

RESEARCH ACTIVITIES VIII

Coordination Chemistry Laboratories

Prof. Youichi Ishii (Chuo 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 CO₂ and Oxidation of Organic Molecules Aiming at Energy Conversion between Chemical Energy and Electricity

Electro- and photochemical reduction of CO₂ 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 -CO₂ adducts by the reaction with coordinatively unsaturated low-valent metal complexes. Metal complexes with η^1 -CO₂ 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 CO₂ 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 CO₂, 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-OH₂ 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}(NH₃)(sq)(trpy)](ClO₄) (**1**, sq = 3,5-di-tert-butyl-1,2-benzosemiquinone, trpy = 2,2':6',2''-terpyridine) and [Ru^{III}(NH₃)(sq)(trpy)](ClO₄)₂ (**2**), were prepared. **2** is quantitatively reduced to **1** in CH₃OH 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 CH₂Cl₂. Both **1** and **2** lose the catalytic activity toward the oxidation of alcohols when the NH₃ ligand of the complexes was replaced by CH₃O⁻ 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*Buacac)](PF₆) (**1**) and [Ni(MePy(Bz)₂)(*t*Buacac)](PF₆) (**2**) have been synthesized. In addition, the corresponding high-spin nickel(II) complexes having a nitrate ion, [Ni(Py(Bz)₂)(*t*Buacac)(NO₃)] (**3**) and [Ni(MePy(Bz)₂)(*t*Buacac)(NO₃)] (**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 $\text{MePy}(\text{Bz})_2$ ligand in **2**, which weakens the Ni-N (pyridine) bond length compared with that of the non-substituted $\text{Py}(\text{Bz})_2$ ligand in **1**.

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

OKAMURA, Rei; WADA, Tohru; AIKAWA, Katsuji; NAGATA, Toshi; TANAKA, Koji

[*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-diboric acid. The reaction of btpyxa with either 1 equiv or an excess of $\text{PtCl}_2(\text{cod})$ (cod = 1,5-cyclooctadiene) followed by anion exchange afforded mono- and dinuclear platinum complexes $[(\text{PtCl})(\text{btpyxa})](\text{PF}_6)$ (**[1]**(PF_6)) and $[(\text{PtCl})_2(\text{btpyxa})](\text{PF}_6)_2$ (**[2]**(PF_6)₂), respectively. The x-ray crystallography of **[1]**(PF_6)-CHCl₃ revealed that the two terpyridine units in the ligand are nearly parallel to each other. Heterodinuclear $[(\text{PtCl})\{\text{Ru}(t\text{Bu}_2\text{SQ})(\text{DMSO})\}(\text{btpyxa})](\text{PF}_6)_2$ (**[4]** (PF_6)₂, $t\text{Bu}_2\text{SQ}$ = 3,5-di-*tert*-butyl-1,2-benzosemiquinone) and the monoruthenium complex $[\text{Ru}(t\text{Bu}_2\text{SQ})(\text{DMSO})(\text{trpy})](\text{PF}_6)$ (**[5]**(PF_6), trpy = 2,2':6',2''-terpyridine) were also synthesized. The CV of **[2]**²⁺ suggests possible electronic interaction between the two Pt(trpy) groups, whereas such an electronic interaction was not suggested by the CV of **[4]**²⁺ between Pt(trpy) and Ru($t\text{Bu}_2\text{SQ}$) 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

SUGIMOTO, Hideki¹; TSUKUBE, Hiroshi¹;

TANAKA, Koji
(¹Osaka City Univ.)

[*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 $[\text{Ru}(\text{bnp})(\text{tpy})](\text{PF}_6)_2$ (**1**) and $[\text{Ru}(\text{bnp})_2](\text{PF}_6)_2$ (**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, $[\text{RuL}(\text{napy-k2 N,N}')(\text{dmsO})](\text{PF}_6)_2$ (**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 CO₂-saturated CH₃CN showed the formation of Ru-($\eta^1\text{-CO}_2$) and Ru-CO complexes under the controlled potential electrolysis of the solution at –1.44 V (vs. The electrochemical reduction of CO₂ catalyzed by **1** at

–1.54 V (vs. Fc/Fc⁺) in DMF –0.1 M Me₄NBF₄ produced CO with a small amount of HCO₂H.

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*-mono-methylated 2,4'- and 2,3'-bipyridine N,C-ligands were prepared and characterized. Reaction of [(bpy)₂RuCl₂] (bpy = 2,2'-bipyridine) with 1-methyl-4-(2-pyridinyl)pyridinium (HL1, PF₆) and 1-methyl-3-(2-pyridinyl)pyridinium (HL2, PF₆) hexafluorophosphates and AgPF₆ afforded cyclometalated complexes [(bpy)₂Ru(L1-C3, N')][PF₆]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)](PF₆) (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 (CH₂Cl₂), 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 CH₂Cl₂ 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 molecules 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

SUGIMOTO, Hideki¹; FURUKAWA, Yuuki¹; TARUMIZU, Makoto¹; MIYAKE, Hiroyuki¹; TANAKA, Koji; TSUKUBE, Hiroshi¹
(¹Osaka City Univ.)

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

The novel complexes (Et₄N)₂[W(bdtCl₂)₃] (**1a**), (Ph₄P)₂[W(bdtCl₂)₃] (**1b**), (Et₄N)[W(bdtCl₂)₃] (**2a**), (Ph₄P)[W(bdtCl₂)₃] (**2b**), (C₅NH₆)[W(bdtCl₂)₃] (**2c**), and (Et₃NH)₂[Mo(bdtCl₂)₃] (**3a**) (bdtCl₂ = 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 (Et₄N)₂[W(bdtCl₂)₃] (**1a**) is changed to an intermediate structure between trigonal prismatic and octahedral upon solid-state oxidation of the complex of (Et₄N)[W(bdtCl₂)₃] (**2a**). Replacement of the counter-cation of (Et₄N)₂[W(bdtCl₂)₃] (**1a**) with Ph₄P⁺ also resulted in geometrical changes and somewhat of an octahedral contribution is included in (Ph₄P)₂[W(bdtCl₂)₃] (**1b**). However, almost the same coordination structures are present in the series of structures (Et₄N)[W(bdtCl₂)₃] (**2a**), (Ph₄P)[W(bdtCl₂)₃] (**2b**), and (C₅NH₆)[W(bdtCl₂)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(bdtCl₂)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

SUGIMOTO, Hideki¹; HARIHARA, Makoto¹; SHIRO, Motoo¹; SUGIMOTO, Kunihiisa¹; TANAKA, Koji; MIYAKE, Hiroyuki¹; TSUKUBE, Hiroshi¹
(¹Osaka City Univ.)

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

The *cis*-dioxo-molybdenum(VI) complexes, [MoO₂(L(H))₂]²⁻ (**1b**), [MoO₂(L(S))₂]²⁻ (**2b**), and [MoO₂(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)O₂ 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*-MoO₂ cores. Because the oxygen atoms of the *cis*-Mo(VI)O₂ 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.

unusually large shift of the $\nu(\text{C}\equiv\text{O})$ band on going from [2]⁰ (1950 cm⁻¹) to [2]⁻ (1587 cm⁻¹) also supports a reversible cyclometalation driven by the bpyO-localized redox reaction.

VIII-A-11 Electrochemical Hydrogenation of [Ru(bpy)₂(napy-*k*N)(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-*k*N)(CO)]²⁺ (**1**²⁺; bpy = 2,2'-bipyridine, napy = 1,8-naphthyridine) at -1.40 V in H₂O. 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)](PF₆)

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

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

Two stereoisomers of [Ru(terpy)(bpyO)(CO)](PF₆) ([**1**]⁺ and [**2**]⁺; terpy = 2,2':6',2''-terpyridine, bpyO = 2,2'-bipyridin-6-onato) were prepared. The pyridonato moiety in the bpyO ligand of [**1**]⁺ and [**2**]⁺ is located *trans* and *cis*, respectively, to CO. Treatment of [**1**]⁺ and [**2**]⁺ with HPF₆ produced [1H]²⁺ and [2H]²⁺, both of which contain bpyOH (bpyOH = 6-hydroxy-2,2'-bipyridine). The difference in the p*K*_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 [**1**](PF₆), [**2**](PF₆)H₂O and [2H](PF₆)₂2H₂O were detd. by x-ray structure analyses. [**1**]⁺ and [**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 [**1**]⁰ results from reductive cleavage of the Ru–CO bond of [**1**]⁻. However, a two-electron oxidation of [**2**]⁻ almost regenerates [**2**]⁺ because of the depression of the reductive Ru–CO bond cleavage of [**2**]⁻ due to cyclometalation formed by an attack of O of bpyO to the C of the Ru–CO bond. An

VIII-B Coordination Chemistry of Sterically Hindered Ligands and Multidentate Ligands, and Activation of Small Molecules

This project is focused on the design and synthesis of new ligands that are capable of supporting novel structural features and reactivity. Currently, we are investigating multidentate ligands based on aryloxy, thiolate, and amidinate. In addition, we set out to study metal complexes with sterically hindered arylthiolate ligands. Our recent efforts have been directed toward activation of small molecules.

VIII-B-1 Synthesis of a Vanadium(III) Tris(arylthiolato) Complex and Its Reactions with Azide and Azo Compounds; Formation of a Sulfenamide Complex *via* Cleavage of an Azo N=N Bond

KOMURO, Takashi; MATSUO, Tsukasa;
KAWAGUCHI, Hiroyuki

[*Inorg. Chem.* **44**, 175–177 (2005)]

Thiolate complexes continue to attract considerable attention due to their unique chemical properties and structural diversity. Since thiolate groups meet the electronic and steric requirements necessary to stabilize a wide variety of metal complexes, they have been used as auxiliary ligands. On the other hand, thiolate complexes are known to undergo chemistry at the sulfur center, including oxidation/reduction and protonation/deprotonation, a complement to traditional chemistry for these complexes centered on the metal. In this study, we report the synthesis of a mononuclear vanadium(III) complex having the $[\text{SC}_6\text{H}_3\text{-2,6-(SiMe}_3)_2]^- (= [\text{SAr}]^-)$ ligands.

The tris(arylthiolate) vanadium(III) complex (**1**) has been synthesized in good yield. This complex is found to undergo CH activation across a V–S bond in the presence of TMEDA to give a cyclometalated species along with free arylthiol. Complex **1** behaves as a two-electron reductant toward Ad-N_3 , yielding an imide complex. Treatment of **1** with azobenzene produces an imide-sulfenamide compound, in which an azo N=N bond cleavage takes place concomitant with formation of a V=N and an S–N bond. These results suggest that the reaction proceeds through a cooperative activation sequence involving both vanadium and sulfur centers.

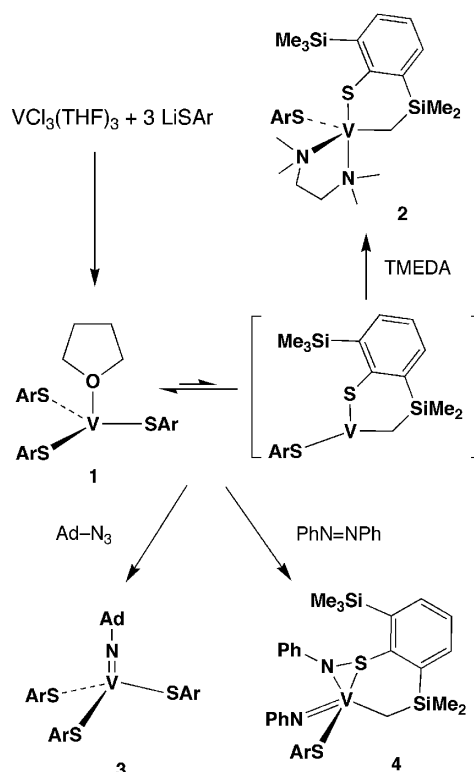


Figure 1.

VIII-B-2 Titanium and Zirconium Complexes of Preorganized Tripodal Triaryloxy Ligands

AKAGI, Fumio; MATSUO, Tsukasa;
KAWAGUCHI, Hiroyuki

[*J. Am. Chem. Soc.* **127**, 11936–11937 (2005)]

Multidentate ligands play an important role in coordination chemistry and catalyst design. An attractive multidentate ligand is a trianionic tetradentate ligand of the tripodal $[\text{X}_3\text{E}]$ type ($\text{X} = \text{N}, \text{O}, \text{S}$; $\text{E} = \text{N}, \text{P}$), which had led to atrane molecules with unique structures and patterns of reactivity. The degree of interaction between the metal center and the neutral E atom can exert a profound influence on the reactivity of the resulting complexes. In this context, a tri(2-oxyphenyl)methane-derived system $[\text{O}_3]^{3-}$ appears practically attractive. This ligand can coordinate to a metal in two forms, which differ mainly as a result of the relative stereochemistry at the methine carbon. Furthermore, intramolecular metalation of the somewhat acidic methine linkage in the $[\text{O}_3]$ complexes is expected to occur quite readily, resulting in formation of 5-carbametalatranes

([O₃C] complexes). In this study, tri(2-oxy-3,5-di-*tert*-butylphenyl)methane has been used to prepare titanium and zirconium complexes of the general formula [O₃]MX (M = Ti, X = NEt₂, Cl, CH₂Ph; M = Zr, X = CH₂Ph). The tripodal [O₃] ligand in titanium complexes adopt the *syn*- and the *anti*-conformation, while the *syn* complex of zirconium undergoes facile C–H activation to give a 5-carbametalatrane [O₃C]Zr(THF)₃. Reactivity studies with these group 4 metal complexes are ongoing.

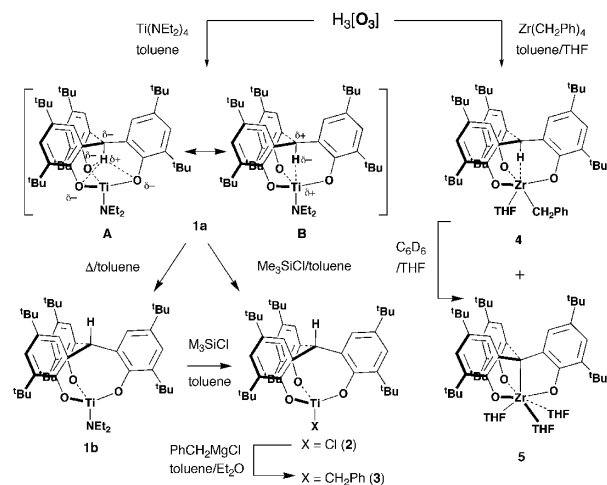


Figure 1.

VIII-C Preparation and Properties of the Homo- and Heterometallic Clusters

This project focuses on the development of a systematic synthetic route to a series of the homo- and heterometallic clusters as templates or catalysts for new types of activation and transformation of organic, inorganic, and organometallic molecules at the well-defined multimetallic reaction sites. Especially, preparation and reactivity of dinuclear Ru(II) complexes having the bridging amido, imido, and alkoxido ligands has been extensively studied.

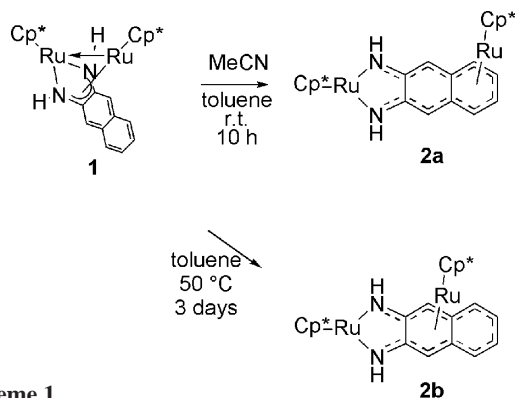
VIII-C-1 A Dinuclear Ru(II) κ^2 -Diamido/ η^6 -Naphthalene Complex Featuring a Coordinatively Unsaturated Yet Highly p-Basic (η^5 -C₅Me₅)Ru Diamide Fragment

TAKEMOTO, Shin¹; OSHIO, Shinya¹; SHIROMOTO, Takayuki¹; MATSUZAKA, Hiroyuki²

(¹Osaka Pref. Univ.; ²IMS and Osaka Pref. Univ.)

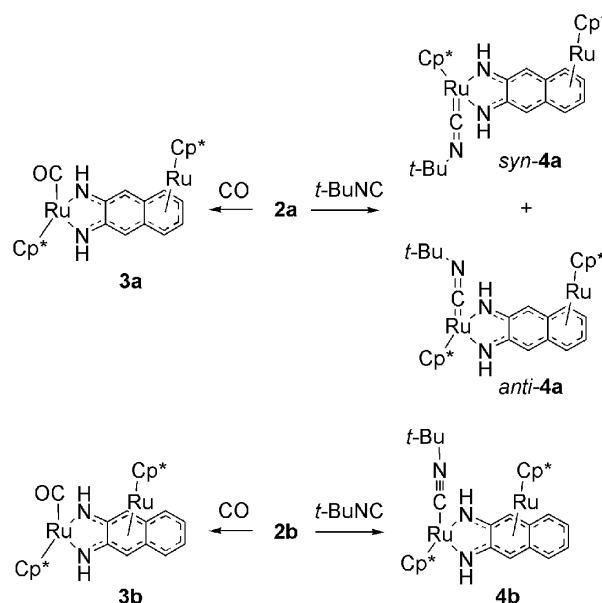
[*Organometallics* **24**, 801–804 (2005)]

Acetonitrile induced a clean isomerization of the amido-bridged diruthenium complex [(Cp*₂Ru)₂{ μ_2 - κ^2 : η^4 -2,3-naphthalenediamido}] (**1**) into a κ^2 : η^6 -bonded dinuclear complex [Cp*₂Ru{ μ_2 - κ^2 : η^6 -2,3-naphthalenediamido}RuCp*] (**2a**) featuring a coordinatively unsaturated Cp*₂Ru terminal diamide fragment. Isomerization of **1** also took place on heating a solution of **1** in hexanes, toluene, or toluene-acetone at 50 °C to give another isomer **2b** selectively, in which the {Cp*₂Ru}⁺ fragment is bound to the inner ring of the naphthalene moiety.



Scheme 1.

Structural and spectroscopic data of its carbon monoxide or *tert*-butyl isocyanide adducts indicated that the Cp*₂Ru diamide fragment can serve as a strong π -base.



Scheme 2.

VIII-C-2 Dinuclear Ruthenium(II) Catecholato and 2,3-Naphthalenediolato Complexes Featuring κ^2 -Diaryloxo/ η^6 -Arene Coordination Mode

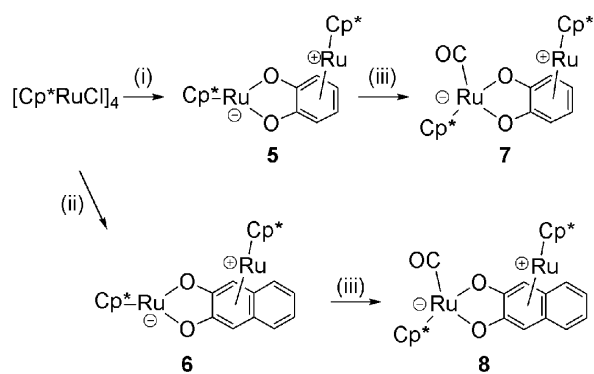
TAKEMOTO, Shin¹; OGURA, Shin-ichiro¹; KAMIKAWA, Ken¹; MATSUZAKA, Hiroyuki²

(¹Osaka Pref. Univ.; ²IMS and Osaka Pref. Univ.)

[*Inorg. Chim. Acta* in press]

A new dinuclear ruthenium(II) catecholato complex [Cp*₂Ru(κ^2 : η^6 - μ_2 -1,2-O₂C₆H₄)RuCp*] (**5**; Cp* = η^5 -C₅Me₅) has been prepared by the reaction of [Cp*₂RuCl]₄ with 2 equiv of disodium catecholato in THF. Complex **5** has a dinuclear structure, in which one of the Cp*₂Ru fragments is κ^2 -bonded to the two oxygen atoms and the other is η^6 -bonded to the aromatic ring. Similar treatment of [Cp*₂RuCl]₄ with disodium 2,3-naphthalenediolato affords an analogous κ^2 : η^6 -bonded dinuclear complex [Cp*₂Ru(κ^2 : η^6 - μ_2 -2,3-O₂C₁₀H₆)RuCp*] (**6**) with selective π -complexation at the oxygen-substituted naphthalene ring. The molecular structure of **6** has been determined by X-ray crystallography. The oxygen-bound ruthenium atoms in complexes **5** and **6** are coordinatively unsaturated and readily uptake 1 equiv of carbon monoxide to give the corresponding carbonyl adducts [Cp*₂Ru(CO)(κ^2 : η^6 - μ_2 -1,2-O₂C₆H₄)RuCp*] (**7**)

and $[\text{Cp}^*\text{Ru}(\text{CO})(\kappa^2:\eta^6\text{-}\mu_2\text{-}2,3\text{-O}_2\text{C}_{10}\text{H}_6)\text{RuCp}^*]$ (**8**), respectively.



Scheme 1. Preparation of Complexes. (i) $\text{Na}_2[1,2\text{-O}_2\text{C}_6\text{H}_4]$, (ii) $\text{Na}_2[2,3\text{-O}_2\text{C}_{10}\text{H}_6]$, (iii) CO (1 atm).

VIII-D Modification of Myoglobin by Replacing the Native Heme with Metalloporphyrinoids

Functionalization of hemoproteins is one of the attractive subjects for creating a new biomaterial. Recently, we have prepared various artificial prosthetic groups and inserted them into apomyoglobin to obtain reconstituted myoglobins. For example, iron porphycene, a structural isomer of iron porphyrin, is a unique prosthetic group to modulate the myoglobin function, since the Lewis acidity of iron atom in the porphycene framework could be strong, and the dz^2 orbital level of the iron atom is stabilized due to the decrease of the macrocycle symmetry compared to porphyrin framework. The physicochemical properties of iron porphycene suggest that the replacement of the native heme in myoglobin with metalloporphycene will improve or convert the myoglobin function. From this project, it is found that the reconstitution of myoglobin with an artificial prosthetic group serves as a new way to create a functionalized hemoprotein.

VIII-D-1 Ligand Binding Properties of Myoglobin Reconstituted with Iron Porphycene: Unusual O₂ Binding Selectivity against CO Binding

MATSUO, Takashi¹; DEJIMA, Hirohisa²; HIROTA, Shun³; MURATA, Dai²; SATO, Hideaki²; IKEGAMI, Takahiro²; HORI, Hiroshi¹; HISAEDA, Yoshio²; HAYASHI, Takashi⁴
(¹Osaka Univ.; ²Kyushu Univ.; ³Kyoto Pharm. Univ.; ⁴IMS and Osaka Univ.)

[*J. Am. Chem. Soc.* **126**, 16007–16017 (2004)]

Sperm whale myoglobin, an oxygen storage hemoprotein, was successfully reconstituted with the iron porphycene having two propionates, 2,7-diethyl-3,6,12,17-tetramethyl-13,16-bis(carboxyethyl)porphycenato-iron. The physicochemical properties and ligand binding events of the reconstituted myoglobin were investigated. The ferric reconstituted myoglobin shows the remarkable stability against acid denaturation and only a low-spin characteristic in its EPR spectrum. The Fe(III)/Fe(II) redox potential (–190 mV vs. NHE) determined by the spectroelectrochemical measurements was much lower than that of the wild-type. These results can be attributed to the strong coordination of His93 to the porphycene iron, which is induced by the nature of the porphycene ring symmetry. The O₂ affinity of the ferrous reconstituted myoglobin is higher by 2,600-fold than that of the wild-type, mainly due to the decrease in the O₂ dissociation rate, whereas the CO affinity is not so significantly enhanced. As a result, the O₂ affinity of the reconstituted myoglobin exceeds its CO affinity ($M' = K_{CO}/K_{O_2} < 1$). The ligand binding studies on H64A mutant support the fact that the slow O₂ dissociation of the reconstituted myoglobin is primarily caused by the stabilization of the Fe–O₂ σ -bonding. The high O₂ affinity and the unique characteristics of the myoglobin with the iron porphycene indicate that the reconstitution with a synthesized heme is a useful method not only to understand the physiological function of myoglobin but also to create a tailor-made function on the protein.

VIII-D-2 Unusual Ligand Discrimination by a Myoglobin Reconstituted with a Hydrophobic Domain-Linked Heme

SATO, Hideaki¹; WATANABE, Masahito¹; HISAEDA, Yoshio¹; HAYASHI, Takashi²
(¹Kyushu Univ.; ²IMS and Osaka Univ.)

[*J. Am. Chem. Soc.* **127**, 56–57 (2005)]

New reconstituted horse heart myoglobins possessing a hydrophobic domain at the terminal of the two heme-propionate side chains were constructed. The O₂ and CO bindings for the reconstituted deoxymyoglobins were examined in detail by laser flash photolysis and stopped-flow rapid mixing techniques. The artificially created domain worked as a barrier against exogenous ligand penetration into the heme pocket, whereas the bound O₂ was stabilized in the reconstituted myoglobin as well as in the native one. In contrast, the CO dissociation rate constant for the reconstituted myoglobin increased by 20-fold compared to the native protein, suggesting that the incorporation of the hydrophobic domain onto the heme pocket perturbs the distal site structure of the reconstituted myoglobin. As a result, the substantial ligand selectivity for the reconstituted myoglobin significantly increases in favor of O₂ over CO with the M' value ($= K_{CO}/K_{O_2}$) of 0.88. The present work concludes that the O₂ selectivity of myoglobin over CO is markedly improved by chemically modifying the heme-propionates without any mutation of the amino acid residues in the distal site.

VIII-D-3 Enhancement of Peroxidase Activity of Myoglobin Reconstituted with Iron Porphycene: Compound III Formation due to the Reaction of Ferric Myoglobin with Hydrogen Peroxide

HAYASHI, Takashi¹; MURATA, Dai²; MATSUO, Takashi²; SATO, Hideaki³; HISAEDA, Yoshio³
(¹IMS and Osaka Univ.; ²Osaka Univ.; ³Kyushu Univ.)

[*Angew. Chem., Int. Ed.* submitted]

The replacement of native heme with an artificially created metal complex is one of the attractive studies in a series of hemoprotein modifications. However, the number of studies that demonstrate the conversion of myoglobin to peroxidase using the reconstitution by non-native prosthetic group have been quite limited. To enhance the peroxidase activity of myoglobin, we

focused on iron porphycene as a structural isomer of iron porphyrin. Reconstituted myoglobin with 2,7-diethyl-3,6,12,17-tetramethyl-13,16-dicarboxyethyl-porphycenatoiron(III) accelerated the H_2O_2 -dependent oxidation of substrates such as guaiacol, thioanisole, and styrene. At pH 7.0, and 20 °C, the initial rate of the guaiacol oxidation is 10-fold faster than that observed for native myoglobin. This finding clearly suggests that the replacement of native heme with iron porphycene enhances the peroxidase activity. In addition, the guaiacol oxidation catalyzed by the reconstituted myoglobin was accelerated at the higher pH values. Moreover, the stopped-flow technique demonstrated that two reaction intermediates, the compound II-like species and compound III, formed from compound II with the excess amounts of H_2O_2 , were detected in the absence of a substrate. It is the first example that compound III is formed *via* compound II in myoglobin chemistry. The enhancement of peroxidase activity and the formation of the stable compound III in myoglobin with iron porphycene could be due to the strong coordination of the Fe–His93 bond.

VIII-D-4 Preparation and O_2 Binding Study of Myoglobin Having a Cobalt Porphycene

MATSUO, Takashi¹; TSURUTA, Takashi²; MAEHARA, Keiko²; SATO, Hideaki²; HISAEDA, Yoshio²; HAYASHI, Takashi³

(¹Osaka Univ.; ²Kyushu Univ.; ³IMS and Osaka Univ.)

[*Inorg. Chem.* **44**, 9391–9396 (2005)]

Sperm whale myoglobin, an oxygen-storage hemo-protein, was reconstituted with 2,7-diethyl-3,6,12,17-tetramethyl-13,16-bis(carboxyethyl)porphycenato-cobalt(II) in order to investigate the reactivity of a cobalt porphycene in a protein matrix. Similar to the previously reported finding for the myoglobin with the iron porphycene, the reconstituted myoglobin with the cobalt porphycene was also found to have a higher O_2 affinity by two orders of magnitude when compared to the myoglobin possessing cobalt protoporphyrin IX. The EPR spectra of the deoxy and oxy myoglobins having the cobalt porphycene at 77 K also have similar features to the myoglobin with cobalt protoporphyrin IX. These spectra suggest that the porphycene cobalt in the deoxy form is coordinated by one nitrogenous ligand postulated to be the imidazole ring of His93, and that the bond configuration of $\text{Co}^{\text{II}}\text{--O}_2$ is regarded as the $\text{Co}^{\text{III}}\text{--O}_2^{\bullet-}$ species.

VIII-E Synthesis of Transition Metal Complexes Containing a Novel Metal-Silicon and Metal-Gallium Bonding

Synthesis of transition metal complexes with unprecedented bonds between a metal and a heavy main group element is one of current topics on inorganic chemistry. In this project, we have investigated the synthesis, structure, and reactivities of metal complexes containing organosilicon and -gallium ligands. We also synthesized a cofacial dimanganese complex, which shows catalytic activity for asymmetric oxidation of sulfides.

VIII-E-1 Synthesis of a Cofacial Schiff-Base Dimanganese(III) Complex for Asymmetric Catalytic Oxidation of Sulfides

HIROTSU, Masakazu¹; OHNO, Naoki²;
NAKAJIMA, Takashi²; UENO, Keiji³
(¹Gunma Univ. and Osaka City Univ.; ²Gunma Univ.;
³IMS and Gunma Univ.)

[*Chem. Lett.* **34**, 848–849 (2005)]

Asymmetric oxidation of sulfides is a key reaction for synthesis of biologically active compounds with chiral sulfoxide centers. It has been reported that optically active salen-type Schiff base manganese(III) complexes are efficient catalysts for the asymmetric oxidation of sulfides. However, the enantioselectivity is not high enough for synthetic applications. Design of chiral macrocyclic dinuclear complexes would be a good approach to efficient asymmetric catalysts, because two metal centers are expected to behave cooperatively as an enantioselective Lewis acid center to catch a sulfide and an active oxidation site upon sulfoxidation, respectively. Among macrocyclic Schiff base complexes, face-to-face salen-type complex dimers have been limited to a few systems. In this work, we report a new catalyst, optically active Schiff base manganese(III) complex dimer **1** (Figure 1). The two Schiff base manganese(III) units in **1** are doubly bridged by two 9,9-dimethylxanthenediyl spacers to form a cofacial structure. The dimanganese complex catalyzed the asymmetric oxidation of methyl phenyl sulfide by iodosobenzene.

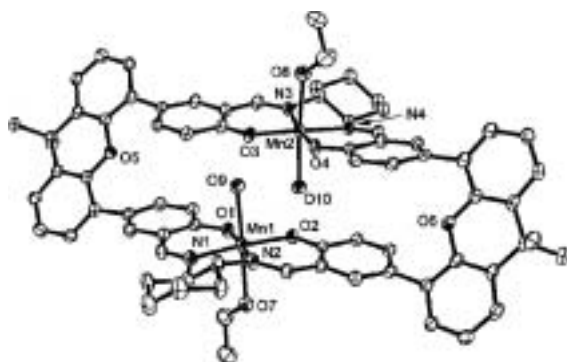


Figure 1. Molecular Structure of Dimanganese Complex 1.

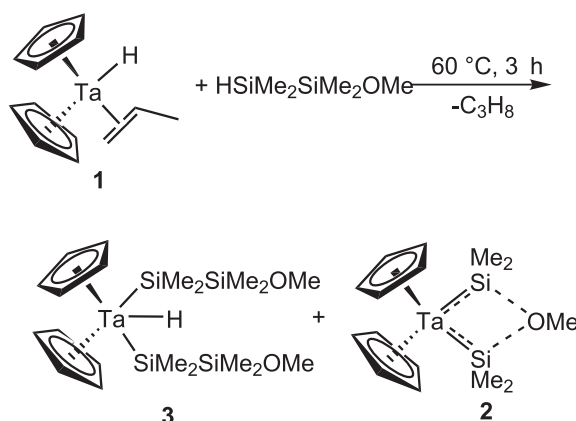
VIII-E-2 Synthesis and Structure of a Base-Stabilized Silyl(silylene)tantalum Complex

KOSHIKAWA, Hidenori¹; OKAZAKI, Masaaki²;
MATSUMOTO, Shun-ichi¹; UENO, Keiji³;

TOBITA, Hiromi¹; OGINO, Hiroshi⁴
(¹Tohoku Univ.; ²Kyoto Univ.; ³IMS and Gunma Univ.;
⁴Univ. Air)

[*Chem. Lett.* in press]

Over the past few decades, transition-metal silylene complexes with metal–silicon double bonds have attracted much interest as silicon analogues of carbene complexes, and as possible intermediates in various transformation reactions of organosilicon compounds. Until now, a wide variety of silylene complexes has been synthesized as not only a base-stabilized form but also a base-free form. To our best knowledge, all these examples are Fischer-type ones, in which the metal–silicon bond is polarized in a $M^{\delta-}-Si^{\delta+}$ manner. Theoretical studies on early transition metal–silylene complexes revealed that the Schrock-type metal–silylene complex $L_nNb=SiR_2$ is more stable than the Fischer-type $L_nM=SiR_2$ ($M = Fe, Cr$), although silylene complexes of group 5 transition metals have not been prepared yet. We herein report the synthesis and structure of methoxy-bridged silyl(silylene)tantalum complex. Thermal reaction of $Cp_2Ta(\eta^2-C_3H_6)$ (**1**) with $HSiMe_2SiMe_2OMe$ in toluene at 60 °C gave $Cp_2Ta\{SiMe_2\cdots O(Me)\cdots SiMe_2\}$ (**2**) (7%) and $Cp_2TaH(SiMe_2SiMe_2OMe)_2$ (**3**) (8%). The former methoxy-stabilized silyl(silylene) complex was characterized by X-ray diffraction study.



VIII-E-3 Synthesis and Structures of the First Titanium(IV) Complexes with Cyclic Tetrasiloxide Ligands: Incomplete and Complete Cage Titanosiloxanes

HIROTSU, Masakazu¹; TARUNO, Shinsuke²;
YOSHIMURA, Takashi²; UENO, Keiji³

(¹Gunma Univ. and Osaka City Univ.; ²Gunma Univ.;
³IMS and Gunma Univ.)

[Submitted for publication]

Group 4 metal complexes immobilized on silica surfaces are industrially and commercially important catalysts. However, the improvement of the catalysts is hindered by the complicated surface structures, making the reaction processes unclear. Several types of siloxido complexes have been synthesized using mono-, di-, and trisiloxido ligands, which can be considered as model compounds for the heterogeneous catalysts. Cyclic tetrasiloxido ligands are also potentially useful as a silica surface model but few complexes with such ligands have been reported so far. Here we report the first titanium(IV) complexes with cyclic tetrasiloxido ligands, $[\text{Ti}(\text{L}^1\text{H})(\text{OSiMe}_3)]_2(\text{H}_2\text{O})$ (**1**) and $(\text{CpTiCl})_4(\text{L}^2)_2$ (**2**), which were synthesized using the all-*cis* isomer of cyclotetrasiloxanetetraols $\text{R}_4(\text{SiO})_4(\text{OH})_4$ (L^1H_4 : $\text{R} = \text{Ph}$, L^2H_4 : $\text{R} = i\text{Pr}$) as ligand precursors. X-ray analysis revealed that **1** is a binuclear complex with bridging siloxy and aqua ligands while **2** has a tetranuclear cage structure capped by two L^2 ligands.

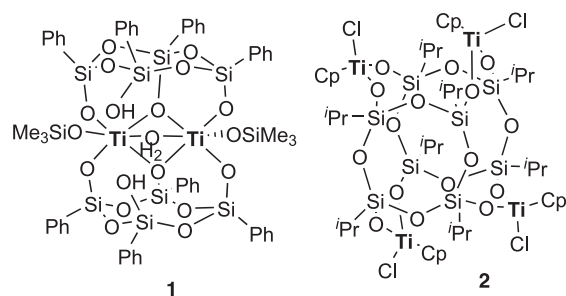


Figure 1. Molecular Structure of Titanium Complexes with Cyclic Tetrasiloxido Ligands.

VIII-F Syntheses, Structures, and Reactivities of Multinuclear Transition Metal Complexes with O- and N-Donor Ligands

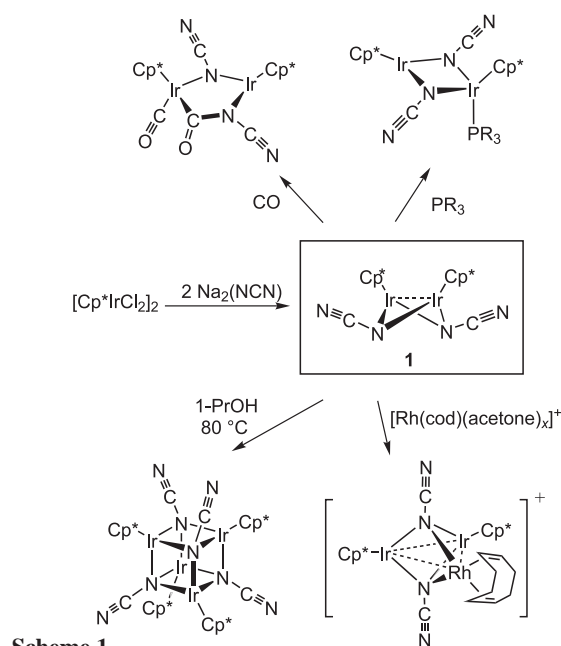
Organotransition metal complexes with O- and N-donor ligands have recently been attracting considerable attention, because they often show structures, reactivities, and physicochemical properties significantly different from those of the complexes with P- and S-donor ligands. In this project it has been disclosed that O- and N-donor ligands such as cyanamide (NCN^{2-}) and cyclophosphate ($\text{P}_3\text{O}_9^{3-}$, $\text{P}_4\text{O}_{12}^{4-}$) ions act as effective bridges to form multinuclear complexes with characteristic structures. The newly synthesized diiridium complex $[\text{Cp}^*\text{Ir}(\mu\text{-NCN-}N,N)]_2$ provides a versatile building block for the synthesis of a series of tri- and tetranuclear cyanamido clusters. On the other hand, di- and trinuclear Ti(IV) complexes built up with Cp^*Ti units and cyclophosphato ligand(s) possess novel three-dimensional structures and exhibit unique fluxional behavior in solution.

VIII-F-1 A Cyanamido-Bridged Diiridium Complex: A Reactive Building Block for Polynuclear Cyanamido Complexes

KAJITANI, Hidenobu¹; TANABE, Yoshiaki²;
KUWATA, Shigeki³; ISHII, Youichi⁴
(¹Univ. Tokyo; ²Chuo Univ.; ³Tokyo Inst. Tech.; ⁴IMS
and Chuo Univ.)

[*Organometallics* **24**, 2251–2254 (2005)]

Treatment of diiridium complex $[\text{Cp}^*\text{IrCl}_2]_2$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) with 2 equiv of Na_2NCN has been found to afford the NCN-bridged diiridium complex $[\text{Cp}^*\text{Ir}(\mu\text{-NCN-}N,N)]_2$ (**1**), which undergoes further reactions with donor molecules such as CO and phosphines. Complex **1** works as an excellent building block for the synthesis of NCN-capped multinuclear complexes: its reactions with cationic group 8–10 metal complexes such as $[\text{Cp-Ru}(\text{MeCN})_3]^+$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$), $[\text{Rh}(\text{cod})(\text{acetone})_n]^+$ ($\text{cod} = 1,5\text{-cyclooctadiene}$), and $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{acetone})_n]^+$ give the heterotrinnuclear complexes $[(\text{Cp}^*\text{Ir})_2(\text{ML})(\mu_3\text{-NCN})_2]^+$ ($\text{ML} = \text{CpRu}$, $\text{Rh}(\text{cod})$, $\text{Pd}(\eta^3\text{-C}_3\text{H}_5)$), while the dimerization of **1** leads to the cubane-type tetrairidium complex $[\text{Cp}^*\text{Ir}(\mu_3\text{-NCN})]_4$ (Scheme 1).

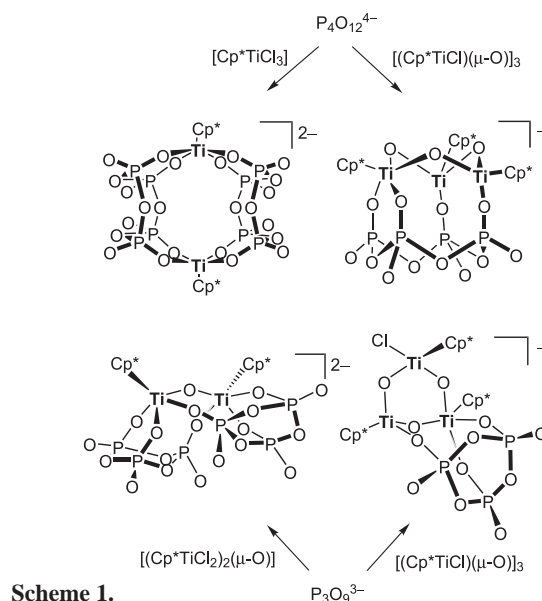


VIII-F-2 Synthesis, Structures, and Solution Behavior of Di- and Trinuclear Titanium(IV)-Cyclophosphato Complexes

KAMIMURA, Sou¹; MATSUNAGA, Tsukasa¹;
KUWATA, Shigeki²; IWASAKI, Masakazu³; ISHII,
Youichi⁴
(¹Univ. Tokyo; ²Tokyo Inst. Tech.; ³Saitama Inst. Tech.;
⁴IMS and Chuo Univ.)

[*Inorg. Chem.* **43**, 6127–6129 (2004)]

The reaction of the cyclotetraphosphate ion ($\text{P}_4\text{O}_{12}^{4-}$) with $[\text{Cp}^*\text{TiCl}_3]$ gives $[(\text{Cp}^*\text{Ti})_2(\text{P}_4\text{O}_{12})_2]^{2-}$ where the P_4O_{12} ligands adopt a saddle conformation, while that with $[(\text{Cp}^*\text{TiCl}_3)(\mu\text{-O})_3]$ leads to $[(\text{Cp}^*\text{Ti})_3(\mu\text{-O})_3(\text{P}_4\text{O}_{12})]^-$ containing a crown form P_4O_{12} ligand; both products feature their unique cage structures. The latter complex is fluxional in solution, and the variable temperature ^1H NMR study has revealed that the Ti_3O_3 unit is rotating on the P_4O_{12} platform. On the other hand, the reactions of the cyclotriphosphate ion ($\text{P}_3\text{O}_9^{3-}$) with $[(\text{Cp}^*\text{TiCl}_2)_2(\mu\text{-O})]$ and $[(\text{Cp}^*\text{TiCl}_3)(\mu\text{-O})_3]$ afford $[(\text{Cp}^*\text{Ti})_2(\mu\text{-O})(\text{P}_3\text{O}_9)_2]^{2-}$ and $[(\text{Cp}^*\text{Ti})_3(\mu\text{-O})_3\text{Cl}(\text{P}_3\text{O}_9)]^-$, respectively, and in both cases the P_3O_9 ligands bridge the two titanium centers with an $\eta^2:\eta^1$ coordination mode (Scheme 1).



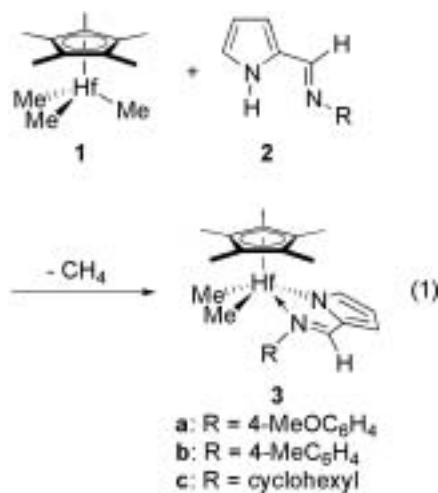
VIII-G Organometallic Chemistry: Synthesis, Characterization, and Catalysts

VIII-G-1 Living Polymerization of 1-Hexene Catalyzed by Half-Metallocene Dimethyl Complexes of Hafnium with Bidentate *N*-Substituted Iminomethylpyrrolyl Ligands

MASHIMA, Kazushi¹; YASUMOTO, Takahiro²; YAMAGATA, Tsuneaki²
(¹IMS and Osaka Univ.; ²Osaka Univ.)

[*Organometallics* **24**, 3375–3377 (2005)]

We have been interested in iminopyrrolyl ligands as a unique unsymmetrical monoanionic ligand capable of supporting non-metallocene type group 4 metal complexes. As an extension of our continuous interest in the iminopyrrolyl ligand system. We here report the syntheses of half-metallocene type hafnium dimethyl complexes with iminopyrrolyl ligand and their catalytic performance for 1-hexene polymerization upon treated with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, giving monodispersed poly(1-hexen) with high isotacticity (up to [mmmm] = 90%). These complexes were the first hafnium catalyst precursors for stereospecific living polymerization of α -olefin. Non-bridged half-metallocene dimethyl hafnium complexes **3a–c** with *N*-substituted iminomethylpyrrolyl ligands **2a–c** have been synthesized and characterized by NMR spectroscopy as well as X-ray analyses for **3a** and **3b**. These complexes were found to be active catalysts for isospecific living polymerization of 1-hexene upon treated with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ below 0 °C.

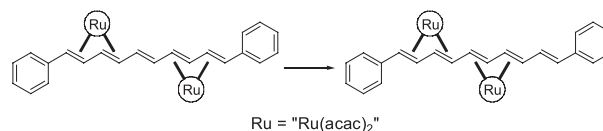


VIII-G-2 Unique Preferential Conformation and Movement of $\text{Ru}(\text{acac})_2$ Fragment(s) Coordinated in an η^4 -*s-trans* Fashion to All Diene Unit(s) of α,ω -Diphenylpolyenes

MASHIMA, Kazushi¹; FUKUMOTO, Hiroki²
(¹IMS and Osaka Univ.; ²TITech)

[*Organometallics* **24**, 3932–3938 (2005)]

α,ω -Diphenylpolyene complexes bearing bis(acetylacetonato)ruthenium(II) of general formula $\text{Ru}_n(\text{acac})_{2n}$ (polyene) [**1**: $n = 1$, polyene = 1,4-diphenylbuta-1,3-diene; **2**: $n = 1$, polyene = 1,6-diphenylhexa-1,3,5-triene; **3**: $n = 2$, polyene = 1,8-diphenylocta-1,3,5,7-tetraene; **4** and **6**: $n = 2$, polyene = 1,10-diphenyldeca-1,3,5,7,9-pentaene; **5**: $n = 3$, polyene = 1,12-diphenyl-dodeca-1,3,5,7,9,11-hexaene] were prepared by reaction of $\text{Ru}(\text{acac})_3$ with the corresponding polyene in the presence of excess amounts of zinc dust. The $\text{Ru}(\text{acac})_2$ fragment(s) in **1–6** coordinated in an η^4 -*s-trans* fashion to each diene unit of the polyene ligands. The Δ - $\text{Ru}(\text{acac})_2$ unit and its counter part Λ - $\text{Ru}(\text{acac})_2$ were assigned to coordinate to the *re*-face and the *si*-face of the diene unit, respectively, on the basis of the crystal structure of complexes **1** and **2** together with the previously reported **3**. The hexaene complex **5** was assumed to have the structure of *anti,anti*- Δ,Λ,Δ -**5a** and its enantiomer *anti,anti*- Λ,Δ,Δ -**5b**. Pentaene complex **4**, in which two ' $\text{Ru}(\text{acac})_2$ ' fragments were bound to C(1)–C(4) and C(7)–C(10) of the pentaene ligand, was isolated. The $\text{Ru}(\text{acac})_2$ fragment of **4** moved over the pentaene in CHCl_3 to settle in the thermodynamically stable **6**, in which two ruthenium fragments located at adjacent positions. Metal migration process, as monitored by decrease of **4**, was found to be first-order for **4**, giving activation parameters (ΔG^\ddagger (25 °C) = 22.5 ± 0.2 kcal/mol; ΔS^\ddagger (25 °C) = -14.2 ± 0.8 cal mol⁻¹ K⁻¹). The negative value of ΔS^\ddagger suggested that the migration of the $\text{Ru}(\text{acac})_2$ fragment is an intramolecular process.



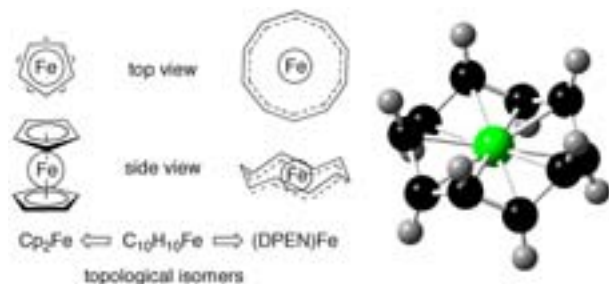
VIII-G-3 A Topological Isomer of Ferrocene: Theoretical Approach for Transition Metal Complexes with Conjugated All Trans Cyclodecapentaene

MASHIMA, Kazushi¹; OHSHIMA, Takashi²; NAKAMURA, Akira³
(¹IMS and Osaka Univ.; ²Osaka Univ.; ³OM Res.)

[*J. Organomet. Chem.* **690**, 4375–4377 (2005)]

Since the discovery of ferrocene in early 1950s, organometallic chemistry of transition metals has been developed extensively in terms of the fundamental bonding, physical properties, and attracting applications as catalysts as well as source for materials. We anticipate that it may be possible to create cyclic polyene coordinating systems, the smallest one being all-trans cyclodeca-1,3,5,7,9-pentaene (DPEN). Thus, by using DFT computation [B3LYP/6-311+G(2d,p) and BP86 level], we examined the capability of all-trans DPEN as a ligand for transition metals. We found that iron(0) and

some other transition metals coordinated by DPEN are stable molecules and unique topological isomers of the corresponding metallocene complexes.



At first, we calculated Fe(0)-DPEN complex. The shape and levels of some orbital interactions including HOMO and LUMO of the iron complex indicate the strong bonding interaction between Fe(0) and DPEN through the aromatic $p\pi$ -electrons of DPEN. Thus, we found on the basis of DFT calculation that DPEN is a potential ligand to hold some transition metals in its center. These complexes are unique topological isomers of ferrocene, $\text{Fe}(\text{C}_5\text{H}_5)_2$, and metallocene derivatives. Computational estimation of general properties of the DPEN complexes is of our interest.

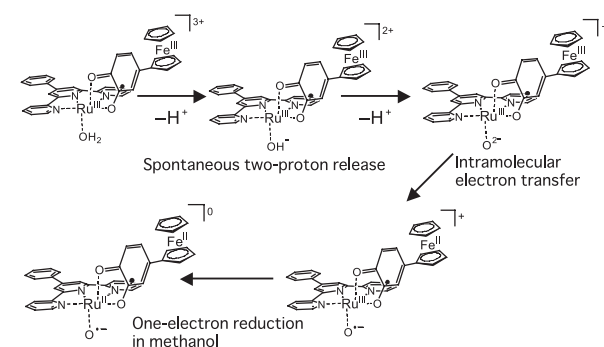
VIII-H Development of Metal-Conjugated Multi-Electron Redox Systems in Metal-Dioxolene Complexes and Activation of Water Ligand

Dioxolenes act as a versatile electron-acceptor and/or -donor through the reversible two-electron redox reaction among three oxidation forms, catechol (Cat), semiquinone (SQ), and quinone (Q). The *o*-dioxolene ligands offer a wide range of the metal complexes showing a unique metal-conjugated intramolecular electron transfer, that is valence tautomerization. Development of the metal-conjugated multi-electron redox systems is one of the most essential in order to design electrocatalysts and electronic molecular devices. The ruthenium-dioxolene complexes exhibit the reversible two-electron redox behavior and each oxidation form has been recognized as the metal-conjugated resonance hybrids, on account of the accessible redox potentials between the metal center and the dioxolene ligands. A new three-electron redox system could be constructed in ruthenium complexes containing a ferrocene-attached dioxolene, leading to metal-conjugated resonance hybrids among the three redox sites, metal, dioxolene, and ferrocene. The ruthenium-dioxolene framework successfully activates its water ligand *via* the intramolecular electron transfer to produce $\text{Ru}^{\text{II}}\text{-O}^{\bullet-}$ species, accompanied by compelling proton release from $\text{Ru}^{\text{III}}\text{-OH}_2$ using an additive strong base. In this study, we prepared a similar $\text{Ru}\text{-OH}_2$ complex bearing the ferrocene-attached dioxolene. In the three-electron redox system, the water molecule is activated through spontaneous two-proton release and the intramolecular electron transfer to the ruthenium-dioxolene-ferrocene framework.

VIII-H-1 Synthesis of a $\text{Ru}\text{-OH}_2$ Complex Bearing a Ferrocene-Attached Catecholato Ligand and Its Spontaneous Proton Release

KURIHARA, Masato¹; OHIZUMI, Tomohiro²;
SAKAMOTO, Masatomi²; WADA, Tohru;
TANAKA, Koji
(¹IMS and Yamagata Univ.; ²Yamagata Univ.)

A ruthenium-acetato-terpyridine complex containing 4-ferrocenyl-1,2-benzosemiquinone, $[\text{Ru}^{\text{II}}(\text{OAc})(\text{SQ-Fc})(\text{ph-terpy})]$ (**1**) was synthesized. Complex **1** showed the reversible three-electron redox behavior, derived from $(\text{1}^-/\text{1})$, $(\text{1}^+/\text{1}^-)$, $(\text{1}^{2+}/\text{1}^+)$ redox couples. The one-electron oxidation form, $[\text{Ru}^{\text{III}}(\text{OAc})(\text{SQ-Fc})(\text{ph-terpy})]$ CF_3SO_3 (**1**⁺) was isolated as a blue precipitate from a dichloromethane solution of **1** on addition of 1 equivalent of AgCF_3SO_3 in the yield of 78%. Our attempt to prepare the two-electron oxidation form, $[\text{Ru}^{\text{III}}(\text{OAc})(\text{SQ-Fc}^+)(\text{ph-terpy})](\text{CF}_3\text{SO}_3)_2$ (**1**²⁺) has been unsuccessful, because **1**²⁺ is labile under the synthetic conditions. The hydrolytic exchange of **1**⁺ from the acetate to an aquo ligand was carried out using HBF_4 in an acetone-water solution. The isolated hydrolysis form, **2** was characterized by ESI-mass and elemental analyses. On the basis of the elemental analysis, **2** consists of 90% of a $\text{Ru}\text{-OH}$ form, $[\text{Ru}^{\text{III}}(\text{OH})(\text{SQ-Fc}^+)(\text{ph-terpy})](\text{BF}_4)_2$ and 10% of a $\text{Ru}\text{-O}$ form, $[\text{Ru}^{\text{III}}(\text{O})(\text{SQ-Fc}^+)(\text{ph-terpy})](\text{BF}_4)$. The mass signals due to the acetate complex completely disappeared in the ESI-mass spectrum of an acetone solution of **2**. The main signal at 719 *m/z* and the isotope pattern are ascribable to a $[\text{Ru}^{\text{III}}(\text{O})(\text{SQ-Fc}^+)(\text{ph-terpy})]^+$. These results suggest that the $\text{Ru}\text{-OH}_2$ and $\text{Ru}\text{-OH}$ forms are changed into the $\text{Ru}\text{-O}$ form through spontaneous two-proton release as an only stable state in the solution, because of the strong electron attraction of $\text{Ru}^{\text{III}}\text{-SQ-Fc}^+$ framework (Scheme 1). The $\text{Ru}\text{-O}$ complex, $[\text{Ru}^{\text{III}}(\text{O})(\text{SQ-Fc}^+)(\text{ph-terpy})]^+$ underwent one-electron reduction in a methanol solution to generate $[\text{Ru}^{\text{II}}(\text{O}^{\bullet-})(\text{SQ-Fc})(\text{ph-terpy})]$, according to the electronic spectral change (Scheme 1).



Scheme 1.