VIII-F Reduction of CO_2 and Oxidation of Organic Molecules Aiming at Energy Conversion between Chemical Energy and Electricity

Electro- and photochemical reduction of CO_2 affording methanol has become crucial issue in line with the progress of fuel energy cells using methanol. Carbon dioxide easily forms η^1- and η^2-CO_2 adducts by the reaction with coordinatively unsaturated low-valent metal complexes. Metal complexes with η^1-CO_2 in protic media are smoothly converted to the corresponding metal-CO ones, which undergo reductive cleavages of the M–CO bonds by accumulation of electrons at the metal centers under electrolysis conditions. A number of metal complexes have proven to catalyze reduction of CO_2 to CO, but the process prevents the CO ligand from hydrogenation leading to methanol formation. To achieve electrochemical reduction of the carbonyl ligand derived from CO_2, we are designing new types of metal complexes that can provide electrons to carbonyl carbon through redox active ligands without increasing electron densities in the metal centers.

Metal complexes that have an ability to oxidize organic molecules at potentials more negative than the reduction potential of dioxygen enable the direct conversion from chemical energy of organic molecules to electricity. Metal-oxo complexes are possible candidates for the smooth oxidation of organic molecules, since metal-oxo species are believed to work as active centers in various metal enzymes, which oxidize various biological substrates under very mild conditions. Mechanistic understandings of the reactivity of metal-oxo species are limited because of the difficulty of selective formation of reactive M–O frameworks in artificial systems. On the other hand, high valent Ru=O complexes can be obtained by sequential electron and proton loss of the corresponding Ru-OH_2 ones, and have proven to work as oxidants of organic molecules. We have succeeded smooth and reversible conversion between aqua and oxo ligands on Ru-dioxolene frameworks without using any oxidants by taking advantage of dioxolene as a redox active ligand. Along this line, we have been preparing a variety of metal-aqua complexes bearing a dioxolene ligand aiming at oxidation of hydrocarbons by the corresponding metal-oxo forms.

VIII-F-1 Regulation of Electron Donating Ability to Metal Center: Isolation and Characterization of Ruthenium Carbonyl Complexes with N,N- and/or N,O-Donor Polypyridyl Ligands

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[*J. Organomet. Chem.* **665**, 107–113 (2003)]

Polypyridyl ruthenium(II) dicarbonyl complexes with an N,O- and/or N,N-donor ligand, $[Ru(pic)(CO)_2Cl_2]^-$ (**1**), $[Ru(bpy)(pic)(CO)_2]^+$ (**2**), $[Ru(pic)_2(CO)_2]$ (**3**), and $[Ru(bpy)_2(CO)_2]^{2+}$ (**4**) (pic = 2-pyridylcarboxylato, bpy = 2,2'-bipyridine) were prepared for comparison of the electron donor ability of these ligands to the ruthenium center. Salts of complexes **1** and **2** were characterized by x-ray crystallography. A carbonyl group of $[Ru(L1)(L2)(CO)_2]^{n+}$ (L1, L2 = bpy, pic) successively reacted with one and two equiv of OH^- to form $[Ru(L1)(L2)(CO)(C(O)OH)]^{(n-1)+}$ and $[Ru(L1)(L2)(CO)(CO_2)]^{(n-2)+}$ (eq 1).

$$[Ru(L1)(L2)(CO)_2]^{n+} \xrightleftharpoons[H^+]{OH^-} [Ru(L1)(L2)(CO)(C(O)OH)]^{(n-1)+} \xrightleftharpoons[H^+]{OH^-} [Ru(L1)(L2)(CO)(CO_2)]^{(n-2)+} \quad (1)$$

These three complexes exist as equilibrium mixtures in aqueous solutions and the equilibrium constants were determined potentiometrically. Electrochemical reduction of **2** in CO_2-saturated CH_3CN-H_2O at –1.5 V selectively produced CO.

VIII-F-2 Mono-Dithiolene Molybdenum(IV) Complexes of *cis*-1,2-Dicyano-1,2-Ethylene-Dithiolate (mnt^{2-}): New Models for Molybdenum Enzymes

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[*Eur. J. Inor. Chem.* **14**, 2633–2638 (2003)]

New mono-dithiolene Mo(IV) complexes of *cis*-1,2-dicyano-1,2-ethylenedithiolato $[(mnt)^{2-}]$ were synthesized as models for Mo enzymes, with 4,4'-di-*tert*-butyl-2,2'-bipyridine (Bu_2bpy) and, *N,N'*-tetraethylethylenediamine (Et_4en) as ancillary ligands, and characterized by IR, UV/visible, elemental anal., ESI-mass and electrochemical techniques. The temperature dependent ^1H NMR spectra, recorded in CD_3CN solution, indicated that $[MoO(mnt)(Bu_2bpy)]$ (**1**) has a rigid structure but $[MoO(mnt)(Et_4en)]$ (**2**) showed dynamic conformational inversion processes involving the chelating ethylenediamine unit. The complexes exhibited different reactivity toward O_2: **1** gave a single oxo-bridged dimolybdenum dimer complex $[Mo_2O_3(mnt)_2(Bu_2bpy)_2]$ (**3**), while **2** did not react with O_2 and kept its mononuclear structure. Both complexes have almost the same redox potential for $Mo^{IV/V}$, and so the steric bulkiness and conformational dynamics probably cause this marked contrast. The obtained dimolybdenum complex **3** was also structurally characterized and studied, and is a new dimolybdenum complex with one dithiolene per Mo. The crystal structure of the starting complex $MoO_2Cl_2(Bu_2bpy)$ (**4**) is also reported.

VIII-F-3 Characterization of a Stable Ruthenium Complex with an Oxyl Radical

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[*J. Am. Chem. Soc.* **125**, 6729–39 (2003)]

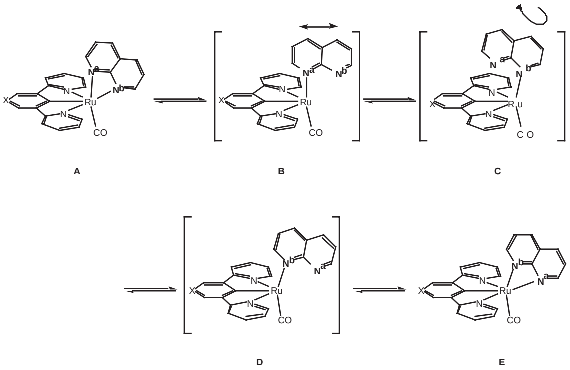
The ruthenium oxyl radical complex, $[Ru^{II}(trpy)(Bu_2SQ)O^{\bullet-}]$ (trpy = 2,2’:6’,2”-terpyridine, Bu_2SQ = 3,5-di-*tert*-butyl-1,2-benzosemiquinone) was prepared for the first time by the double deprotonation of the aqua ligand of $[Ru^{III}(trpy)(Bu_2SQ)(OH_2)](ClO_4)_2$. $[Ru^{III}(trpy)(Bu_2SQ)(OH_2)](ClO_4)_2$ is reversibly converted to $[Ru^{III}(trpy)(Bu_2SQ)(OH^-)]^+$ upon dissociation of the aqua proton (pK_a 5.5). Deprotonation of the hydroxo proton gave rise to intramolecular electron transfer from the resultant O^{2-} to Ru-dioxolene. The resultant $[Ru^{II}(trpy)(Bu_2SQ)O^{\bullet-}]$ 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 $[Ru^{II}(trpy)(Bu_2SQ)O^{\bullet-}]$ 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, $[Ru^{III}(trpy)(4ClSQ)(OH_2)](ClO_4)_2$ (4ClSQ = 4-chloro-1,2-benzosemiquinone) was prepared and we compared the deprotonation behavior of the aqua ligand with that of $[Ru^{III}(trpy)(Bu_2SQ)(OH_2)](ClO_4)_2$. Deprotonation of the aqua ligand of $[Ru^{III}(trpy)(4ClSQ)(OH_2)](ClO_4)_2$ induced intramolecular electron transfer from OH^- to the $[Ru^{III}(4ClSQ)]$ moiety affording $[Ru^{II}(trpy)(4ClSQ)(OH^{\bullet})]^+$, which then probably changed to $[Ru^{II}(trpy)(4ClSQ)O^{\bullet-}]$. The antiferromagnetic interactions (J values) between Ru^{II}-semiquinone and the oxyl radical for $[Ru^{II}(trpy)(Bu_2SQ)O^{\bullet-}]$ and for $[Ru^{II}(trpy)(4ClSQ)O^{\bullet-}]$ were $2J$ = –0.67 cm^{-1} and –1.97 cm^{-1}, respectively.

VIII-F-4 Synthesis, Structures and Fluxional Behavior of Ruthenium(II) Complexes Bearing a Bidentate 1,8-Naphthyridine Ligand

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

[*Bull. Chem. Soc. Jpn.* **76**, 1969–1975 (2003)]

The Ru complexes bearing 1,8-naphthyridine (napy) and terpyridine analogous (N,C,N)-tridentate ligands were synthesized and characterized. The reaction of $[RuCl_2(napy\text{-}k^2N,N')(DMSO)_2]$ with **2** equiv of $AgPF_6$ and subsequent addition of LH and CO gave $[RuL(napy\text{-}k^2N,N')(CO)](PF_6)_n$ (**6a**: L = *N*-methyl-3,5-di(2-pyridyl)-4-pyridyl, n = 2; **6b**: L = 2,6-di(2-pyridyl)phenyl, n = 1) *via* $[RuL(napy\text{-}k^2N,N')(DMSO)](PF_6)_n$ (**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 distorted octahedral coordination with the tridentate (N,C,N)-ligand as mer-fashion, two nitrogens of bidentate napy and the S of DMSO (**5a**) or the C of the CO ligand (**6a**). Detailed expts. for irradn. and variable-temperature ^1H NMR studies reveal a fluxional process of the chelated napy ligand in solutions.



VIII-F-5 Selective Formation of Inter- and Intramolecular A-D-A π-π Stacking: Solid-State Structures of Bis(pyridiniopropyl)benzenes

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

[*Eur. J. Org. Chem.* **23**, 4528–4532 (2003)]

The synthesis and mol. structures of bis(pyridiniopropyl)benzene derivatives $[p\text{-}(4\text{-}RC_5H_4N^+CH_2CH_2CH_2)_2C_6H_4](X^-)_2$ [R = H, X = I (**I**); R = CMe_3, X = Br (**II**)] have been investigated. **I** adopts a linear structure in the solid state and the crystal packing geometry can be defined as isolated triplets formed by the phenylene ring of one mol. and two pyridinium rings of two neighboring molecules. In contrast, **II** 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 mol. Such a distinct difference in the crystal structures of **I** and **II** can be ascribed to the substituent on the pyridinium unit. The steric repulsion of the bulky *tert*-Bu group hinders internal. A-D-A π-π stacking.

VIII-F-6 Equilibrium of Low- and High-Spin States of Ni(II) Complexes Controlled by the Donor Ability of the Bidentate Ligands

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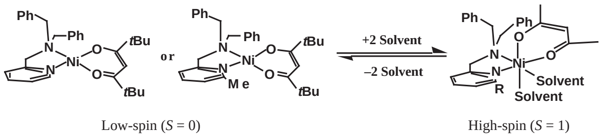
([1]IMS, CREST/JST)

[*Inorg. Chem.* **43**, 3024–30 (2004)]

Low-spin nickel(II) complexes containing bidentate ligands with modulated nitrogen donor ability, $Py(Bz)_2$ or $MePy(Bz)_2$ ($Py(Bz)_2$ = *N*,*N*-bis(benzyl)-*N*-[(2-pyridyl)methyl]amine, $MePy(Bz)_2$ = *N*,*N*-bis(benzyl)-*N*-[(6-methyl-2-pyridyl)methyl]amine), and a β-diketonate derivative, *t*BuacacH (*t*BuacacH = 2,2,6,6-tetramethyl-3,5-heptanedione), represented as $[Ni(Py(Bz)_2)(t\text{Buacac})](PF_6)$ (**1**) and $[Ni(MePy(Bz)_2)(t\text{Buacac})](PF_6)$ (**2**) have been synthesized. In addition, the corresponding high-spin nickel(II) complexes having a nitrate ion, $[Ni(Py(Bz)_2)(t\text{Buacac})(NO_3)]$ (**3**) and $[Ni(MePy(Bz)_2)(t\text{Buacac})(NO_3)]$ (**4**), have also been synthesized for comparison. Complexes **1** and **2** have tetracoordinate low-spin square-planar structures, whereas the coordination environment of the nickel ion in **4** is a hexacoordinate high-spin octahedral geometry. The absorption spectra of low-spin complexes **1** and **2** in a noncoordinating solvent, dichloromethane (CH_2Cl_2), display the characteristic absorption bands at 500 and 540 nm, respectively. On the other hand, the spectra of a CH_2Cl_2 solution of high-spin complexes **3** and **4** exhibit the absorption bands centered at 610 and 620 nm, respectively. The absorption spectra of **1** and **2** in *N*,*N*-dimethylformamide (DMF), being a coordinating solvent, are quite different from those in CH_2Cl_2, which are nearly the same as those of **3** and **4** in CH_2Cl_2. This result indicates that the structures of **1** and **2** are converted from a low-spin square-planar to a high-spin octahedral configuration by the coordination of two DMF molecules to the nickel ion. Moreover, complex **1** shows thermochromic behavior resulting from the equilibrium between low-spin square-planar and high-spin octahedral structures in acetone, while complex **2** exists only as a high-spin octahedral configuration in acetone at any temperature.

Such drastic differences in the binding constants and thermochromic properties can be ascribed to the enhancement of the acidity of the nickel ion of **2** by the steric effect of the *o*-methyl group in the MePy(Bz)$_2$ ligand in **2**, which weakens the Ni-N(pyridine) bond length compared with that of the nonsubstituted Py(Bz)$_2$ ligand in **1**.



VIII-F-7 Acid-Base Equilibria of Various Oxidation States of Aqua-Ruthenium Complexes with 1,10-Phenanthroline-5,6-Dione in Aqueous Media

FUJIHARA, Tetsuaki; WADA, Tohru; TANAKA, Koji

[*Dalton Trans.* 645–52 (2004)]

Syntheses and pH dependent electrochemical properties of aqua-ruthenium(II) complexes, [Ru(trpy)(PDA-*N*,*N*’)(OH_2)](ClO_4)$_2$ ([**1**](ClO_4)$_2$) and [Ru(trpy)(PD-*N*,*N*’)(OH_2)](ClO_4)$_2$ ([**2**](ClO_4)$_2$) (trpy = 2,2’:6’,2”-terpyridine, PDA = 6-acetonyl-6-hydroxy-1,10- phenanthroline-5-one, PD = 1,10-phenanthroline-5,6-dione) are presented. Treatment of [Ru(trpy)(PD-*N*,*N*’)Cl](PF_6) with $AgClO_4$ in a mixed solvent of acetone and H_2O selectively produced the acetonyl-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. The proton dissociation constants of various oxidations state of [**1**]$^{2+}$ and [**2**]$^{2+}$ were evaluated by simulation of $E_{1/2}$ values of those redox potentials depending on pH. The simulation revealed that the acetonyl-PD complex [**1**]$^{2+}$ underwent successive Ru(II)/Ru(III) and Ru(III)/Ru(IV) redox couples though the two redox reactions were not separated in the cyclic voltammograms. The redox behavior of [**2**]$^{2+}$ in H_2O is reasonably explained by not only the similar successive metal-centered redox reactions but also simultaneous two-electron quinone/catechol redox couple of the PD ligand including the contribution of hydration on a carbonyl carbon.

VIII-F-8 Syntheses and Electrochemical Properties of Ruthenium(II) Complexes with 4,4’-Bipyrimidine and 4,4’-Bipyrimidinium Ligands

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[*Inorg. Chim. Acta* **357**, 1205–1212 (2004)]

The syntheses and electrochem. properties of novel ruthenium(II) polypyridyl complexes with 4,4’-bipyrimidine, [Ru(trpy)(bpm)Cl](X) ([**1**](X; X = PF_6^-, BF_4^-)) and with a quaternized 4,4’-bipyrimidinium ligand, [Ru(trpy)(Me_2bpm)Cl](BF_4)$_3$ ([**2**](BF_4)$_3$, trpy = 2,2’:6’,2”-terpyridine, bpm = 4,4’-bipyrimidine, Me_2 bpm = 1,1’-dimethyl-4,4’-bipyrimidinium) are presented. The bpm complex [**1**]$^+$ was prepared by the reaction of Ru(trpy)Cl_3 with 4,4’-bipyrimidine in EtOH/H_2O. The structural characterization of [**1**]$^+$ revealed that the bpm ligand coordinated to the ruthenium atom in a bidentate fashion. Diquaternization of the noncoordinating nitrogen atoms on bpm of [**1**]$^+$ by Me_3OBF_4 in CH_3 CN gave [**2**](BF_4)$_3$. The electrochemical and spectroelectrochemical properties of the complexes are described.

VIII-F-9 Strong Interaction between Carbonyl and Dioxolene Ligands Caused by Charge Distribution of Ruthenium-Dioxolene Frameworks of Mono- and Dicarbonylruthenium Complexes

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[*Bull. Chem. Soc. Jpn.* **77**, 741–749 (2004)]

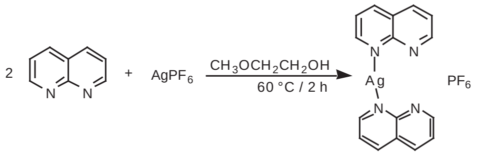
Monocarbonylruthenium complexes with a semiquinone ligand, [Ru(CO)(sq)(L)]$^{n+}$ (sq = 3,5-di-*tert*-butyl-1,2-benzosemiquinone, n = 1 or 0, L = 2,2’:6’,2”-terpyridine ([**1**]$^+$), 2,6-bis(*N*,*N*-dimethylaminomethyl) pyridine ([**2**]$^+$), 2,6-di-2’-pyridylphenyl ([**3**]^0), or 2-(2,2’-bipyridin-6-yl)phenolato ([**4**]^0)), and dicarbonylruthenium complexes with two semiquinone ligands, [Ru(CO)$_2$(sq)$_2$] ([**5**]^0) and [Ru(CO)$_2$(phsq)$_2$] (phsq = 9,10-phenanthrasemiquinone, [**6**]^0), were synthesized and the structures of [**1**]$^+$ and [**6**] were determined by x-ray crystal anal. Monocarbonyl Ru(II)-dioxolene complexes displayed the ligand localized catecholato/semiquinone and semiquinone/quinone redox couples, and two sets of those redox couples were obsd. in the dicarbonyl Ru(II)-bis(dioxolene) complexes. Spectroelectrochemical study revealed that the Ru(II)-catecholato and Ru(II)-semiquinone complexes were stable in solutions, while the Ru(II)-quinone complexes underwent fragmentation in solutions. One-electron reduction of the monocarbonyl Ru(II)-semiquinone complexes caused a red shift of the ν(CO) bands at 41–56 cm^{-1}, which was substantially larger than those of carbonyl Ru(II)-polypyridyl complexes. Two ν(CO) bands of dicarbonyl Ru(II)-bis(semiquinone) complexes also shifted to lower wavelength at 53–99 cm^{-1} upon two electron reduction of the complexes. The unusually large red shift of ν(CO) bands upon redn. of carbonyl Ru(II)-dioxolene complexes compared with those of Ru(II)-polypyridyl complex is ascribed to a strong electronic interaction between carbonyl and dioxolene ligands.

VIII-F-10 Synthesis and Crystal Structures of Mono- and Dinuclear Silver(I) Complexes Bearing 1,8-Naphthyridine Ligand

KOIZUMI, Take-aki; TANAKA, Koji

[*Inorg. Chim. Acta* **357**, 3666–3672 (2004)]

Mononuclear and dinuclear silver(I) complexes bearing 1,8-naphthyridine (napy) were prepd. The crystal structures of $[Ag(napy\text{-}\kappa N)_2](PF_6)$ (**1**) and $[Ag_2(\mu\text{-}napy)_2](PF_6)_2\cdot 3CH_3CN$ (**2**$\cdot 3CH_3CN$) were determined by X-ray diffraction studies. In complex **1**, intermol. π-π interaction of napy ligands between neighboring molecules forms left-handed hexagonal columns in the solid state. On the other hand, two napy ligands bridging two Ag ions in the dinuclear complex **2** shape a face-to-face π-π stacking with those of the neighboring molecule to form the dimeric unit. Besides, two of four napy ligands, which are located in a diagonal position in the dimeric unit, build intermolecular back-to-back π-π stackings with those of the adjacent dimeric unit, and a ladder-like stairway structure is generated in the solid state. Irrespective of such characteristic structures of **1** and **2** in the solid state, both complexes show very rapid dynamic behavior in solutions. No conversion between **1** and **2** took place even in the presence of excess amts. of Ag^+ or napy in solutions.



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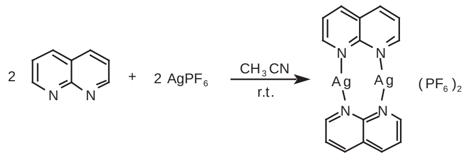

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