqua-Cr(III)-dioxolene complexes,
[\text{Cr(OH}_2)(3,5,-\text{Bu}_2\text{SQ})(\text{trpy})][\text{ClO}_4] \text{(1s), [Cr(OH}_2)(3,5,-
\text{Bu}_2\text{Cat})(\text{trpy})][\text{ClO}_4] \text{(1c), [Cr(OH}_2)(3,6,-\text{Bu}_2\text{SQ})(\text{trpy})-
(\text{Cl}_4\text{Cat})][\text{ClO}_4] \text{(2), [Cr(OH}_2)(3,5,-\text{Bu}_2\text{Cat})(\text{trpy})][\text{ClO}_4] \text{(3), [Cr(OH}_2)(-
3,6\text{-Bu}_2\text{SQ})(\text{Cl}_4\text{Cat})(\text{trpy})][\text{ClO}_4] \text{(4), [Cr(OH}_2)(3,5,-
\text{Bu}_2\text{SQ})(\text{Me}_3\text{-tacn})][\text{ClO}_4] \text{(5), [Cr(OH}_2)(\text{Cat})(\text{Me}_3\text{-tacn})][\text{ClO}_4] \text{(6),}
and [\text{Cr(OH}_2)(\text{Cl}_3\text{Cat})(\text{Me}_3\text{-tacn})][\text{ClO}_4] \text{(7) (Bu}_2\text{SQ} = di-
terr-butyl-1-o-benzosemiquinonate anion, Bu}_2\text{Cat} = di-
terr-butylcatecholate dianion, Cat = catecholate dianion,
Cl}_3\text{Cat} = tetrachlorocatecholate dianion, trpy = 2,2':
6',2''-terpyridine, and 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 \textit{pKa} value of the
aqua-Cr(III) complexes increased in the order
6 \succ 5 \succ 4 \succ 1c \succ 7 \succ 3 \succ 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 H$_2$O/THF at pH 11 under
illumination of visible light.

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

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[Chem. Lett. 868–869 (2002)]

Ru-quinone complex containing an aqua ligand,
[\text{Ru(II)(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\textsuperscript{2-} ligand to quinone ligand generating
O\textsuperscript{2-} ligand.

VII-D-7 Multi-Electron Reduction of CO$_2$ via
Ru-CO$_2$, -C(O)OH, -CO, -CHO, and -CH$_2$OH Species
A review about preparations and the molecular structures determined by x-ray analyses of [Ru(bpy)$_2$-(CO)$_L$]$^{n+}$ (L = CO$_2$, (CO)OH, CO, CHO, CH$_2$OH, CH$_3$, and C(O)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$_3$OH, 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 [Ru(bpy)$_2$]$_2$-(CO)$_L$]$^{n+}$ was assessed by the ν(Ru–L) bands and the Ru–L bond distances from the viewpoint of elucidation of the relationship 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 [Ru(bpy)$_2$-(CO)$_L$]$^{n+}$ largely depends on the hybrid orbital of the C atom bonded to Ru and lengthens in the order Ru–Csp$^3$ < Ru–Csp$^2$ < Ru–Csp$^1$. An unusual shift of the ν(Ru–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, Tetsuaki$^1$; WADA, Tohru; TANAKA, Koji

Synthesis and electrochemical behavior of aqua-ruthenium(II) complexes, [Ru(trpy)(PDA-N$^\cdot$N')(OH)$_2$]- (ClO$_4$)$_2$ (I[ClO$_4$]), and [Ru(trpy)(PD-NN')(OH)$_2$]- (ClO$_4$)$_2$ (I[ClO$_4$]) (trpy = 2,2':6',2"-terpyridine, PDA = 6-acetonyl-6-hydroxy-5-oxo-1,10-phenanthroline, PD = 1,10-phenanthroline-5,6-dione) are presented. Treatment of [Ru(trpy)(PD-NN')(Cl]PF$_6$) with AgClO$_4$ in a mixed solvent of acetone and H$_2$O selectively produced the acetyl-PD complex I[ClO$_4$], and the similar treatment in a mixed solvent of 2-methoxyethanol and H$_2$O gave the PD complex I[ClO$_4$]. The molecular structures of both complexes were determined by X-ray structural analysis. Simulation of pH dependent redox potentials ($E_{1/2}$) of I$^{2+}$ and I$^{2+}$ in H$_2$O revealed that the acetyl-PD complex I$^{2+}$ underwent closely successive Ru(II)/Ru(III) and Ru(II)/Ru(IV) redox reactions. In addition to the similar successive Ru(II)/Ru(III) and Ru(II)/Ru(IV) redox reactions, the aqua complex I$^{2+}$ 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, Tetsuaki$^1$; WADA, Tohru; TANAKA, Koji

The synthesis and electrochemical properties of novel ruthenium(II) polypyridyl complexes with 4,4'-bipyrimidine, [Ru(trpy)(bpm)Cl]$^{n+}$ (L = CO$_2$, BF$_4$), and with a quaternized bipyrimidinium ligand, [Ru(trpy)(Me$_2$bpm)Cl]BF$_4$ (trpy = 2,2':6',2"-terpyridine, bpm = 4,4'-bipyrimidine, Me$_2$bpm = 1,1'-dimethyl-4,4'-bipyrimidinium) are presented. The bpm complex of [I$^+$] was prepared by the reaction of Ru(trpy)Cl$_3$ with 4,4'-bipyrimidine in EtOH/H$_2$O. The structural characterization of [I$^+$] revealed that the bpm ligand was coordinated to the ruthenium atom with the bidentate fashion. Disquaternization of the non-coordinating nitrogen atoms on bpm of [I$^+$] by (CH$_3$)$_3$OBF$_4$ in CH$_3$CN 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, Tetsuaki$^1$; TOMORI, Mizuno$^2$; OYOYAMA, Dai$^2$; TANAKA, Koji

Monocarbonyl Ru(II) Complexes with semiquinone, ([Ru(CO)(sq)(L)]$^{n}$ (sq = 3,5-di-tert-butyl-1,2-benzosemiquinone, n = 0, 1+ or 0), and dicarbonyl Ru(II) complexes with two semiquinones, [Ru(CO)$_2$(sq)$_2$] (I$^+$), and [Ru(CO)$_2$-(phsq)$_2$] (phsq = 9,10-phenanthrasemiquinone, [6]$^n$), were synthesized. Red shift of ν(CO) bands caused by one-electron reduction of semiquinone is in a range of –41 to –56 cm$^{-1}$. Unusual large red shift of ν(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 Intramolecular 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, 2,4-(4-R-C₅H₄N⁺CH₂)₂C₆H₄][X – ]₂ (1, R = H, X = I; 2, R = t-Bu, X = Br) are investigated. The compound 1 has an S-shaped arrangement, and an intermolecular A–D–A π–π stacking. Solid State π-stacking. Intramolecular A–D–A repulsion of the bulky tert-butyl group hinders steric difference in the crystal structures of 1 and 2 compared with analogous Ru(II)–polypyridyl results from the strong interaction between carbonyl and dioxolene across Ru(II).

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

KOIZUMI, Take-aki; TOMON, Takashi; TANAKA, Koji

The ruthenium complexes bearing 1,8- naphthyridine (nap) and terpyridine analogous (N,C,N)-tridentate ligands were synthesized and characterized. Reaction of RuCl₂(N₃-napy)(DMSO)₂ with 2 equiv of AgPF₆ and subsequent addition of LH and CO gave [RuL(η²-napy)(CO)][PF₆]₆ (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(η²-napy)-(DMSO)][PF₆]₆ (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 nap 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.

(¹IMS, CREST/JST)

The ruthenium complexes bearing 1,8- naphthyridine (nap) and terpyridine analogous (N,C,N)-tridentate ligands were synthesized and characterized. Reaction of RuCl₂(N₃-napy)(DMSO)₂ with 2 equiv of AgPF₆ and subsequent addition of LH and CO gave [RuL(η²-napy)(CO)][PF₆]₆ (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(η²-napy)-(DMSO)][PF₆]₆ (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 nap 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.

(¹IMS, CREST/JST)