RESEARCH ACTIVITIES VIII
Coordination Chemistry Laboratories

Prof. Youichi Ishii (Chuou Univ.) and Prof. Takashi Hayashi (Osaka Univ.) took the position of Laboratory of Coordination Bond from April 2005. Prof. Hiroyuki Matsuzaka (Osaka Prefecture Univ.) and . Prof. Keiji Ueno (Gunma Univ.) finished their term as Adjunct Prof. of the Laboratory of Coordination Bond in March 2005. Their effort during their term is gratefully appreciated. Prof. Kazushi Mashima (Osaka Univ.) and Assoc. Prof. Masato Kurihara (Yamagata Univ.) continue the position of the Laboratory of Complex Catalyst.

VIII-A 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-A-1 Redox Behavior of New Ru-Dioxolene-Ammine Complexes and Catalytic Activity toward Electrochemical Oxidation of Alcohol under Mild Conditions

HINO, Takami; WADA, Tohru; FUJIWARA, Tetsunori; TANAKA, Koji

[*Chem. Lett.* **33**, 1596–1597 (2004)]

The new Ru-dioxolene-ammine complexes, $[Ru^{II}(NH_3)(sq)(trpy)](ClO_4)$ (**1**, sq = 3,5-di-tert-butyl-1,2-benzosemiquinone, trpy = 2,2’:6’,2”-terpyridine) and $[Ru^{III}(NH_3)(sq)(trpy)](ClO_4)_2$ (**2**), were prepared. **2** is quantitatively reduced to **1** in CH_3OH in the presence of base. Furthermore, both MeOH and *i*-PrOH are catalytically oxidized under the controlled potential electrolysis of **1** at 0 V (*vs.* SCE) in CH_2Cl_2. Both **1** and **2** lose the catalytic activity toward the oxidation of alcohols when the NH_3 ligand of the complexes was replaced by CH_3O^- during the electrolysis conditions.

VIII-A-2 Equilibrium of Low- and High-Spin States of Ni(II) Complexes Controlled by the Donor Ability of the Bidentate Ligands

OHTSU, Hideki; TANAKA, Koji

[*Inorg. Chem.* **43**, 3024–3030 (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 beta-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 non-substituted $Py(Bz)_2$ ligand in **1**.

VIII-A-3 A Platinum-Ruthenium Dinuclear Complex Bridged by Bis(terpyridyl)xanthene

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[*Inorg. Chem.* **43**, 7210–7217 (2004)]

4,5-Bis(2,2’:6’,2”-terpyrid-4’-yl)-2,7-di-*tert*-butyl-9,9-dimethylxanthene (btpyxa) was prepared. to serve as a new bridging ligand *via* Suzuki coupling of terpyridin-4’-yl triflate and 2,7-di-tert-butyl-9,9-dimethylxanthene-4,5-diboronic acid. The reaction of btpyxa with either 1 equiv or an excess of $PtCl_2$(cod) (cod = 1,5-cyclooctadiene) followed by anion exchange afforded mono- and dinuclear platinum complexes [(PtCl)(btpyxa)](PF_6) ([**1**](PF_6)) and $[(PtCl)_2$(btpyxa)]$(PF_6)_2$ ([**2**]$(PF_6)_2$), respectively. The x-ray crystallography of [**1**](PF_6)·$CHCl_3$ revealed that the two terpyridine units in the ligand are nearly parallel to each other. Heterodinuclear [(PtCl){Ru($t$$Bu_2$SQ)(DMSO)}(btpyxa)]$(PF_6)_2$ ([**4**] $(PF_6)_2$, $t$$Bu_2$SQ = 3,5-di-*ter*t-butyl-1,2-benzosemiquinone) and the monoruthenium complex [Ru($t$$Bu_2$SQ) (DMSO) (trpy)]($PF_6$) ([**5**]($PF_6$), trpy = 2,2’:6’,2”-terpyridine) were also synthesized. The CV of $[\mathbf{2}]^{2+}$ suggests possible electronic interaction between the two Pt(trpy) groups, whereas such an electronic interaction was not suggested by the CV of $[\mathbf{4}]^{2+}$ between Pt(trpy) and Ru($t$$Bu_2$SQ) frameworks.

VIII-A-4 Immobilization of a High-Valent Rhenium Complex on an Indium-Doped Tin-Oxide Electrode: Enhanced Catalytic Activity of a *trans*-Dioxorhenium(V) Complex in Electrochemical Oxidation of Alcohols

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[*Eur. J. Inorg. Chem.* 4550–4553 (2004)]

A high-valent trans-dioxorhenium(V) complex containing pyridine ligands was successfully immobilized on an ITO (indium-doped tin-oxide) electrode. The complex formed a monolayer structure on the electrode surface and promoted electrochemical catalytic oxidation of 1-phenylethanol to acetophenone in CH_2Cl_2. Oxidation hardly occurred in CH_2Cl_2 solution containing the free rhenium(V) complex. Immobilization of other high-valent metal complexes will present opportunities for design of functional electrodes with high activities.

VIII-A-5 Synthesis, Chemical- and Electrochemical Properties of Ruthenium(II) Complexes Bearing 2,6-Bis(2-naphthyridyl)pyridine

KOIZUMI, Take-aki; TANAKA, Koji

[*Inorg. Chim. Acta* **358**, 1999–2004 (2005)]

Ruthenium complexes with a terpyridine-analogous ligand, 2,6-bis(2-naphthyridyl)pyridine (**I**, bnp), were synthesized and their chem. and electrochemical properties studied. The structures of [Ru(bnp)(tpy)]$(PF_6)_2$ (**1**) and $[Ru(bnp)_2](PF_6)_2$ (**2**) were determined by x-ray structure analysis. The bnp localized redox potentials of **1** and **2** showed significant pos. shift by 260–290 mV relative to the analogous Ru-terpyridine complexes.

VIII-A-6 Synthesis, Structures and Electrochemical Properties of Ruthenium (II) Complexes Bearing Bidentate 1,8-Naphthyridine and Terpyridine Analogous (N,N,C)-Tridentate Ligands

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

[*J. Organomet. Chem.* **690**, 4272–4279 (2005)]

1,8-Naphthyridine (napy) and terpyridine-analogous (N,N,C) tridentate ligands coordinated ruthenium (II) complexes, [RuL(napy-*k*2 N,N’) (dmso)]$(PF_6)_2$ (**1**: L = L 1 = N”-methyl-4’-methylthio-2,2’:6’,4”-terpyridinium, **2**: L = L 2 = N”-methyl-4’-methylthio-2,2’: 6’,3”-terpyridinium) were prepared and their chem. and electrochemical properties were characterized. The structure of complex **1** was determined. by X-ray crystallographic study, showing that it has a distorted octahedral coordination style. The cyclic voltammogram of **1** in DMF exhibited two reversible ligand-localized redox couples. On the other hand, the CV of **2** shows two irreversible cathodic peaks, due to the Ru–C bond of **2** containing the carbenic character. The IR spectra of **1** in CO_2-satulated CH_3CN showed the formation of Ru-(η1-CO_2) and Ru-CO complexes under the controlled potential electrolysis of the solution at –1.44 V (*vs.* The electrochemical reduction of CO_2 catalyzed by **1** at

–1.54 V (*vs.* Fc/Fc^+) in DMF –0.1 M Me_4NBF_4 produced CO with a small amount of HCO_2H.

VIII-A-7 Synthesis and Electrochemical Properties of Bis(bipyridine)ruthenium(II) Complexes Bearing Pyridinyl- and Pyridinylidene Ligands Induced by Cyclometalation of N'-Methylated Bipyridinium Analogs

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

[*J. Organomet. Chem.* **690**, 1258–1264 (2005)]

Ruthenium cyclometalated complexes with *N*-monomethylated 2,4'- and 2,3'-bipyridine N,C-ligands were prepared and characterized. Reaction of [$(bpy)_2RuCl_2$] (bpy = 2,2'-bipyridine) with 1-methyl-4-(2-pyridinyl) pyridinium (HL1. PF_6) and 1-methyl-3-(2-pyridinyl)-pyridinium (HL_2. PF_6) hexafluorophosphates and $AgPF_6$ afforded cyclometalated complexes [$(bpy)_2$Ru(L1-C3, N')][PF_6]$_2$ (**1**) and carbenoid complex I (**2**), respectively. Structure of **2** was confirmed by low-field shift of the C4-carbon of the cyclometalated bipyridinium ligand and by x-ray structure determine. The ligand-localized redox potentials of **1** and **2** also revealed the substantial difference in the electron donating ability of both ligands.

VIII-A-8 Electronic Structural Changes Between Nickel(II)-Semiquinonato and Nickel(III)-Catecholato states Driven by Chemical and Physical Perturbation

OHTSU, Hideki; TANAKA, Koji

[*Chem. Eur. J.* **11**, 3420–3426 (2005)]

The selective synthesis of tetracoordinate square-planar low-spin nickel(II)-semiquinonato (NiII-SQ) and nickel(III)-catecholato (NiIII-Cat) complexes, [Ni(L)(SQ/CAT)](PF_6) (L = dibenzyl(2-pyridylmethyl)amine, SQ = 3,5-di-*tert*-butylsemiquinonate, CAT = 3,5-di-*tert*-butylcatecholate), **1** and **2**, respectively, was achieved by using bidentate ligands with modulated nitrogen-donor ability to the nickel ion. The electronic structures of **1** and **2** were revealed by XPS and EPR measurements. The absorption spectra of **1** and **2** in a non-coordinating solvent, dichloromethane (CH_2Cl_2), are completely different from those in THF, being a coordinating solvent. As expected the gradual addition of DMF, which is also a coordinating solvent like THF, into a solution of **1** or **2** in CH_2Cl_2 leads to color changes from blue (for **1**) and brown (for **2**) to light green, which is the same color observed for solutions of **1** or **2** in THF. Also, the same color changes are induced by varying the temp. Such spectral changes are attributable to the transformation from square-planar low-spin NiII-SQ and NiIII-Cat complexes to octahedral high-spin NiII-SQ ones, caused by the coordination of two solvent moleculars to the nickel ion.

VIII-A-9 Synthesis and Crystal Structures of [W(3,6-Dichloro-1,2-Benzenedithiolate)$_3$]$^{n-}$ (n = 1, 2) and [Mo(3,6-Dichloro-1,2-Benzenedithiolate)$_3$]$^{2-}$: Dependence of the Coordination Geometry on the Oxidation Number and Counter-Cation in Trigonal-Prismatic and Octahedral Structures

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[*Eur. J. Inorg. Chem.* 3088–3092 (2005)]

The novel complexes $(Et_4N)_2[W(bdtCl_2)_3]$ (**1a**), $(Ph_4P)_2[W(bdtCl_2)_3]$ (**1b**), $(Et_4N)[W(bdtCl_2)_3]$ (**2a**), $(Ph_4P)[W(bdtCl_2)_3]$ (**2b**), $(C_5NH_6)[W(bdtCl_2)_3]$ (**2c**), and $(Et_3NH)_2[Mo(bdtCl_2)_3]$ (**3a**) ($bdtCl_2$ = 3,6-dichloro-1,2-benzenedithiolate) were prepared and characterized by X-ray crystallography, UV/Vis spectroscopic, and electrochemical methods. Versatile geometrical changes around the tungsten centers were observed. The trigonal-prismatic structure of the tungsten center in $(Et_4N)_2[W(bdtCl_2)_3]$ (**1a**) is changed to an intermediate structure between trigonal prismatic and octahedral upon solid-state oxidation of the complex of $(Et_4N)[W(bdtCl_2)_3]$ (**2a**). Replacement of the counter-cation of $(Et_4N)_2[W(bdtCl_2)_3]$ (**1a**) with Ph_4P^+ also resulted in geometrical changes and somewhat of an octahedral contribution is included in $(Ph_4P)_2[W(bdtCl_2)_3]$ (**1b**). However, almost the same coordination structures are present in the series of structures $(Et_4N)[W(bdtCl_2)_3]$ (**2a**), $(Ph_4P)[W(bdtCl_2)_3]$ (**2b**), and $(C_5NH_6)[W(bdtCl_2)_3]$ (**2c**), with an oxidation no. of +5. These structures adopt an intermediate geometry between trigonal prismatic and octahedral. No geometrical change was observed upon changing the metal center from tungsten to molybdenum in $[M(bdtCl_2)_3]^{2-}$ (M = W and Mo).

VIII-A-10 Dioxo-Molybdenum(VI) and Mono-oxo-Molybdenum(IV) Complexes Supported by New Aliphatic Dithiolene Ligands: New Models with Weakened Mo=O Bond Characters for the Arsenite Oxidase Active Site

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[*Inorg. Chem.* **44**, 6386–6392 (2005)]

The *cis*-dioxo-molybdenum(VI) complexes, $[MoO_2(L(H))_2]^{2-}$ (**1b**), $[MoO_2(L(S))_2]^{2-}$ (**2b**), and $[MoO_2(L(O))_2]^{2-}$ (**3b**) (L(H) = cyclohexene-1,2-dithiolate, L(S) = 2,3-dihydro-2H-thiopyran-4,5-dithiolate, and L(O) = 2,3-dihydro-2H-pyran-4,5-dithiolate), with new aliphatic dithiolene ligands were prepared and investigated by infrared (IR) and UV-vis spectroscopic and electrochemical methods. The mono-oxo-molybdenum(IV) complexes, $[MoO(L(H))_2]^{2-}$ (**1a**), $[MoO(L(S))_2]^{2-}$ (**2a**), and $[MoO(L(O))_2]^{2-}$ (**3a**), were further characterized by X-ray crystal structural determinations. The IR and resonance Raman spectroscopic studies suggested that these *cis*-dioxo molybdenum(VI) complexes (**1b-3b**) had weaker Mo=O bonds than the common Mo(VI)O_2 complexes. Complexes **1b-3b** also exhibited strong absorption bands in the visible regions assigned as charge-transfer bands from the dithiolene ligands to the *cis*-MoO_2 cores. Because the oxygen atoms of the *cis*-Mo(VI)O_2 cores are relatively nucleophilic, these complexes were unstable in protic solvents and protonation might occur to produce Mo(VI)O(OH), as observed with the oxidized state of arsenite oxidase.

VIII-A-11 Electrochemical Hydrogenation of $[Ru(bpy)_2(napy\text{-}kN)(CO)]^{2+}$: Inhibition of Reductive Ru–CO Bond Cleavage by a Ruthenacycle

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

[*Angew. Chem., Int. Ed.* **44**, 2229–2232 (2005)]

A 5-membered metallacycle (2+) hydrogenated at the 4-position of the naphthyridine ligand results from the reduction of $[Ru(bpy)_2(napy\text{-}kN)(CO)]^{2+}$ ($\mathbf{1}^{2+}$; bpy = 2,2’-bipyridine, napy = 1,8-naphthyridine) at –1.40 V in H_2O. Chemical or electrochemical oxidation of 2+ regenerates 1+ in almost quantitative yield.

VIII-A-12 Stabilization and Destabilization of the Ru–CO Bond During the 2,2’-Bipyridin-6-onato (bpyO)-Localized Redox Reaction of $[Ru(terpy)(bpyO)(CO)](PF_6)$

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

[*Eur. J. Inorg. Chem.* 285–293 (2005)]

Two stereoisomers of $[Ru(terpy)(bpyO)(CO)](PF_6)$ ($[\mathbf{1}]^+$ and $[\mathbf{2}]^+$; terpy = 2,2’:6’,2”-terpyridine, bpyO = 2,2’-bipyridin-6-onato) were prepared. The pyridonato moiety in the bpyO ligand of $[\mathbf{1}]^+$ and $[\mathbf{2}]^+$ is located trans and *cis*, respectively, to CO. Treatment of $[\mathbf{1}]^+$ and $[\mathbf{2}]^+$ with HPF_6 produced $[1H]^{2+}$ and $[2H]^{2+}$, both of which contain bpyOH (bpyOH = 6-hydroxy-2,2’-bipyridine). The difference in the pK_a values of $[1H]^{2+}$ (3.5) and $[2H]^{2+}$ (3.9) reflects the stronger electronic interaction between CO and the pyridonato moiety in the bpyO ligand in the trans position compared with that in the cis position. The molecular structures of $[\mathbf{1}](PF_6)$, $[\mathbf{2}](PF_6)H_2O$ and $[2H](PF_6)_22H_2O$ were detd. by x-ray structure analyses. $[\mathbf{1}]^+$ and $[\mathbf{2}]^+$ undergo one, reversible reduction at $E_{1/2}$ = –1.65 V and –1.51 V, respectively, and one irreversible reduction at $E_{p,c}$ = –2.07 and $E_{p,c}$ = –2.13 V, respectively. Both reductions are assigned to redox reactions localized at the terpy and bpyO ligands. Irreversible reduction of $[\mathbf{1}]^0$ results from reductive cleavage of the Ru–CO bond of $[\mathbf{1}]^-$. However, a two-electron oxidation of $[\mathbf{2}]^-$ almost regenerates $[\mathbf{2}]^+$ because of the depression of the reductive Ru–CO bond cleavage of $[\mathbf{2}]^-$ due to cyclometalation formed by an attack of O of bpyO to the C of the Ru–CO bond. An unusually large shift of the ν(C≡O) band on going from $[\mathbf{2}]^0$ (1950 cm^{-1}) to $[\mathbf{2}]^-$ (1587 cm^{-1}) also supports a reversible cyclometalation driven by the bpyO-localized redox reaction.