RESEARCH ACTIVITIES VII
Coordination Chemistry Laboratories

Prof. Mitsuhiko Shionoya and Dr. Kentaro Tanaka in laboratory of Complex Catalysis moved to Faculty of Science, Tokyo University in April 1999. Prof. Makoto Fujita and Dr. Takahiro Kusukawa in laboratory of Functional Coordination Chemistry also moved to Faculty of Engineering, Nagoya University in April 1999. Prof. Yuzo Nishida, Prof. Masahiro Ebihara, Dr. Tomohiro Ozawa and Dr. Hiroyuki Kawaguchi continued the position of Synthetic Coordination Chemistry from April 1998. Prof. Ginya Adachi (Osaka University) and Assoc. Prof. Hiromi Tobita (Tohoku University) finished their term as Adjunct Prof. in March 1999 in the Laboratory of Coordination Bond. Their effort during their term is gratefully appreciated. Prof. Hiromu Sakurai (Kyoto pharmacy University) and Assoc. Prof. Yuji Mizobe (Tokyo University) continued their position as Adjunct Prof. of Laboratory of Complex Catalysis. Prof. Takuzo Aida (Tokyo University) and Assoc. Prof. Itaru Hamachi (Kyushu University) took the position of the laboratory of Coordination Bond.

VII-A New Insight into Mechanism of Oxygen Activation in Biological Oxygenases

One of the remaining frontiers in organic chemistry is the direct functionalization of saturated hydrocarbons. The catalytic cycle that oxidizes a hydrocarbon R-H to an alcohol R-OH employing cytochrome P-450 and methane monooxygenase is a well-established process, however no reasonable mechanism for dioxygen activation and for formation of the R-OH is available at present. Recently the present author has proposed a new idea that elucidates many biological oxygenation reactions including monooxygenases and dioxygenases comprehensively. In this new concept, the importance of electrophilic nature of a metal-peroxide adduct and the role of the substrate as an electron donor to the peroxide adduct were emphasized. This idea suggests that formation of a high-valent iron-oxo species, which has been frequently pointed out by the previous authors, occurs most likely when the metal-peroxide intermediate is activated through electronic interaction with both the substrate and the peripheral organic group; the latter two act as an electron donor to the peroxide adduct (see Figure 1: Y. Nishida, *Trends Inorg. Chem.* **5**, 89 (1998)). We are now continuing the study on the reactivity of the metal-peroxide adducts in order to ascertain that my idea is applicable to other reactions, such as degradation of DNA and proteins by the metal-peroxide adducts.

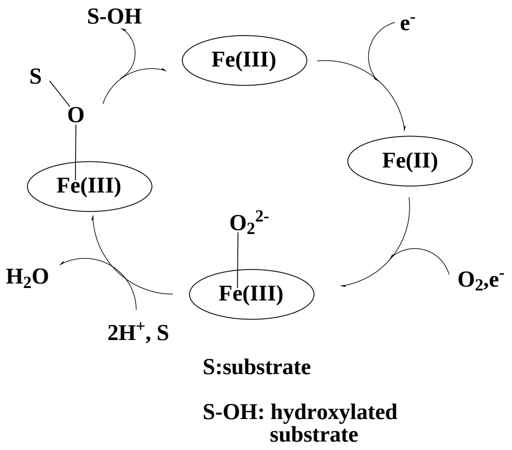


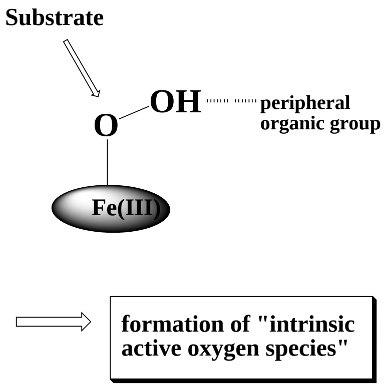
Figure 1. Nishida's mechanism for hydroxylation reaction catalyzed by cytochrome P-450

VII-A-1 Important Role of Substrate in Activation of Dioxygen in Biological Oxygenases

NISHIDA, Yuzo

[*Trends Inorg. Chem.* **5**, 89 (1998)]

In this paper, I have discussed the reaction mechanism of monooxygenases and dioxygenases based on the results obtained for the model systems. Monooxygenases and dioxygenases activate peroxide ion and dioxygen molecule, respectively, and in both cases the substrate plays an important role in the activation of the oxygen species, generating an "intrinsic active oxygen species." (see the Scheme shown below)



My idea is completely different from those of the previous papers; in the latter cases it has been believed that the active oxygen species generates from the reaction between oxygen and the metal enzymes, and then it reacts with a substrate. According to our scheme, the oxygen atom of the peroxide adduct which is coordinate to the iron(III), is inserted to the substrate in P-450 reaction (see the figure above). On the contrary, terminal oxygen atom of the peroxide adduct is inserted to the porphyrin ring in Heme-oxygenase; in the latter case the substrate is identical to the peripheral group. Thus, it seems quite likely that oxygen atom, which interacts strongly with the substrate is transferred to the organic group, and that electronic interaction between the orbitals of a metal-peroxide and substrate induces heterolytic cleavage of O-O bond, and the electron transfer is not necessary in this process.

In the monooxygenases such as cytochrome P-450 and methane monooxygenase, at first a metal peroxide forms via two electron transfer reduction, and heterolysis of the O-O bond of the metal-peroxide occurs in the presence of substrate and also peripheral organic moiety near the metal ion, and one oxygen atom is incorporated into the substrate.

In the dioxygenases, the metal ion plays a role to bring the substrate near to oxygen molecule and to promote the electron transfer from the substrate to oxygen, giving a C-OOH bond formation. In this case, since the activation of oxygen molecule occurs, O-O bond cleavage does not occur. The substrate in the dioxygenases are generally oxidizable than those in the monooxygenases.

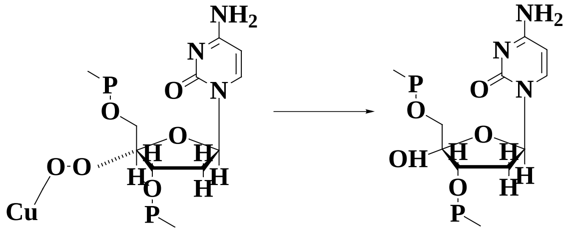
In the case of phenylalanine hydroxylase and tyrosine hydroxylase, which are one of the monooxygenases, dioxygenase reaction proceeds in the first step, and in the next step, monooxygenase, does. In the first step the substrate is pterin, and in the second step, amino acid, such as phenylalanine or tyrosine.

VII-A-2 Structural Variety of Copper(II)-Peroxide Adducts and its Relevance to DNA Cleavage

NISHINO, Satoshi; KOBAYASHI, Teruyuki; KUNITA, Mami; ITO, Sayo; NISHIDA, Yuzo

[*J. Bioscience* **54C**, 94 (1999)]

The reactivity of copper(II) compounds with several tetradentate ligands towards some spin-trapping reagents was studied in the presence of hydrogen peroxide. The compounds used in this study are roughly divided into two groups based on the reactivity towards 2,2,6,6-tetramethy-4-piperidinol (and also 2,2,6,6-tetramethyl-4-piperidone), which are trapping agents for singlet oxygen, $^1O_2(^1\Delta_g)$. The A-group compounds exhibited a high activity to form the corresponding nitrone radical, which was detected by ESR spectrometry, but the corresponding activity of the B-group compounds was very low. The A-group compounds defined as above exhibited high activity for cleavage of DNA (supercoiled Form I DNA in the presence of hydrogen peroxide, yielding DNA Form II (relaxed circular) or Form III (linear duplex) under our experimental conditions. On the other hand, the B-group compounds effected complete degradation of the DNA (double-strand scission) under he same experimental conditions; formation of Form II or Form III DNA is negligible. Two different DNA cleavage patterns observed for A- and B-group compounds were elucidated by different structural properties of the copper(II)-peroxide adducts, which is controlled by the interaction through both DNA and the peripheral group of the ligand system. Based on these results, it was assumed that double-strand break by Cu(bdpg)/H_2O_2 system(one of the B-group compound) may proceed via formation of 4'-OH as shown in Scheme.

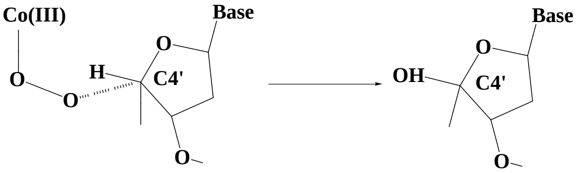


VII-A-3 Mechanism of DNA Cleavage due to Green Cobalt(III)-Bleomycin Hydroperoxide Irradiated by Visible Light

NISHIDA, Yuzo; KUNITA, Mami; NISHINO, Satoshi

[*Inorg. Chem. Commun.* **2**, 156 (1999)]

The origin of the DNA cleavage reaction due to green cobalt(III)-bleomycin hydroperoxide irradiated by visible light (366 nm) was developed on the molecular orbital theory. The importance of the activation of the peroxide ion by transferring an electron from the occupied orbital to σ*-orbital of the peroxide ion was pointed out. We have proposed that the irradiation of the system by the light (366 nm) induces a direct hydroxylation reaction at the 4' position associated with a concerted heterolytic O-O cleavage reaction (*i.e.*, insertion of an atomic oxygen into the C-H bond) without formation of a C4' radica l(see the Scheme shown below). This consideration is quite consistent with the observed results, and a study on the reaction mechanism of hydroxylation by heme-oxygenase, and our previous theoretical consideration.

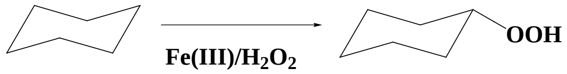


VII-A-4 Selective Dioxygenation of Cyclohexane Catalyzed by Hydrogen Peroxide and Dinuclear Iron(III) Complexes with μ-Alkoxo Bridge

NISHINO, Satoshi; HOSOMI, Hiroyuki; OHBA, Shigeru; MATSUSHIMA, Hideaki; TOKII, Tadashi; NISHIDA, Yuzo

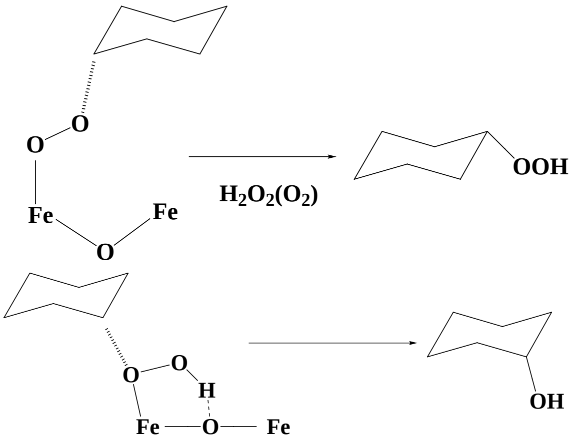
[*J. Chem. Soc., Dalton Trans.* 1509 (1999)]

Several dinuclear iron(III) complexes with μ-alkoxo bridge gave predominantly cyclohexyl hydroperoxide in the reaction with cyclohexane and hydrogen peroxide



and similar results were observed when linear n-alkanes, such as n-nonane and n-octane, were used instead of cyclohexane.

These facts clearly indicate that the Fish's mechanism for the hydroxylation of cyclohexane by Fe(III)/H_2O_2 system is wrong. We have proposed new mechanism for the functionalization of alkanes by Fe(III)/H_2O_2 system; the active species which catalyze dioxygenation and monooxygenation are different from each other, and theoretical elucidation was also provided to our conclusion.

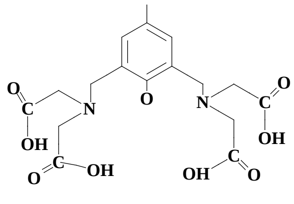


VII-A-5 Interaction between the Peroxide Ion and Acetate Moiety of the Ligand System in a Cobalt(II) Complex with a Binucleating Ligand

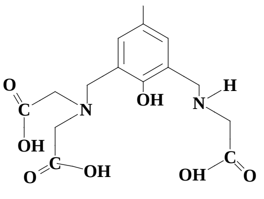
SASAKI, Yumiko; KOBAYASHI, Teruyuki; MASUDA, Hideki; EINAGA, Hisahiko; OHBA, Shigeru; NISHIDA, Yuzo

[*Inorg. Chem. Commun.* **2**, 244 (1999)]

We have found that reaction between Na_3H_2(HXTA) and $Na_3Co(CO_3)_3$ in an aqueous solution gave a binuclear cobalt(III) complex, Na_2Co_2(HXTRA), where in $(HXTRA)^{4-}$ ligand one of the four acetato arms of the original $(HXTA)^{5-}$ ligand is lost.

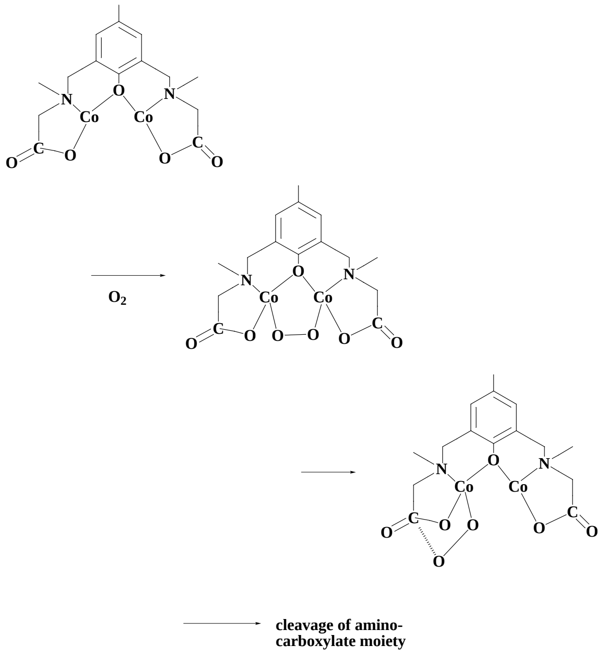


$(HXTA)^{5-}$



$(HXTRA)^{4-}$

This may be attributed to the oxidative degradation of one acetato arm of $(HXTA)^{5-}$ ligand due to an electrophilic peroxide-cobalt(III) species with end-on type, as illustrated in Scheme.



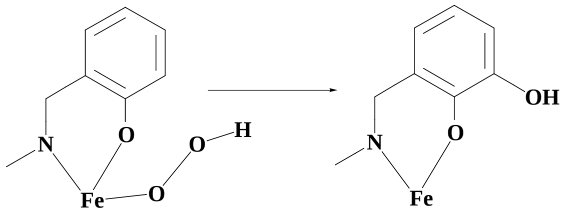
VII-A-6 Electrospray Mass Spectrometry of Peroxide Adduct of Monomeric Fe(III) Complex Containing Phenol Group

OKUTSU, Wataru; ITO, Sayo; NISHIDA, Yuzo

[*Inorg. Chem. Commun.* **2**, 308 (1999)]

Peroxoiron(III) complexes are increasingly being considered as potential intermediates in oxidation catalyzed by both non-heme and heme iron centers. In 1994, Sam *et al.* reported that an "activated bleomycin" is a monomeric iron(III)-peroxide adduct with end-on type, however evidence for the formation of a monomeric iron(III)-peroxide adduct with end-on type is scarce, and their reactivity is unknown at present. In our previous paper, we have reported the preparation, crystal structure determinations of the monomeric iron(III) compounds with ligands containing phenol group, and proposed that the phenol group plays an important role in formation of a peroxide adduct, and in activation of he peroxide ion.

In this study we have confirmed the formation of a peroxide adduct of the monomeric iron(III) complex with end-on type in terms of the electrospray mass spectrometry, and discussed the activation of the peroxide ion and hydroxylation of phenol ring(see Scheme) based on these facts.

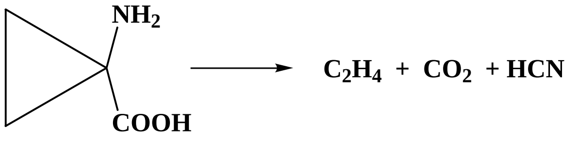


VII-A-7 High Activity of Binuclear Cobalt(II) Complex for Ethylene Evolution from 1-Aminocyclopropane-1-carboxylic Acid in the presence of Hydrogen Peroxide

KOBAYASHI, Teruyuki; SASAKI, Yumiko; AKAMATSU, Tetsuya; ISHII, Toshihiro; MASUDA, Hideki; EINAGA, Hisahiko; NISHIDA, Yuzo

[*Z. Naturforsch., C: Biosci.* **54**, 534 (1999)]

The binuclear Co(II) and Mn(II) complexes with H_5-(HXTA), where H_5(HXTA) represents *N*,*N*'-(2-hydroxy-5-methyl-1,3-xylylene)bis(*N*-carboxylmethyglycine) induced a strong ethylene evolution from 1-aminocyclopropane-1-carboxylic acid (ACC) in the presence of hydrogen peroxide (see Scheme), whereas the activities of the corresponding Fe(III), Ni(II) and V(III) compounds were found negligible.



ACC

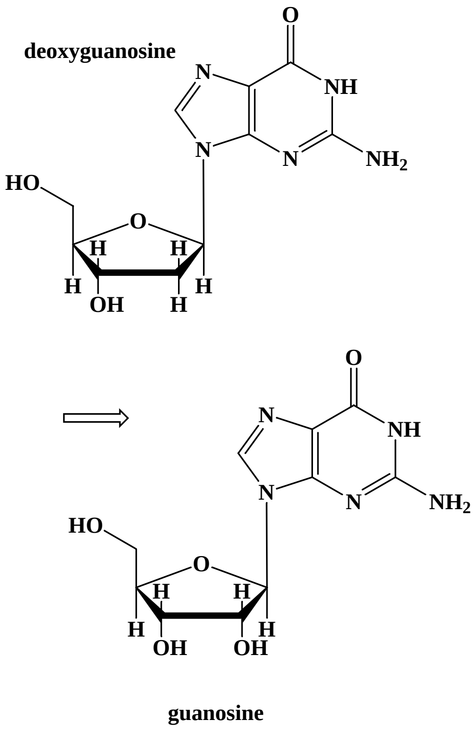
Based on the spectroscopic and mass-spectral data it is proposed that a peroxide adduct of binuclear Co(II) (and Mn(II)) complex with η^1-coordination mode interacts with ACC, which is chelated to a binuclear cobalt(II) complex leading to facile oxidative degradation of ACC and to evolution of ethylene.

VII-A-8 Oxygenation of Nucleosides by Peroxide Adduct of Binuclear Iron(III) Complex with a μ-Oxo Bridge

ITO, Sayo; SASAKI, Yumiko; TAKAHASHI, Yasuyuki; OHBA, Shigeru; NISHIDA, Yuzo

[*Z. Naturforsch., C: Biosci.* **54**, 554 (1999)]

The (μ-oxo)(μ-carbonato)diiron(III) complex with H_2(tfda) (H_2(tfda) = 2-aminomethyltetrahydrofuran-*N*,*N*-diacetic acid) exhibited high activity for hydroxylation of 2'-deoxyguanosine in the presence of hydrogen peroxide, giving 8-hydroxydeoxyguanosine, but its hydroxylation activity towards other nucleosides, such as 2'-deoxyadenosine, adenosine, or thymidine was found negligible. In the case of the Fe(III)-(eda) complex (H_2(eda) = 2-methoxyethylamine-*N*,*N*-diacetic acid), hydroxylation reaction occurred mainly at the sugar site, converting 2'-dexoyguanosine to guanosine (see the Scheme). Based on the spectroscopic and structural properties of these iron(III) compounds, it seems most likely that an intrinsic active species for hydroxylation should be an electrophilic peroxide adduct of the (μ-oxo)diiron(III) core with η^1-coordination mode, while the contribution of OH• to the hydroxylation reaction of nucleosides is ruled out.



VII-B Electronic Structure and Reactivity of Metal Cluster Complexes

Because trimetal cluster complex is a fundamental framework for constructing high nuclearity cluster, electronic structure and reactivity of trimetal cluster complex is important. We have studied the electronic structure and reactivity of bis(μ_3-benzylidyne)tris(cyclopentadienylcobalt) complex. It reacts halogens and silver(I) to give halide and silver bridged complexes.

VII-B-1 Synthesis, Structure and Redox Behavior of Tricobalt Cluster with Capping Benzylidyne and Bridging halogen $[Co_3Cp_3(\mu_3\text{-}CPh)_2(\mu\text{-}X)]^+$ (X = Cl, Br, I)

EBIHARA, Masahiro; IIBA, Masami[1]; MATSUOKA, Hiroaki[1]; KAWAMURA, Takashi[1]
([1]Gifu Univ.)

Reactions of the benzylidyne capped tricobalt cluster $[Co_3Cp_3(\mu_3\text{-}CPh)_2]$ (**1**) with halogens ($X_2 = Cl_2, Br_2, I_2$) in CH_2Cl_2 gave oxidative addition products of halogen to **1**. X-ray structures of four salts, $[Co_3Cp_3(\mu_3\text{-}CPh)_2(\mu\text{-}Cl)]PF_6{\cdot}CH_3CN$ ($\mathbf{2}^+PF_6^-{\cdot}CH_3CN$), $[Co_3Cp_3(\mu_3\text{-}CPh)_2(\mu\text{-}Br)]SbF_6$ ($\mathbf{3}^+SbF_6^-$), $[Co_3Cp_3(\mu_3\text{-}CPh)_2(\mu\text{-}I)]SbF_6{\cdot}CH_2Cl_2$ ($\mathbf{4}^+SbF_6^-{\cdot}CH_2Cl_2$) and $[Co_3Cp_3(\mu_3\text{-}CPh)_2(\mu\text{-}I)]I_3$ ($\mathbf{4}^+I_3^-$) were determined. In all structures the halogen atom was in the Co_3 plane. The halogen-bridged Co–Co distance was elongated ($\mathbf{2}^+PF_6^-{\cdot}CH_3CN$: 2.6072(5) Å, $\mathbf{3}^+SbF_6^-$: 2.6097(9) Å, $\mathbf{4}^+SbF_6^-{\cdot}CH_2Cl_2$: 2.621(2) Å) and the Co–Co distances without halogen-bridge remained unchanged ($\mathbf{2}^+PF_6^-$: 2.4038(9) and 2.3947(7) Å, $\mathbf{3}^+SbF_6^-$: 2.3902(8) and 2.4015(9) Å, $\mathbf{4}^+SbF_6^-{\cdot}CH_2Cl_2$: 2.392(2) and 2.388(2) Å) from that of **1** (2.38 Å). Cyclic voltammogram of $\mathbf{2}^+PF_6^-$ in CH_2Cl_2 with 0.1 M *n*-Bu_4NPF_6 as supporting electrolyte showed an quasi-reversible oxidation (+0.75 V, potential vs Fc/Fc^+) and an irreversible reduction wave (–0.57 V) (Figure 1). The irreversible reduction caused recovery of neutral cluster complex **1**. The redox properties of $\mathbf{3}^+$ and $\mathbf{4}^+$ were similar to that of $\mathbf{2}^+$. Cyclic voltammetry of **1** in 0.1 M *n*-Bu_4NCl/CH_3CN with various scan rates indicated that the formation of $\mathbf{2}^+$ was a multi-step reaction. First **1** was oxidized to $\mathbf{1}^+$ and it was coordinated by Cl^- and immediately oxidized to $\mathbf{2}^+$.

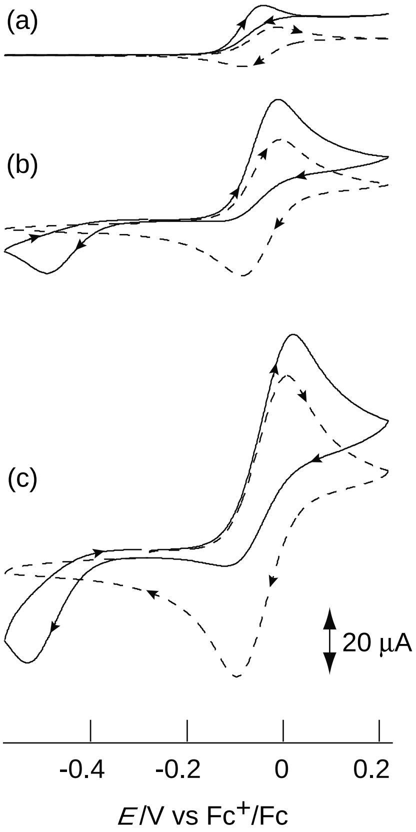


Figure 1. Cyclic voltammograms of **1** (2.0 mM) in CH_3CN with 0.1 M *n*-Bu_4NCl. Scan rate (a) 10 mVs^{-1}, (b) 100 mVs^{-1} and (c) 500 mVs^{-1} with cyclic voltammograms of **1** (2.0 mM) in 0.1 M *n*-Bu_4NPF_6 (broken line).

VII-B-2 Bis-μ_3-Benzylidyne Tri(cyclopentadienylcobalt) Cluster with Edge-bridging Silver(I): Synthesis, Structure and Solution Properties of $[Co_3Cp_3(\mu_3\text{-}CPh)_2\{\mu\text{-}Ag(X)\}]$ (X = CF_3CO_2, NO_3) and $[Co_3Cp_3(\mu_3\text{-}CPh)_2\{\mu\text{-}Ag(NCCH_3)\}]PF_6$

EBIHARA, Masahiro; IIBA, Masami[1]; MATSUOKA, Hiroaki[1]; KAWAMURA, Takashi[1]
([1]Gifu Univ.)

Reactions of the benzylidyne capped tricobalt cluster $[Co_3Cp_3(\mu_3\text{-}CPh)_2]$ (**1**) with various silver salts are examined. The salts of weakly- or non-coordinating anions (BF_4^-, PF_6^-) oxidize **1** to its cationic radical $[Co_3Cp_3(\mu_3\text{-}CPh)_2]^+$ ($\mathbf{1}^+$) in CH_2Cl_2. The reaction with the salts of strongly-coordinating anions ($CF_3CO_2^-$, NO_3^-) gives silver(I) adducts of **1**, $[Co_3Cp_3(\mu_3\text{-}CPh)_2\{\mu\text{-}Ag(X)\}]$ (X = $CF_3CO_2^-$ (**2**, Figure 1), NO_3^- (**3**)). Even for $AgBF_4$ or $AgPF_6$ the reaction in CH_3CN produces silver(I) adduct $[Co_3Cp_3(\mu_3\text{-}CPh)_2\{\mu\text{-}Ag(NC\text{-}$

$CH_3)\}]^+$ (**4**$^+$). The Co_3Ag skeleton in structures of **2**, **3** and **4**$^+$ resembles each other. The Co–Co bonds bridged by the Ag atom (**2**: 2.4783(9) Å, **3**: 2.481(1) Å, **4**$^+$: 2.4600(9) Å) are longer than that of **1** (2.38 Å). The other Co–Co bonds are slightly shorter than that in **1**. The Co_2Ag triangle is not coplanar with the Co_3 triangle; the dihedral angles between these triangles for **2**, **3**, and **4**$^+$ are 162.7°, 157.8°, and 151.3°, respectively. Dissolution of **4**$^+PF_6{}^-$ in CH_2Cl_2 causes formation of **1**$^+$ with deposition of Ag metal. ^1H NMR spectra of **2** and **3** in CD_2Cl_2 indicates partial dissociation of the AgX group. The ^1H NMR spectra of CD_3CN solutions and the ESR spectra in frozen CH_3CN solutions of **2**, **3**, and **4**$^+PF_6{}^-$ shows generation of **1**$^+$ without deposition of Ag metal. It suggests that equilibrium of Ag^+ and **1** with Ag^0 and **1**$^+$ is established in acetonitrile. Addition of AgO_2CCF_3 to the solution causes disappearance of the ESR signal. It indicates that **1**$^+$ is generated from **4**$^+$ or the reaction of **1** with anion-uncoordinated Ag^+.

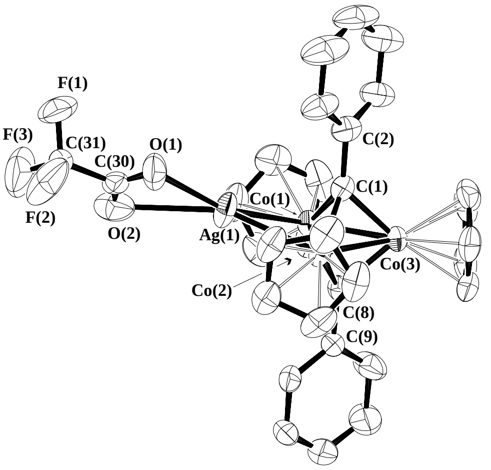


Figure 1. Structure of $[Co_3Cp_3(\mu_3\text{-}CPh)_2\{\mu\text{-}Ag(O_2CCF_3)\}]$.

VII-C Bio-Inspired Molecular Architecture

Nature has produced a limited number of molecular modules such as nucleosides and nucleotides, amino acids, and lipids. However, the chemical diversity of these biomolecules and the different ways they can be polymerized or assembled into precisely-defined three-dimensional shapes provide a wide range of possible structures and functions. Furthermore, owing to advances in chemical synthesis and biotechnology we can combine or chemically modify these molecular building blocks, almost at will, to produce new functional molecules that have not yet been made in Nature. Based on these concepts, we have been working on the following research projects. Our research programs also consciously focus on structures and functions that have been unknown in living, biological systems.

VII-C-1 Synthesis of a Novel Nucleoside for Alternative DNA Base Pairing through Metal Complexation

TANAKA, Kentaro; SHIONOYA, Mitsuhiko

[*J. Org. Chem.* **64**, 5002 (1999)]

A novel artificial nucleoside was synthesized, in which artificial bases are introduced as metal coordination sites for alternative base-pairing through metal complexation instead of hydrogen bonding in natural DNA. The artificial β-C-nucleoside (4-[1,2-dideoxy-β-D-ribofuranos-1-yl)-*o*-phenylenediamine) **1** which has a phenylenediamine moiety as a metal coordination site was prepared by coupling reaction of a lithiated *o*-phenylenediamine derivative and 2,3,5-tri-*O*-benzyl-D-ribonic γ-lactone followed by several reactions to remove 2'-hydroxyl group. ^{1}H NMR and ESI mass spectroscopic studies clearly showed that **1** and Pd^{2+} form a stable 2:1 complex in aqueous media (Figure 1).

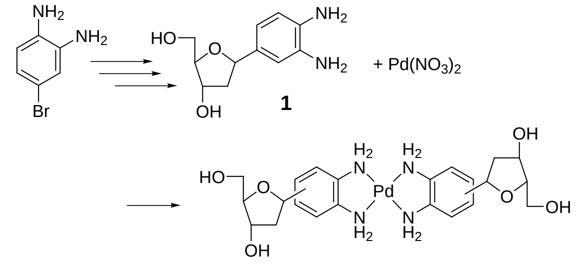


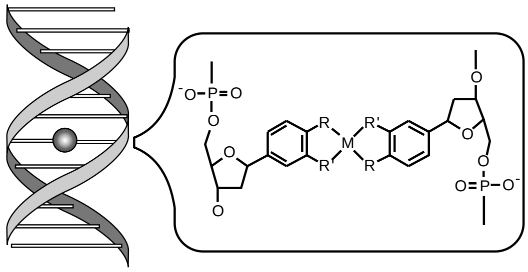
Figure 1. Complex formation of phenylenediamine-nucleoside **1** with Pd^{2+}.

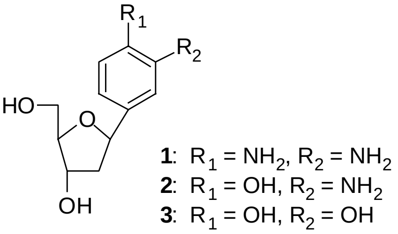
VII-C-2 An Approach to Metal-Assisted DNA Base Pairing: Novel β-C-Nucleosides with a 2-Aminophenol or a Catechol as the Nucleobase

TANAKA, Kentaro; TASAKA, Motoyuki[1]; CAO, Honghua[1]; SHIONOYA, Mitsuhiko
([1]GUAS)

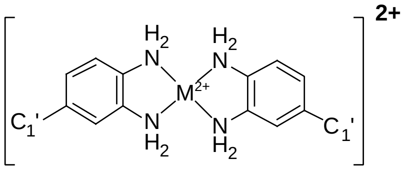
[*Eur. J. Pharm. Sci.* in press]

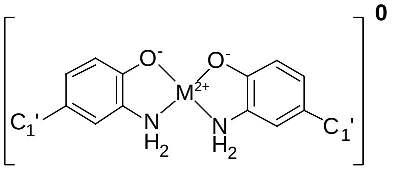
The metal-chelating β-C-nucleoside having a phenylenediamine moiety as the nucleobase was previously found to form a stable 2:1 complex with a Pd^{2+} ion in aqueous media, where hydrogen bonding is replaced by metal coordination in the base pairing thereby creating a novel hybridization motif in duplex DNA. In this regard, we have further designed two types of artificial β-C-nucleosides possessing a metal-chelating site (a 2-aminophenol or a catechol) as the nucleobase moiety. These artificial nucleosides are directed toward controlling the net charges of the metal-assisted base pairs. This paper describes convenient syntheses of the artificial nucleosides bearing a 2-aminophenol or a catechol moiety. Each nucleoside was directly synthesized through 2'-deoxy derivative via a Friedel-Crafts coupling reaction as the key step between the aromatic ring and ribose moiety, whereas the nucleoside having a phenylenediamine moiety was prepared in rather longer steps through an RNA type intermediate followed by the removal of 2'-hydroxy group.

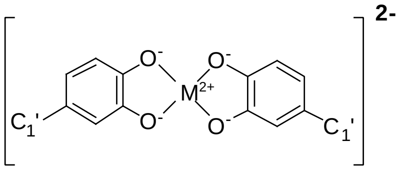




1: $R_1 = NH_2$, $R_2 = NH_2$
2: $R_1 = OH$, $R_2 = NH_2$
3: $R_1 = OH$, $R_2 = OH$





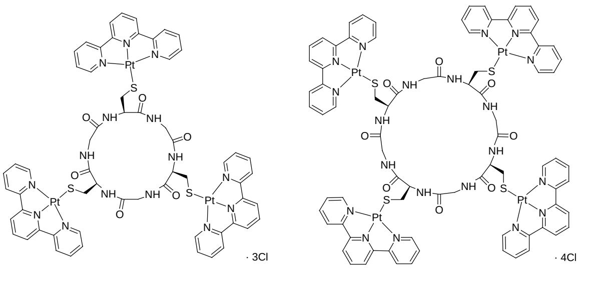


VII-C-3 Cyclic Metallopeptides, *cyclo*[-Gly-L-Cys(terpyPt^{II})-]$_n$Cl$_n$

TANAKA, Kentaro; SHIGEMORI, Kazuki[1]; SHIONOYA, Mitsuhiko
([1]GUAS)

[*Chem. Commun.* in press]

A new efficient synthetic methodology has been developed that can be utilized for the iterative construction of a new family of cyclohexa and cycloocta metallopeptides of the general formula, *cyclo*[-Gly-L-Cys(terpyPt^{II})-]$_n$Cl$_n$, **1** (n = 3) and **2** (n = 4). The linear peptides, TFA·H-[Gly-L-Cys(terpyPt^{II})]$_n$-OH·(CF_3CO_2)$_n$, (n = 3) and (n = 4), were cyclized in H_2O-CH_3CN (7:3) at 25 ˚C to the corresponding cyclopeptides, **1** and **2**, in the presence of excess HOBt and EDC in 58% yield in both cases. The ring size of each cyclopeptide was determined by high-resolution ESI mass spectroscopy. The cyclohexapeptide **1** selectively separated benzene 1,3,5-tricarboxylate from a mixture of three tricarboxylates (benzene 1,3,5-tricarboxylate and its 1,2,4- and 1,2,3-isomers) in neutral water. The ^{1}H NMR and ESI mass spectra of the precipitate immediately appeared clearly evidenced the 1:1 complexation of **1** and benzene 1,3,5-tricarboxylate. The Pt^{II}-terpyridine complex moieties of **1** were readily removed by acid treatment to afford the corresponding cyclohexapeptides, *cyclo*[-Gly-L-Cys-]$_3$. The synthetic strategy developed in this work would provide a powerful tool for arraying functional metal complexes on cyclopeptide frameworks.



1 2

Figure 1. Chemical structures of the cyclic metallopeptides newly synthesized in this study.

VII-C-4 Construction of a Unique Alternating-Chain Array with Copper(II) and a New Diazamesocycle Bearing One Functional Pendant

BU, Xian-He[1]; XU, Qiang[1], SHANG, Zhi-Liang[1]; ZHANG, Ruo-Hua[1]; ZHAO, Qi-Hua[1]; TANAKA, Kentaro; SHIONOYA, Mitsuhiko
([1]Nankai Univ.)

[*Inorg. Chem. Commun.* submitted]

The polymeric Cu^{II} complex of 1-[(1-methylimidazol-2-yl)methyl]-1,5-diazacyclooctane (**L**), {[Cu_2(**L**)$_2$(μ-Cl)$_2$](ClO_4)$_2$}$_\infty$ (***I***), has been constructed from the self-assembling reaction of Cu^{II} perchlorate and **L** in water; and the X-ray crystallographic analysis of the complex showed that it has a zigzag alternating-chain structure consisting of two distinct coordination geometries.

VII-C-5 Spontaneously Resolved Chiral Molecular Box: A Cyclic Tetranuclear Zn(II) Complex with DPTZ (DPTZ = 3,6-Di-2-Pyridyl-1,2,4,5-Tetrazine)

BU, Xian-He[1]; MORISHITA, Hiromasa[2]; TANAKA, Kentaro; BIRADHA, Kumar; SHIONOYA, Mitsuhiko
([1]Nankai Univ.; [2]GUAS)

[*J. Am. Chem. Soc.* submitted]

Interest in coordination architectures constructed by metal ions and bridging ligands has been driven by the expectation of developing new materials with unique electronic, magnetic, and optical properties, or catalytic activities. Their structure and functions have a close relationship with the geometry and chemical properties of the metal ions and bridging ligands used in the architectures. Our recent studies make clear that 3,6-di-2-pyridyl-1,2,4,5-tetrazine (DPTZ) is a promising ligand which can be used in the construction of highly organized supramolecular structures.

We report herein a novel tetranuclear Zn(II) molecular square complex that exhibits a chiral structure in the crystal state. The reaction of Zn(ClO_4)$_2$·6H_2O with DPTZ in a 1:1 ratio in a mixed solvent of $CHCl_3$ and CH_3CN at room temperature produced a tetranuclear zinc(II) complex as orange prisms in *ca.* 90% yield. Its X-ray crystal structure is shown in Figure 1. This compound crystallizes in the chiral space group *C*222$_1$. In contrast, a similar reaction of DPTZ with Cd(II) in a 1:1 ratio afforded a linear complex of Cd(II) with 1D chain structure almost quantitatively.

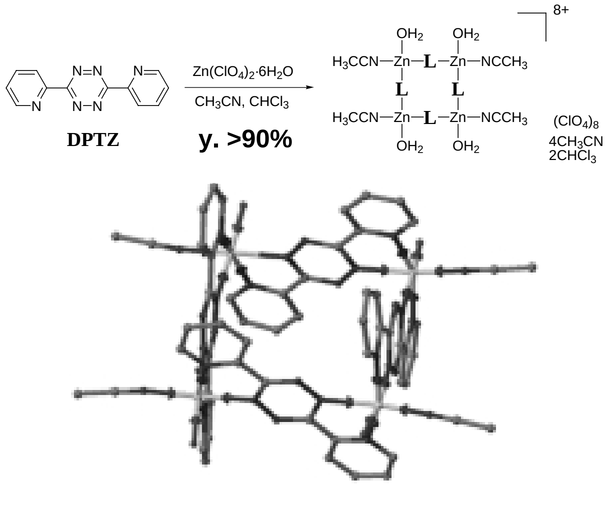


Figure 1. A chiral molecular box Zn(II) complex.

VII-D Research on the Relationship between Structure of Vanadyl Complex and Insulin-Mimetic Activity

Insulin-dependent diabetes mellitus (IDDM) shows hyperglycemia owing to deficiency of insulin, causing many serious secondary complications. To prevent the complications, IDDM is controlled by daily injections of insulin. Therefore, we have developed orally active insulin-mimetic vanadyl complexes.

VII-D-1 Syntheses, Structure, and Insulin-like Activities of Oxovanadium (IV) Complexes with Tetra- and Penta-Dentate Histidine Derivatives

KAWABE, Kenji[1]; SUEKUNI, Tomonari[1]; INADA, Takanori[1]; YAMATO, Kazuhiro[1]; TADOKORO, Makoto[1]; KOJIMA, Yoshitane[1]; FUJISAWA, Yae[2]; SAKURAI, Hiromu[3]
([1]Osaka City Univ.; [2]Kyoto Pharm. Univ.; [3]IMS and Kyoto Pharm. Univ.)

[*Chem. Lett.* 1155 (1998)]

$[\mathrm{VO}(^{pm}\mathrm{H})(\mathrm{ClO}_4)]$, $[\mathrm{VO}(\mathrm{Me}_4)]$, and $[\mathrm{VO}(^{(pm)2}\mathrm{H})](\mathrm{ClO}_4)$ complexes were prepared and their X-ray structures were analyzed. Among them, in vitro insulin-mimetic activity of $[\mathrm{VO}(^{pm}\mathrm{H})(\mathrm{ClO}_4)]$ was found to be higher than that of vanadyl sulfate as a positive control.

VII-D-2 Insulin-Mimetic Vanadyl-Dithiocarbamate Complexes

SAKURAI, Hiromu[1]; WATANABE, Hiromi[2]; TAMURA, Hideyuki[2]; YASUI, Hiroyuki[2]; MATSUSHITA, Rokuji[3]; TAKADA, Jitsuya[3]
([1]IMS and Kyoto Pharm. Univ.; [2]Kyoto Pharm. Univ.; [3]Res. Reactor Inst., Kyoto Univ.)

[*Inorg. Chim. Acta* **283**, 175 (1998)]

Five vanadyl-dithiocarbamate complexes with VO-(S_4) coordination mode such as VO-DMD, VO-DED, VO-PYD, VO-MGD and VO-SAD were prepared and their *in vitro* and *in vivo* insulin-like activities were examined. VO-PYD complex was concluded to be a potent agent on daily oral administration to treat insulin-dependent diabetes in experimental animals.

VII-D-3 A New Insulin-mimetic Vanadyl Complex, (*N*-Pyridylmethylaspartate) Oxovanadium (IV) with $\mathrm{VO}(\mathrm{N}_2\mathrm{O}_2)$ Coordination Mode, and Evaluation of its Effect on Uptake of *D*-Glucose by Ehrlich Ascites Tumor Cells

TAWA, Riichi[1]; UCHIDA, Keiko[1]; TANIYAMA, Junko[1]; FUJISAWA, Yae[1]; FUJIMOTO, Seiki[1]; NAGAOKA, Takashi[2]; KANAMORI, Kan[2]; SAKURAI, Hiromu[3]
([1]Kyoto Pharm. Univ.; [2]Toyama Univ.; [3]IMS and Kyoto Pharm. Univ.)

[*J. Pharm. Pharmacol.* **51**, 119 (1999)]

A new *in vitro* assay method using Ehrlich ascites tumor cells for the insulin-mimetic activity of a compound was proposed. By using this method, VO-(PASP), VO(PA) and VO(MPA) complexes have been found to have good insulin-mimetic activities.

VII-E Syntheses of Transition Metal-Sulfur Clusters and Development of Their Catalysis

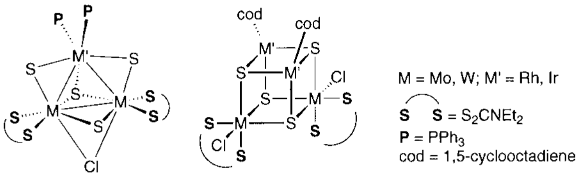
This project focuses on the development of the new, reliable synthetic routes towards the transition metal-sulfur clusters with the tailored core structures in high yield, and also on the determination of the detailed structures of the novel clusters prepared in this study by the X-ray crystallography. Activation of the small molecules will be attempted by the use of polynuclear homo- or heterometallic site in these clusters to exploit the new catalytic reactions that are inaccessible by the mononuclear complex catalyst.

VII-E-1 Syntheses and Structures of Mixed-Metal Sulfido Clusters Containing Incomplete Cubane-Type $M_2M'S_4$ and Cubane-Type $M_2M'_2$-S_4 Cores (M = Mo, W; M' = Rh, Ir)

IKADA, Tomotake[1]**; KUWATA, Shigeki**[1]**; MIZOBE, Yasushi**[2]**; HIDAI, Masanobu**[1]
([1]Univ. Tokyo; [2]Univ. Tokyo and IMS)

[*Inorg. Chem.* **38**, 64 (1999)]

The reactions of sulfido-bridged dimolybdenum and ditungsten complexes $[M_2S_2(\mu\text{-}S)_2(S_2CNEt_2)_2]$ (**1**; M = Mo, W) with an equimolar amount of $[M'Cl(PPh_3)_3]$ (M' = Rh, Ir) gave a series of mixed-metal incomplete cubane-type sulfido clusters $[M'(PPh_3)_2(\mu_3\text{-}S)(\mu_2\text{-}S)_3\{M(S_2CNEt_2)\}_2(\mu_2\text{-}Cl)]$. On the other hand, mixed-metal cubane-type sulfido clusters $[\{M'(cod)\}_2\{MCl(S_2CNEt_2)\}_2(\mu_3\text{-}S)_4]$ (M' = Rh, Ir; cod = 1,5-cyclooctadiene) were obtained by the reactions of **1** with an equimolar amount of $[M'Cl(cod)]_2$. Detailed structures of $[Ir(PPh_3)_2(\mu_3\text{-}S)(\mu_2\text{-}S)_3\{W(S_2CNEt_2)\}_2(\mu_2\text{-}Cl)]$ and $[\{Rh(cod)\}_2\{MoCl(S_2CNEt_2)\}_2(\mu_3\text{-}S)_4]$ have been determined by X-ray crystallography.



VII-E-2 Synthesis and Reactivities of Ir_2Ru Heterobimetallic Sulfido Clusters Derived from a Hydrogensulfido-Bridged Diiridium Complex

KOCHI, Takuya[1]**; NOMURA, Yasuo**[1]**; TANG, Zhen**[1]**; ISHII, Youichi**[1]**; MIZOBE, Yasushi**[2]**; HIDAI, Masanobu**[1]
([1]Univ. Tokyo; [2]Univ. Tokyo and IMS)

[*J. Chem. Soc., Dalton Trans.* 2575 (1999)]

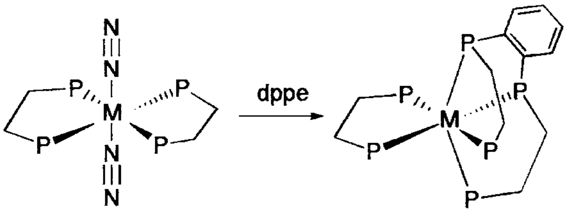
The hydrogensulfido-bridged diiridium complex $[ClCp^*Ir(\mu\text{-}SH)_2IrCp^*Cl]$ reacted with $[RuH_2(PPh_3)_4]$ to give a mixed-metal trinuclear cluster $[(Cp^*Ir)_2(\mu_3\text{-}S)_2RuCl_2(PPh_3)]$ **1**. which was further converted into the cationic diphosphine derivatives $[(Cp^*Ir)_2(\mu_3\text{-}S)_2\text{-}RuCl(L)]Cl$ (L = dppe = $Ph_2PCH_2CH_2PPh_2$ **2** or depe = $Et_2PCH_2CH_2PEt_2$ **3**). The reaction of **2** with Me_2CuLi followed by anion metathesis with KPF_6 afforded the methyl cluster $[(Cp^*Ir)_2(\mu_3\text{-}S)_2RuMe(dppe)][PF_6]$, while treatment of **2** with $CHCl_2Li$ led to formation of $[(Cp^*Ir)\{\eta^4\text{-}C_5Me_5CHCl_2)Ir\}(\mu_3\text{-}S)_2RuCl(dppe)]$, in which one of the Cp* ligands was alkylated by $CHCl_2Li$ to form an η^4-diene. Clusters **2** and **3** were also transformed into the dihydrido clusters $[(Cp^*Ir)_2(\mu_3\text{-}S)_2\text{-}(\mu\text{-}H)_2Ru(L)]$ (L = dppe or depe) by the reaction with $NaBH_4$. On the other hand, **1** was converted into the carbonyl cluster $[(Cp^*Ir)_2(\mu_3\text{-}S)_2RuCl(CO)(PPh_3)]Cl$, the isocyanide clusters $[(Cp^*Ir)_2(\mu_3\text{-}S)_2RuCl(CNXy)\text{-}(PPh_3)]Cl$ (Xy = 2,6-$C_6H_3Me_2$) and $[(Cp^*Ir)_2(\mu_3\text{-}S)_2Ru\text{-}Cl(CNXy)_2(PPh_3)][BPh_4]_2$ and the co-ordinatively unsaturated thiolato clusters $[(Cp^*Ir)_2(\mu_3\text{-}S)_2Ru(SAr)_2]$ (Ar = 2,4,6-$C_6H_2Pr^i{}_3$ **12** or Xy) on treatment with CO, XyNC and LiSAr, respectively.

VII-E-3 Formation of Linear Tetradentate Phosphine Ligand *o*-$C_6H_4(PPhCH_2CH_2PPh_2)_2$ by Coupling of Two Diphosphine Ligands Bound to Low-Valent Mo or W Center. Synthesis and Structure of $[M\{o\text{-}C_6H_4(PPhCH_2CH_2PPh_2)_2\}\text{-}(Ph_2PCH_2CH_2PPh_2)]$ (M = Mo, W)

ARITA, Chirima[1]**; SEINO, Hidetake**[1]**; MIZOBE, Yasushi**[2]**; HIDAI, Masanobu**[1]
([1]Univ. Tokyo; [2]Univ. Tokyo and IMS)

[*Chem. Lett.* 611 (1999)]

A mixture of *trans*-$[M(N_2)_2(dppe)_2]$ (M = Mo or W; dppe = $Ph_2PCH_2CH_2PPh_2$) and dppe was heated to reflux in benzene or toluene to give the M(0) complex $[M(\mathbf{P}_4)(dppe)]$, which contains the novel tetradentate phosphine *o*-$C_6H_4(PPhCH_2CH_2PPh_2)_2$ ($\mathbf{P}_4$) arising from the coupling of two dppe ligands. The reaction of $[Mo(\mathbf{P}_4)(dppe)]$ with CO afforded the carbonyl complex $[Mo(CO)_2(\mathbf{P}_4)]$.



VII-F Activation of Carbon Dioxide and Creation of Reactive Hydroxy- and Oxo-metal Complexes through Activation of Water Molecules on Metals

An electrophilic attack of CO_2 to coordinatively unsaturated low valent metal complexes produces M-η^1-CO_2 complexes, which can be smoothly converted to M-CO ones. Metal complexes with a chelate ring that smoothly opens and closes depending on reaction conditions must be suitable for generation of M-η^1-CO_2 complexes by considering thermal lability of coordinatively unsaturated low valent metal complexes. A major problem of multi-electron reduction of CO_2 in homogeneous reactions is predominant cleavages of metal-CO bonds derived from CO_2 under reductive conditions, because accumulation of too many electrons in the central metals causes reductive cleavage of M-CO bonds. Electro- and photochemical reduction of CO_2 by using ligand localized redox reactions, therefore, may afford a new methodology for multi-electron reduction of CO_2.

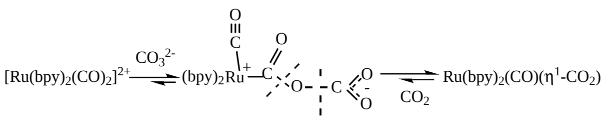
The proton gradient (Δp) between inside and outside of a cell is depicted as the sum of electric activity ($\Delta\psi$) and chemical activity (ΔpH) components. $\Delta p = \Delta\psi - Z\Delta\mathrm{pH}$ ($Z = 2.303\ RT/F$) Proton gradient is equivalent to the neutralization energy because the neutralization reaction takes place if the separating membrane is removed. Biological system creates various valuable energies from the neutralization. Although acids or bases generated in industrial process are just wasted as thermal energy, neutralization energy is originated from the binding energy of acid and base, which is able to be converted directly to chemical energy. Along this line, we tried to convert the neutral energy to electronic energy by using ruthenium-aqua complexes.

VII-F-1 Stabilization of $[Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)]$ and Unprecedented Reversible Oxide Transfer Reactions from CO_3^{2-} to $[Ru(bpy)_2(CO)_2]^{2+}$ and from $[Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)]$ to CO_2

NAKAJIMA, Hiroshi; TSUGE, Kiyoshi; TOYOHARA, Kiyotsuna; TANAKA, Koji

[*J. Organomet. Chem.* **561**, 61 (1998)]

Metal complexes with an η^1-CO_2 group, which is formed by overlap of the filled dz^2 orbital of d^8 metals and the empty CO_2 π^* orbital, are generally extremely labile to air, moisture and temperature. Unusual thermal stability of $[Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)]$ (**1**) as a metal-η^1-CO_2 complex was examined both in the solid state and in solutions. $LiCF_3SO_3$ assists solubilization of **1** in CH_3CN due to the interaction between Li^+ and the η^1-CO_2 group. Electron flow from Ru to the CO_2 ligand induced by Li^+ also largely stabilizes the Ru-CO_2 bond. Oxide transfer from $[Crown{\cdot}K]_2CO_3$ to $[Ru(bpy)_2(CO)_2](PF_6)_2$ smoothly took place in dry CH_3CN to afford **1** through the 1 : 1 adduct with the RuC(O)-OCO_2 moiety. On the other hand, Li^+ caused the oxide transfer from **1** to CO_2 giving $[Ru(bpy)_2(CO)_2]^{2+}$ and CO_3^{2-} due to insolubility of the Li_2CO_3 in organic solvents. Unprecedented reversible oxide transfer from **1** to CO_2 and from CO_3^{2-} to $[Ru(bpy)_2(CO)_2]^{2+}$ proceeds via their 1 : 1 adduct, which was confirmed by the NMR spectra.



VII-F-2 First Artificial Energy Conversion from Proton Gradient to Electricity

TSUGE, Kiyoshi; TANAKA, Koji

[*Chem. Lett.* 1069 (1998)]

Metal-aqua, -hydroxy and -oxo complexes are expected to exist as equilibrium mixtures depending on proton concentrations in solutions (eq 1) when dimerization and

$$[M(H_2O)]^{2+} \rightleftarrows [M(OH)]^{+} \rightleftarrows [M(O)] \qquad (1)$$

oligomerization of these complexes can be effectively depressed. Electron withdrawing ligands will decrease nucleophilicity of the terminal hydroxy and oxo groups, which would serve to depress the formation of μ-OH and μ-O bridged oligomers. We, therefore, introduce redox active quinone ligands to stabilize the aqua, hydroxy and oxo complexes to accommodate extra electrons generated deprotonation of the aqua and hydroxy ligands. As a result, the redox potentials of the complexes reversibly change depending on pH in solutions. The cyclic voltammogram (CV) of [Ru(trpy)-(3,5-di-tert-butylquinone)$(H_2O)]^{2+}$ ($[Ru\text{-}H_2O]^{2+}$) in acetone showed two reversible redox couples at $E_{1/2} = -0.47$ V and $E_{1/2} = 0.38$ V ($E_{1/2} = (E_{pc} + E_{pa})/2$) assigned to the $[Ru\text{-}H_2O]^{0/+}$ and $[Ru\text{-}H_2O]^{+/2+}$ couples, respectively. When 0.7 equiv of OH^- was added to the solution, the rest potential of the solution (V_{rest}) shifted from 0.60 V to 0.30 V across the $E_{1/2}$ of the $[Ru\text{-}H_2O]^{+/2+}$ couple, and new redox couples appeared at $E_{1/2} = -0.80$ V and 0.00 V assignable to the $[Ru\text{-}OH]^{0/+}$ and $[Ru\text{-}OH]^{+/2+}$ couples (eq 2, 3).

$$[Ru\text{-}H_2O]^{2+} + OH^- \rightarrow [Ru\text{-}OH]^{+} + H_2O \qquad (2)$$

$$[Ru\text{-}H_2O]^{2+} + [Ru\text{-}OH]^{+} \rightarrow [Ru\text{-}H_2O]^{+} + [Ru\text{-}OH]^{2+} \qquad (3)$$

Further addition of OH^- caused deprotonation of $[Ru\text{-}OH]^{2+}$ to produce [Ru-O] (eq 4), which equilibrates with the reactant (eq 5).

$$[Ru\text{-}OH]^{2+} + OH^- \rightarrow [Ru\text{-}O]^{+} + H_2O \qquad (4)$$

$$[Ru\text{-}OH]^{2+} + [Ru\text{-}O]^{+} \rightarrow [Ru\text{-}OH]^{+} + [Ru\text{-}O]^{2+} \qquad (5)$$

The energy conversion was conducted with two compartment cells (I and II) separated by an anion exchange membrane filled with an acetone solution of $[Ru\text{-}H_2O]^{2+}$ (7.0 μmol/15 ml in each cell). Upon an addition of 1.6 equivalent of OH^- to cell(I), $[Ru\text{-}H_2O]^{+}$ and $[Ru\text{-}OH]^{+}$ formed and Vrest shifted from 0.60 V to –0.13 V (eqs 2-5). The connection of two cells induced current flow from the cell(II) to cell(I). At the end of the discharge (12 hr later), Vrest of two cells were 0.33 ±

0.02 V, and 0.50 C of electricity was obtained. Thus the proton gradient is catalytically converted to electricity by ruthenium aqua complex [Ru(trpy)(3,5-di-tert-butylquinone) $(H_2O)]^{2+}$.

VII-F-3 Two-Electron Reduction of $[\{(bpy)_2Ru(dmbbbpy)\}_3Ru]^{8+}$ from $(BNA)_2$ via Photoinduced Electron Transfer [dmbbbpy = 2,2'-Bis-(*N*-Methylbenzimidazole-2-yl)-4,4'-bipyridine]

ALI, Md. Meser[1]; SATO, Hiroyasu[1]; TANAKA, Koji; HAGA, Masa-aki; YOSHIMURA, Akio[2]; OHNO, Takeshi[2]
([1]Mie Univ.; [2]Osaka Univ.)

[*Inorg. Chem.* **37**, 6176 (1998)]

Photoirradiation (λ > 500 nm) of $[\{(bpy)_2Ru(dmbbbpy)\}_3Ru]^{8+}$ ($\mathbf{1}^{8+}$) (dmbbbpy = 2,2'-Bis(*N*-methylbenzimidazole-2-yl)-4,4'-bipyridine and bpy = 2,2'-bipyridine) in the presence of dimeric *N*-benzyl-dihydronicotinamide, $(BNA)_2$ produced stable two-electron reduced species ($\mathbf{1}^{6+}$). Laser flash photolysis and emission spectroscopy were used to understand the reductive reaction pathways. The emission quenching k_q value (4.1×10^9 $M^{-1}s^{-1}$) obtained from Stern-Volmer plot is in excellent agreement with the electron transfer rate constant, k_{et} (4.7×10^9 $M^{-1}s^{-1}$) determined from the decay kinetics of transient $^3\mathbf{1}^{8+}$ triplet-triplet absorption at 650 nm indicating that photoreduction of $\mathbf{1}^{8+}$ proceeds via photoinduced electron transfer from $(BNA)_2$ to $^3\mathbf{1}^{8+}*$. After bimolecular electron transfer process, $\mathbf{1}^{8+}$ was reduced to $\mathbf{1}^{7+}$ and electron donor $(BNA)_2$ was oxidized. Oxidation of $(BNA)_2$ leads to the formation of highly reactive species, BNA• which then reduces $\mathbf{1}^{7+}$ to $\mathbf{1}^{6+}$. The quantum yield for the formation of the photo-reduction product was 0.026.

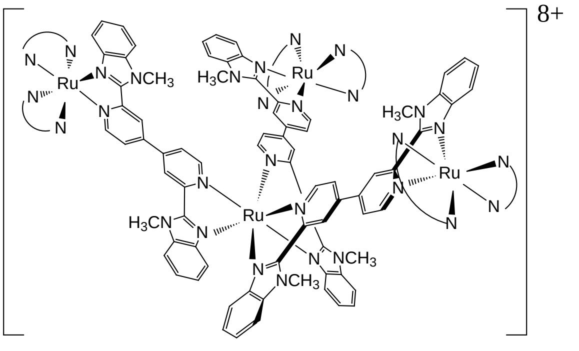


Figure 1. $[\{(bpy)_2Ru(dmbbbpy)\}_3Ru]^{8+}$.

VII-F-4 Selective Production of Acetone in Electrochemical Reduction of CO_2 Catalyzed by Ru-naphthyridine Complex

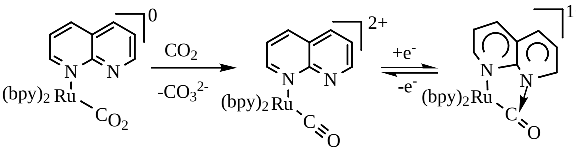
MIZUKAWA, Tetsunori; TSUGE, Kiyoshi; NAKAJIMA, Hiroshi; TANAKA, Koji

[*Angew. Chem., Int. Ed. Engl.* **111**, 373 (1999)]

Carbon dioxide is smoothly converted to CO on metals by oxide transfer from M-CO_2 to CO_2, while reductive cleavage of the resultant metal-CO bond (eq 1) is the major problem in utilization of CO_2 as a C1 resource. Acylation of the metal-CO complexes

$$[M\text{-}\eta^1\text{-}CO_2]^0 \xrightarrow[-CO_3^{2-}]{CO_2} [M\text{-}CO]^{2+} \xrightarrow{2e^-} [M]^0 + CO \quad (1)$$

derived from CO_2 under reductive conditions, therefore, would provide new methodologies for utilization of CO_2 as a staring material in organic synthesis. One and two-electron reductions of $[Ru(bpy)_2(napy)(CO)](PF_6)_2$ (napy = 1,8-naphthyridine-κN) take place in napy localized orbitals, which induce nucleophilic attack of the free nitrogen of napy to the carbonyl carbon (eq2). Electron transfer from the reduced form of napy to the CO group in the metallacycle enables reductive activation of the CO group without the metal-CO bond cleavage and gives rise to electrophilic attack of $(CH_3)_4N^+$ to the carbonyl carbon. As a result, $CH_3C(O)CH_3$ and CO_3^{2-} were catalytically produced in the electrochemical reduction of $[Ru(bpy)(napy\text{-}\kappa N)_2(CO)_2](PF_6)_2$ in the presence of in CO_2-saturated DMSO when $(CH_3)_4NBF_4$ was used as an electrolyte (eq 3).



(2)

$$2CO_2 + 4e^- + 2(CH_3)_4N^+ \rightarrow CH_3C(O)CH_3 + CO_3^{2-} + 2(CH_3)_3N \quad (3)$$

VII-F-5 Basicity of μ_3-X and η^1-Y Ligands (X, Y = S, Se) of Reduced, Oxidized and Super-Oxidized Forms of $[Fe_4X_4(YAd)_4]^{2-}$ (Ad = 1-Adamantane) in Aqueous Solutions

NAKAMOTO, Masami; FUKAISHI, Kenji; TAGATA, Tsuyoshi; KAMBAYASHI, Hide; TANAKA, Koji

[*Bull. Chem. Soc. Jpn.* **72**, 407 (1999)]

Synthetic 4Fe4S clusters are subject to hydrolysis under aqueous conditions. A series of $[Fe_4X_4(YAd)_4]^{2-}$ (X, Y= S, Se; Ad= 1-adamantane) solubilized in aqueous poly[2-dimethylamino(hexanamide)] (PDAH) solutions were stable due to the enbedding effect in hydrophobic environment and inhibition of dissociation of the terminal ligand into the aqueous media. Cyclic voltammetry of the clusters in the solutions showed pH dependent redox potentials of not only $[Fe_4X_4]^{+/2+}$ but also $[Fe_4X_4]^{2+/3+}$ (X, Y = S and Se) couples, resulting from redox-linked protonation reactions of the three oxidation states of $[Fe_4X_4(YAd)_4]^{n-}$ (n = 1–3), which enabled to determine the pK of each oxidation state. Computer simulation of the pH dependent redox potentials indicated the basicity of the μ_3-X cores (X = S and Se) of $[Fe_4X_4(YAd)_4]^{n-}$ (n = 1, 2, 3) is stronger than the YAd (Y = S and Se) ligands. In the case of the mono-protonated $[Fe_4X_4(YAd)_4]^{3-}(H^+)$ and $[Fe_4X_4(YAd)_4]^{2-}(H^+)$, thre basicity of the η^1-Y ligand of $[Fe_4X_4(YAd)_4]^{2-}(H^+)$ becomes stronger than that of μ_3-X cores. On the other hand, the μ_3-X of $[Fe_4X_4(YAd)_4]^{3-}$-(H^+) still show strong basicity compared with those of η^1-Y ligands.

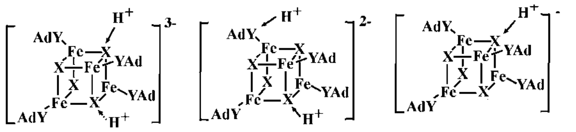


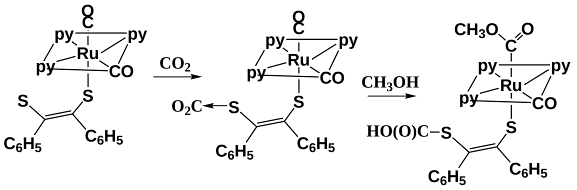
Figure 1. Protonation of $[Fe_4X_4(YAd)_4]^{n-}$ (X,Y = S, Se: n = 2, 1, 0) in aqueous PDAH solutions: dotted arrow is estimated by computer simulation.

VII-F-6 Double Addition of CO_2 and CH_3OH to Ruthenium Carbonyl Complex with Novel Mono-Dentate Dithiolene

SUGIMOTO, Hideki; TSUGE, Kiyoshi; TANAKA, Koji

[*Chem. Lett.* in press.]

The reaction of $[Ru(CO)_2Cl(terpy)]PF_6$ and Na_2mnt in CH_3OH gave a yellow complex (**1**) with mono-dentate mnt. On the other hand, the reaction between $[Ru(CO)_2Cl(terpy)]^+$ and $Cs_2S_2C_2Ph_2$ in CH_3OH under aerobic conditions gave a complex (**2**) with thio-carboxylic acid and methoxy carbonyl groups rather than the expected $[Ru(CO)_2(SSC_2Ph_2\text{-}\kappa^1S)(terpy\text{-}\kappa^3N,N',N'')]$. The most characteristic feature of **2** is that the carbonyl and the uncoordinate thiolate of **1** are changed to methoxy carbonyl and thio-carboxylato units, respectively. Although it is not clear that the carboxylato moiety of **2** exists as protonated or deprotonated form by X-ray analysis, the former is deduced from the elemental analysis and the charge balance of **2**. Unprecedented double addition of CO_2 and methanol to thiolate and carbonyl ligands located far from each other is apparently caused by the long-range π-π interaction between basic $Ph_2C_2SS^{2-}$ and acidic carbonyl units through d-orbitals of the rutheniurn atom.



VII-G Molecular Self-assembly Through Coordination

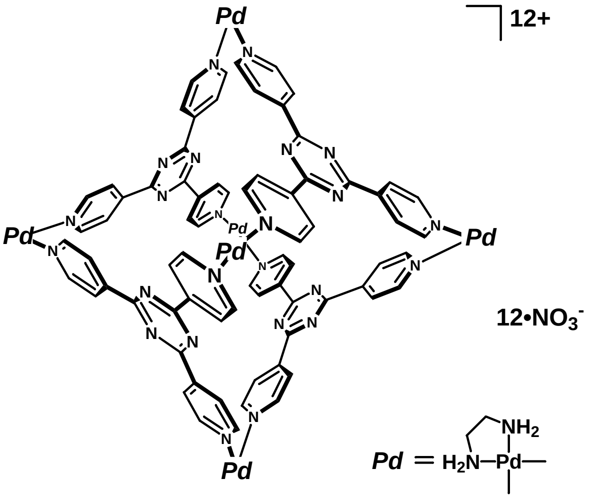
Molecular self-assembly refers to the spontaneous generation of well-defined structures from component molecules under a well-defined set of conditions. Since 1990, we have been studying the self-assembly of descrete structures based on coordination chemistry, where coordinate bonds induce the generation of defined structures. Studies during 1998-1999 are focused on the self-assembly of such three dimensional systems as cages, capsules, tubes, bowls, and 3D-interlocked molecules. Our strategy is characterized by the use of a cis-protected Pd(II) unit as a convergent block for molecular assembly, providing 90 degree coordination angle.

VII-G-1 Encapsulation of Large, Neutral Molecules in a Self-Assembled Nanocage Incorporating Six Palladium(II) Ions

KUSUKAWA, Takahiro; FUJITA, Makoto

[*Angew. Chem., Int. Ed. Engl.* **37**, 3142 (1998)]

Cage compound **1** encapsulates as many as four molecules of *o*-carborane (8 Å in diameter). A large guest, 1,3,5-tri-*tert*-butylbenzene, once encapsulated by thermally-activated slippage, cannot escape from the cavity at room temperature since its dimension is slightly larger than that of the cavity window.



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VII-G-2 “Ship-in-a-Bottle” Formation of Stable Hydrophobic Dimers of *cis*-Azobenzene and -Stilbene Derivatives in a Self-assembled Coordination Nanocage

KUSUKAWA, Takahiro; FUJITA, Makoto

[*J. Am. Chem. Soc.* **121**, 1397 (1998)]

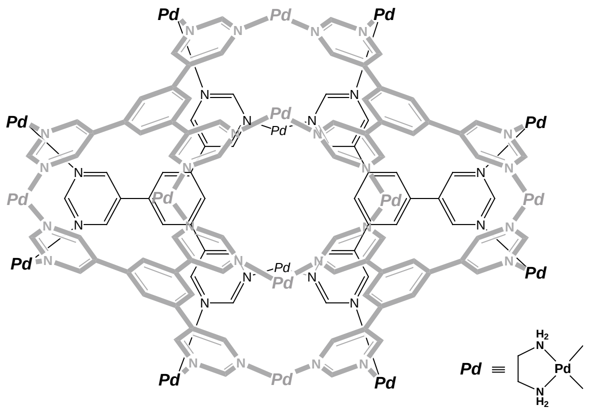
Nano-sized coordination cage **1** (see compound **1** in **VII-G-1**) has been shown to enclathrate large neutral guest molecules. Here we report the selective enclathration of “C-shaped” molecules such as *cis*-azobenzene and -stilbene derivatives by cage **1**. These guest molecules are enclathrated in the cavity through the “ship-in-a-bottle assembly” into a hydrophobically interacted dimer. The hydrophobic dimers of azobenzene derivatives are considerably stabilized and do not undergo *cis-trans* isomerization.

VII-G-3 A Nonometer-Sized Hexahedral Coordination Capsule Assembled from 24 Components

TAKEDA, Nobuhiro[1]; UMEMOTO, Kazuhiko[2]; YAMAGUCHI, Kentaro[3]; FUJITA, Makoto
([1]CREST, Jpn. Sci. Tech. Co. (JST); [2]GUAS; [3]Chiba Univ.)

[*Nature* **398**, 794 (1999)]

Molecular capsules consist of closed, hollow frameworks within which encapsulated molecules are isolated from interaction with external molecules. In this environment, otherwise reactive molecules can be stabilized. Although some molecular capsules have been prepared by conventional synthetic chemistry, recent progress in non-covalent synthesis has allowed the creation of capsules held together by hydrogen bonds. Here we report the use of transition-metal based coordination chemistry to assemble a stable, nanometre-scale capsule **1** from 24 small components: 18 metal ions and six triangular ligands. The capsule is roughly hexahedral and comprises six edge-sharing triangles with two metal ions on each edge. This internal space has a volume of 900 Å and is fully closed to all but very small molecules.



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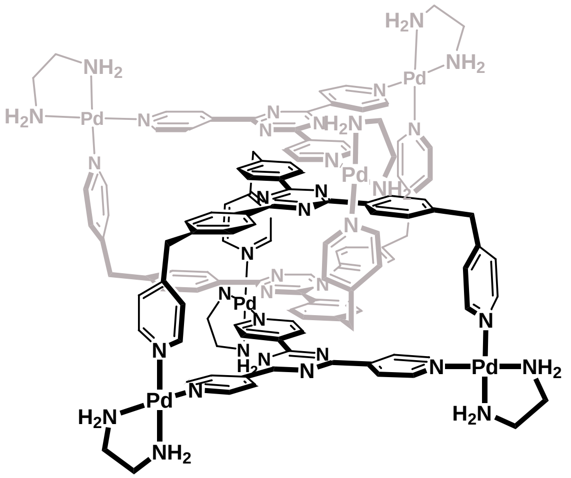
VII-G-4 Spontaneous Assembly of Ten Components into a Two Interlocked, Identical Coordination Cages

FUJITA, Makoto; FUJITA, Norifumi[1]; OGURA, Katsuyuki[2]; YAMAGUCHI, Kentaro[2]
([1]GUAS; [2]Chiba Univ.)

[*Nature* **400**, 52 (1999)]

Supermolecules consisting of interlinked ring-like molecules (catenanes) are an interesting target for chemical synthesis both for their intrinsic interest as non-covalently bound but robust assemblies and because of the perspective they offer on materials chemistry. Catenanes have been prepared by metal-ion templating and self-assembly through other non-covalent interactions. Here we report the synthesis of catenane **1** composed not of two interlocking rings but of two cages. This structure is prepared by metal-mediated self-assembly. The framework of each cage is assembled from five components: two tridentate legands held together with three metal ions. Because each cage framework can bind an aromatic ring, two cage units will bind one another during their assembly process through the formation of a quadruple aromatic stack, giving rise to the ten-component interlocked supermolecule.



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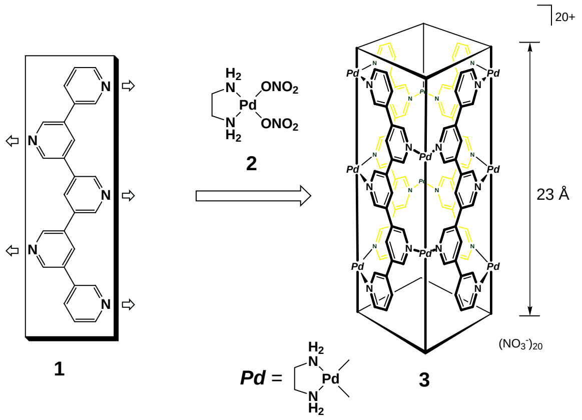
VII-G-5 Quantitative Formation of Coordination Nanotubes Templated by Rod-like Guests

AOYAGI, Masaru[1]; BIRADHA, Kumar[2]; FUJITA, Makoto
([1]GUAS; [2]JSPS)

[*J. Am. Chem. Soc.* **121**, 7457 (1999)]

Molecular-based tubular structures have attracted considerable current interest because of their potential abilities for selective inclusion and transportation of ions and molecules and catalysis for specific chemical transformations, by exploiting the interior space of the tubes. In the present study, coordination nanotubes **3** are constructed by linking oligo(3,5-pyridine)s **1** with a cis-protected Pd(II) building block, (en)Pd$(NO_3)_2$ (**2**, en = ethylenediamine). This transformation was in fact accomplished with the remarkable template effect of biphenyl derivatives. Thus, the reaction of **1** and **2** first resulted in the formation of uncharacterizable products. However, the addition of sodium 4,4'-biphenylenedicarboxylate to the solution induced the smooth assembly of nanotubes **3** wherein four oligo(3,5-pyridine) molecules were held together with six to ten Pd(II) units. A nanotube structure templated by a guest was confirmed by an X-ray crystallographic analysis.

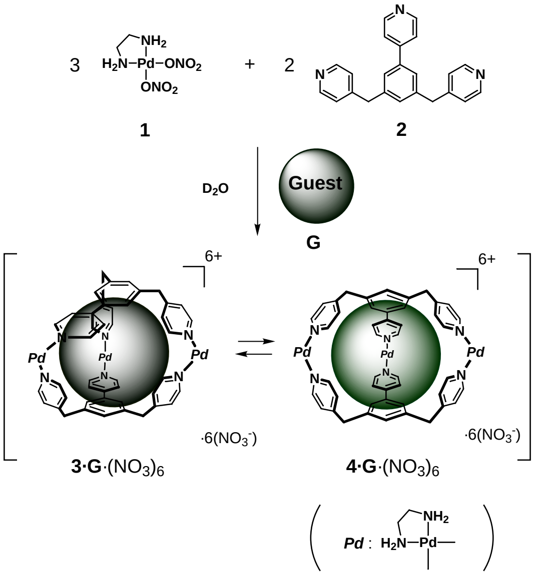


VII-G-6 Guest-Selected Formation of Pd(II)-Linked Cages from a Prototypical Dynamic Library

HIRAOKA, Shuichi[1]; FUJITA, Makoto
([1]CREST, Jpn. Sci. Tech. Co. (JST))

[*J. Am. Chem. Soc.* in press]

Biological receptors modulate the shape and size of their recognition sites to bind substrate molecules, generating numerous receptor structures from which the most suitable one is selected (or induced-fit) by their substrates. Modeling such a system is particularly important to develop a new receptor design wherein artificial receptors are constructed through a selection process by their own guests. Although previous examples are dealing with the induced-fit control of receptor conformations, there are only several reports on the control of receptor linkages. Here we report the guest-selected formation of its optimal cage-like receptor from an equilibrium mixture of receptors. In the following scheme, Pd(II)-linked cages, **3** and **4**, and some oligomeric compounds, accessible from the same components **1** and **2**, are in equilibrium. From this thermodynamic mixture, each cage structure is selected upon the addition of appropriate guest molecules. This phenomenon is a prototype for "dynamic receptor library," which represents one of important goals in the field of molecular recognition.



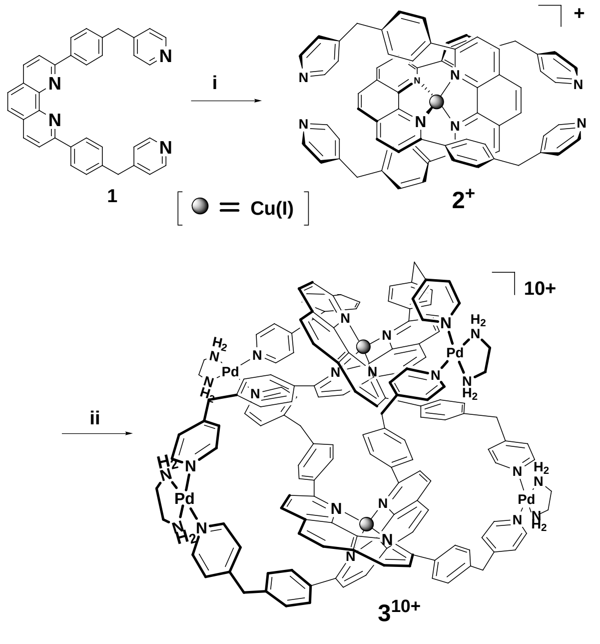
VII-G-7 Quantitative and Spontaneous Formation of a Doubly Interlocking [2]Catenane using Copper(I) and Palladium(II) as Templating and Assembling Centers

IBUKURO, Fumiaki[1]; FUJITA, Makoto; YAMAGUCHI, Kentaro[2]; SAUVAGE, Jean-Pierre[3]
([1]GUAS; [2]Chiba Univ.; [3]Univ. Louis Pasteur)

[*J. Am. Chem. Soc.* in press]

A new strategy based on pure coordination chemistry has been used to construct a 4-crossing [2]catenane. The ligand **1** contains a central 1,10-phenanthroline site attached to two pendent/4-pyridyl groups. The central site is used to complex a copper(I) center whereas the lateral pyridine groups are coordinated to palladium(II).

The stepwise complexation procedure is virtually quantitative. It can be carried out both ways (copper(I) followed by palladium(II) or reverse). The final complex **3** is a chiral species incorporation 4 ligands, 2 copper(I) and 4 palladium(II) centres. It has been characterized in solution and its structure has been evidenced by ESI-MS.



VII-G-8 Flexible Coordination Networks with Fluorinated Backbones. Remarkable Ability for Made-to-Order Enclathration of Organic Molecules

KASAI, Kayoko[1]; AOYAGI, Masaru[2]; FUJITA, Makoto
([1]Miyagi Univ. Education; [2]GUAS)

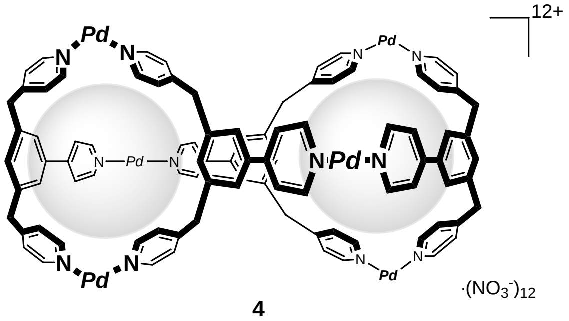
We have designed and prepared flexible ligands containing fluorinated aromatic rins: $PyCH_2$-R_f-CH_2Py; Py = 4-pyridyl, R_f = -C_6F_4-, -C_6F_4-C_6F_4-, and -$C_{10}F_6$-. Because of very weak intermolecular forces among fluorinated compounds, networks from these ligands and metal ions are not apt to be constricted or interpenetrated, but prefer to interact with guest molecules to form clathrate compounds. In these clathrate complexes, we have found that the network topologies are induced-fit by guest molecules owing to the flexibility of the ligand frameworks giving rise to 1D, 2D, and 3D structures with large cavities. Consequently, we have achieved "made-to-order" enclathration of a variety of organic guests with the flexible, fluorinated coordination networks.

VII-G-9 Kinetic and Thermodynamic Aspects in the Substrate-Induced Assembly of Optimal Receptors from a Dynamic Library

HIRAOKA, Shuichi[1]; KUBOTA, Yasuo[2]; BIRADHA, Kumar[3]; FUJITA, Makoto
([1]CREST, Jpn. Sci. Tech. Co. (JST); [2]Nagoya Univ.; [3]JSPS)

Pyridine functionalized C_{2v} ligand **1** (see compound **2** in **VII-G-6**) has been recently shown to provide a mixture of more than two cage-like receptors upon complexation with (en)Pd^{2+} coordination block. The mixture thus obtained can be termed as "dynamic receptor library" because appropriate substrates induce the assembly of their optimal receptors from the mixture. Further studies on this thermodynamic phenomenon have elucidated some important structural and mechanistic aspects.

We report here that, in addition to M_3L_2 type receptors **2** and **3** (see compounds **3** and **4** in **VII-G-6**, respectively), dimeric M_6L_4 cage 4 is involved in the equilibrium mixture. Interestingly, **2** and **3** interconvert via the dimeric M_6L_4 form as revealed by a kinetic study. Furthermore, symmetrical M_3L_2 cage **2** and M_6L_4 dimer **4** are isolated and characterized by X-ray crystallography. These results emphasize how easily a variety of host frameworks with different conectivities and stoichiometries are generateed from only one ligand component and how precisely the optimal receptor frameworks are selected from the equilibrated cage molecules or a "dynamic receptor library."



4

VII-G-10 Dynamic Behavior of Rod-like Guest Accomodated in Coordination Nanotubes

AOYAGI, Masaru[1]; FUJITA, Makoto
([1]GUAS)

Oligo(3,5-pyridine) ligands **1** self-assemble into coordination nanotubes 2 with the aid of remarkable templete effect of rod-like guest (For the structures of **1** and **2**, see those of **1** and **3** in **VII-G-5**, respectively). Studies on the dynamic behavior of guest molecules accomodated in the tubes are particularly interesting because guests are expected to move only in a one-dimensional way within a tightly fitted tubular space and such a restricted guest motion would lead to novel functions of tubular molecules: *e.g.*, shape-selective molecular transportation and (catalytic) chemical transformation. Here, we report NMR studies on the dynamic motion of the guests accommodated in the coordination nanotube. Guest molecules are found to shuttle in the tube without turning their head and tail at room temperature, but intermolecularly exchange at elevated temperature.

VII-G-11 Wacher Oxidation in an Aqueous Phase Through the Reversed Phase-Transfer Catalysis of a Self-Assembled Nanocage

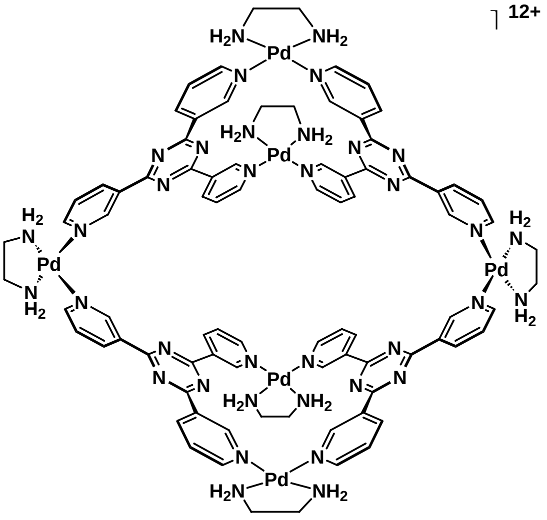
ITO, Hirokazu[1]**; KUSUKAWA, Takahiro; FUJITA, Makoto**
([1]GUAS)

Chemical transformation in aqueous media is a current trend in synthetic chemistry in view of developing clean technology. One of the best approaches to water-based reactions is to develope reversed phase-transfer catalysts which bring organic substrates into aqueous phase, let them react with aqueous reagents, and take out products from the aqueous phase. This paper reports that the coordination nanocage **1** (see compound **1** in **VII-G-1**) shows the reversed phase-transfer catalysis toward Wacker oxidation of olefins which is a typical Pd(II)-promoted catalytic reaction. Thus, styrene is effectively and catalytically oxidized to acetophenone (86% yield) by treating it with aqueous solution of (en)Pd(NO_3)$_2$ (10 mol%) and cage **1** (10 mol%).

VII-G-12 Hydrophobic Assembling of a Coordination Nanobowl into a Dimeric Capsule Which can Accommodate upto Six Large Organic Molecules

YU, Shu-Yan[1]**; KUSUKAWA, Takahiro; KUMAR, Biradha**[1]**; FUJITA, Makoto**
([1]JSPS)

Dimerization of bowl-shaped molecules is an atractive approach to molecular capsules which are capable of accommodating organic moleucles within their interior space. Both covalent and non-covalent dimers of bowl-shaped molecules have been studied during the last decade. Recently reported coordination nanobowl **1** provides a unique component for a dimeric capsule because the nature of the bowl is amphiphilic: *i.e.*, the open cavity of **1** is surrounded by 16 aromatic rings and thus hydrophobic, whereas the outside surface of the bowl is hydrophilic due to the explosure of six charged Pd(II) centers. Threfore, bowl **1** is expected to assemble in aqueous media into a dimeric capsule creating a large hydrophobic pocket inside the framework. Reported here is that such a dimeric strucure assembles in a solid state accommodating as many as six neutral organic molecules. Spectroscopic studies elucidated that the same structure also exsists even in solution.



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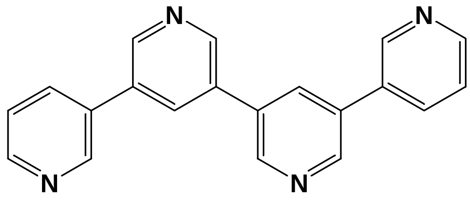
VII-G-13 Porous Coordination Polytubes

BIRADHA, Kumar[1]**; AOYAGI, Masaru**[2]**; FUJITA, Makoto**
([1]JSPS; [2]GUAS)

Despite great interest in porous coordination polymers assembled from metals and bridging ligands, there remains difficulty in predicting cavities in the polymer frameworks because of the frequently encountered unfavorble interpenetration of the networks. This problem can be solved by designing organic lignads which are unable to give interpenetrated networks. In this regard, use of a panel-like ligand such as **1** is attractive because its coordination assembly is expected to give polytube structures which are not allowed to interpenetrate. In this report we show that, upon treatment with atransition metal (CuI), ligand **1** assembles into polytube structures which accomodate organic guests in the tubuler cavities. Interesingly, the polytube structures are templated by the guest employed; *i.e.*, two polytubes possessing different linkage conectivities with the accessible porosity of *ca.* 30–50% have been obtained by using different organic guests.



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VII-G-14 X-Ray And NMR Observation of Encapsulated Molecules in a Self-Assembled Coordination Nanocage

KUSUKAWA, Takahiro; FUJITA, Makoto

Nano-sized coordination cage **1** (see compound **1** in **VII-G-1**) has been shown to enclathrate "C-shaped" molecules such as *cis*-azobenzene and -stilben derivatives. The dimeric assembly of the guests was evidenced for a diaryl diketone guest **2**, by X-ray crystallography (Figure 1), which showed the formation of M and P helical conformations for the guest molecule. Due to the formation of a desymmetrized M/P meso dimeric structure, the ^{1}H-NMR showed 12 signals for the pyridine protons of the triazine ligand. This observation indicated that the conformation of guest molecule **2** was fixed as a meso-dimeric form even in a solution.

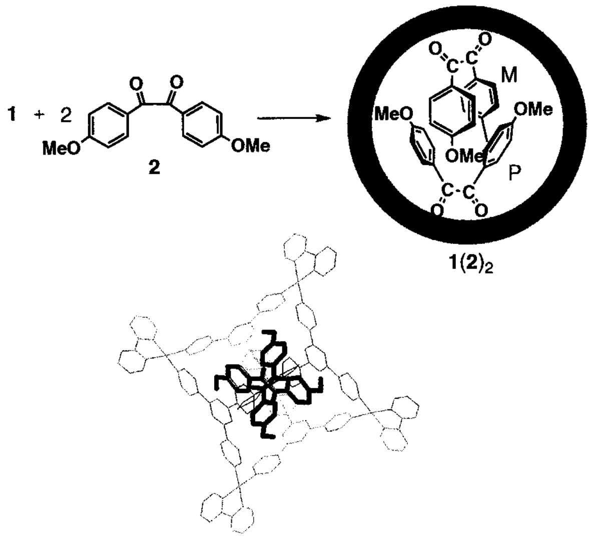


Figure 1. The crystal structure of **1**(**2**)$_2$.

VII-H Synthesis and Reactivity of Complexes Containing Peculiar Bonds between Transition Elements and Main Group Elements

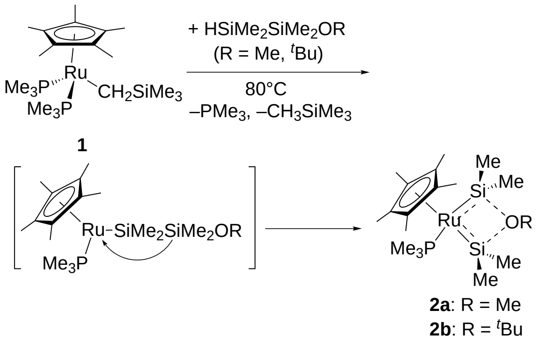
The bonds between transition elements and main group elements are attracting increasing attention in recent years. This is attributable not only to the great variety of the combination of elements but also to the peculiarity of their physical and chemical properties. We are currently focusing on transition metal complexes containing novel and peculiar bonds between transition elements and some main group elements, particularly single and multiple bonds to silyl, silene, and sulfido ligands. We are examining the synthesis, structures, fluxional behaviors, and reactivity of these complexes to gain a better understanding on the characters of these bonds.

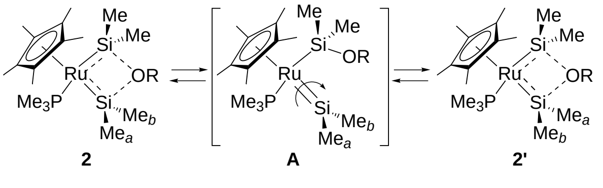
VII-H-1 Fluxional Behavior of Alkoxy-Bridged Bis(silylene)ruthenium Complexes $Cp^*(Me_3P)Ru\{SiMe_2{\cdot\cdot}O(R){\cdot\cdot}SiMe_2\}$ (R = Me, ^{t}Bu) Caused by Rotation of the Silylene Ligands

WADA, Hiroaki[1]**; TOBITA, Hiromi**[1,2]**; OGINO, Hiroshi**[1]
([1]Tohoku Univ.; [2]IMS)

[*Chem. Lett.* 993 (1998)]

Heating a hexane solution of $Cp^*(Me_3P)_2RuCH_2SiMe_3$ (**1**; Cp* = η^5-C_5Me_5) and $HSiMe_2SiMe_2OR$ (R = Me, ^{t}Bu) at 80 °C overnight in a sealed tube gave alkoxy-bridged bis(silylene)ruthenium complexes $Cp^*(Me_3P)Ru\{SiMe_2{\cdot\cdot}O(R){\cdot\cdot}SiMe_2\}$ (**2a**: R = Me; **2b**: R = ^{t}Bu) in 77 and 39% yields, respectively. The exchange of Si-Me groups in **2a** and **2b** through silylene ligand rotation on the intermediate **A** was observed by variable temperature ^{1}H NMR spectroscopy. Such a fluxionality was not observed in $CpLRu\{SiMe_2{\cdot\cdot}O(Me){\cdot\cdot}SiMe_2\}$ (L = PPh_3, CO) nor in the iron analogues. Thus, this fluxionality is considered to be due to the weakened Si··O partial bonds caused by the strong electron-releasing effect of Cp* and PMe_3 ligands.



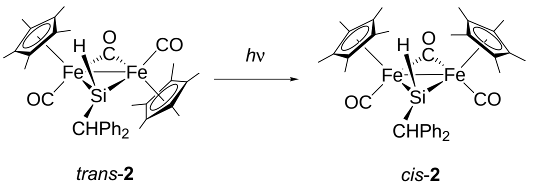


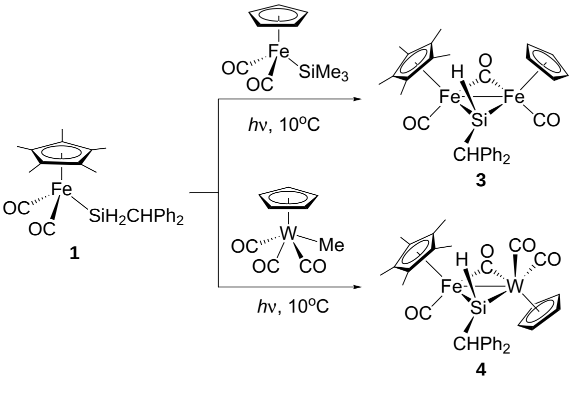
VII-H-2 Preparation of Silanediyl-Bridged Fe-Fe and Fe-W Dinuclear Complexes. X-Ray Structures of $[Cp^*Fe(CO)(\mu\text{-}CO)\{\mu\text{-}Si(H)CHPh_2\}(CO)_nMCp]$ (Cp* = C_5Me_5, Cp = C_5H_5, M = Fe, n = 1; M = W, n = 2)

LUH, Lung-Shiang[1]**; WEN, Yuh-Sheng**[1]**; TOBITA, Hiromi**[2,3]**; OGINO, Hiroshi**[3]
([1]Academia Sinica, Taipei; [2]IMS; [3]Tohoku Univ.)

[*Bull. Chem. Soc. Jpn.* **71**, 2865 (1998)]

Photolysis of a 2:1 mixture of $[Cp^*Fe(CO)_2Me]$ and Ph_2CHSiH_3 produces the mononuclear silyl complex $[Cp^*Fe(CO)_2\{Si(H)_2CHPh_2\}]$ (**1**) as a main product in 41% yield together with two silanediyl-bridged diiron complexes, *cis*- and *trans*-$[Cp^*_2(CO)_2Fe_2(\mu\text{-}CO)\{\mu\text{-}Si(H)CHPh_2\}]$ (**2**), and $[\{Cp^*Fe(CO)_2\}_2]$. The *trans*-**2** complex isomerizes to *cis*-**2** photochemically, but no *cis-trans* isomerization occurs thermally below 100 °C. Photolysis of $[CpFe(CO)_2SiMe_3]$ or $[CpW(CO)_3Me]$ in the presence of **1** produces novel unsymmetrical silanediyl-bridged complexes $[Cp^*Fe(CO)(\mu\text{-}CO)\{\mu\text{-}Si(H)CHPh_2\}(CO)_nMCp]$ (**3**: M = Fe, n = 1; **4**: M = W, n = 2) in moderate yields. Complexes **3** and **4** have been characterized by X-ray diffraction analysis. To the best of our knowledge, complex **4** is the first example of silanediyl-bridged Fe-W complex. The Cp and Cp* rings are mutually *cis* with the dihedral angle of 78.7(2)° in complex **3** but they are *trans* with the dihedral angle of 13.1(6)° in complex **4**.



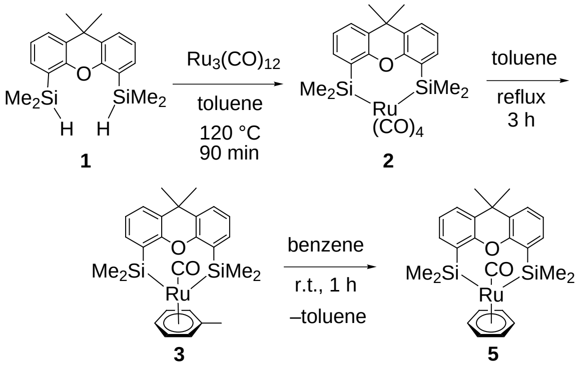


VII-H-3 Extremely Facile Arene Exchange on a Ruthenium(II) Complex Having a Novel Bis(silyl) Chelate Ligand (9,9-Dimethylxanthene-4,5-diyl)bis(dimethylsilyl) (Xantsil)

TOBITA, Hiromi[1,2]**; HASEGAWA, Kenji**[2]**; MINGLANA, Jim Josephus Gabrillo**[2]**; LUH, Lung-Shiang**[3]**; OKAZAKI, Masaaki**[2]**; OGINO, Hiroshi**[2]
([1]IMS; [2]Tohoku Univ.; [3]Academia Sinica, Taipei)

[*Organometallics* **18**, 2058 (1999)]

Heating a solution of 4,5-bis(dimethylsilyl)-9,9-dimethylxanthene (xantsilH_2) (**1**) and 0.4 molar equivalent of $Ru_3(CO)_{12}$ in toluene at 120 ºC for 90 min afforded a ruthenium complex having a novel bis(silyl) chelate ligand (9,9-dimethylxanthene-4,5-diyl)bis-(dimethylsilyl) (xantsil), *cis*-$Ru(CO)_4$(xantsil) (**2**), as a main product. The X-ray crystal structure analysis showed that the Ru-Si bonds in **2** (2.562(2) and 2.564(2) Å) represent the longest known Ru-Si bonds ever reported probably because of the intramolecular steric repulsion. Isolated **2** reacted with toluene on refluxing for 3 h to give *cis*-Ru(CO)(xantsil)(η^6-$C_6H_5CH_3$) (**3**) in 95% yield. When **3** was dissolved in benzene, the η^6-toluene ligand was cleanly substituted by the solvent at room temperature within 1 h to afford *cis*-Ru(CO)-(xantsil)(η^6-C_6H_6) (**5**) quantitatively.



VII-H-4 Synthesis and Structures of Heterometallic Trinuclear Clusters $[CpFe(CO)_2]_2(\mu_3\text{-}S_2)W(CO)_5$ and $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu_3\text{-}S)W(CO)_5$ and Kinetic Study of Migration of the $W(CO)_5$ Moiety in the Disulfido Complex

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Reaction of $CpFe(CO)_2Br$ with an excess of NaSH in THF at room temperature resulted in formation of a brown solution. Addition of $W(CO)_5(THF)$ after 2 h to the reaction mixture gave two heterometallic trinuclear clusters $[CpFe(CO)_2]_2(\mu_3\text{-}S_2)W(CO)_5$ (**1**) and Cp_2Fe_2-$(CO)_2(\mu\text{-}CO)(\mu_3\text{-}S)W(CO)_5$ (**2**) in 30 and 11% yields, respectively. X-ray crystal structures of both **1** and **2** were determined. Complex **1** is the first example of a trinuclear cluster connected by only one disulfido ligand in an η^1:η^1:η^1 fashion. Variable-temperature ^1H NMR spectroscopy of **1** clearly showed that the $W(CO)_5$ moiety is migrating between two sulfur atoms faster than the NMR time scale to make the two Cp ligands equivalent. A mechanism involving oxidative addition-reductive elimination of the S-S bond was proposed for this fluxional behavior.