

RESEARCH ACTIVITIES VII

Coordination Chemistry Laboratories

Prof. Nobuhiro Tokito, Prof. Kiyotaka Onizuka took the position of Laboratory of Coordination Bond from April 2001. Prof. Takuzo Aida (Tokyo University) and Assoc. Prof. Kaku Hamachi (Kyushu University) finished their term as Adjunct Prof. of the Synthetic Coordination Chemistry in March 2001. Their effort during their term is gratefully appreciated. Prof. Isao Taniguchi (Kumamoto University) and Assoc. Prof. Yasutaka Tanaka (Shizuoka University) continue the position of the Synthetic Coordination Chemistry.

VII-A A Diversity-Based Approach to Novel Chiral Units

Catalytic asymmetric reactions have attracted significant interest for their synthetic utility. One of the most exciting and challenging subjects in research on the catalytic asymmetric synthesis is development of the novel and basic chiral units. Homochiral organic molecules bearing hetero atoms (*e.g.* nitrogen, phosphorus, *etc.*) occupy a prominent position in organic chemistry as both useful synthetic reagents and molecules of biological interest. Highly functionalized optically active bicyclic amines having a pyrrolo[1,2-*c*]imidazolone framework were identified as effective chiral agents through a diversity-based approach to new chiral amine catalysts.

VII-A-1 A Parallel Preparation of A Bicyclic *N*-Chiral Amine Library and Its Use for Chiral Catalyst Screening

UOZUMI, Yasuhiro; MIZUTANI, Kanako; NAGAI, Shin-ichi

[*Tetrahedron Lett.* **42**, 407 (2001)]

A parallel library of optically active bicyclic tertiary amines bearing *N*-chiral bridgehead nitrogen atoms was readily prepared by condensation of primary amines, cyclic amino acids, and aldehydes. The enantiocontrolling ability of each of the library members was examined for the asymmetric alkylation of benzaldehyde with diethylzinc, and (3*R*,6*R*,7*aS*)-(2,3-diphenyl-6-hydroxy)hexahydro-1*H*-pyrrolo[1,2-*c*]imidazol-1-one, which contains β -amino alcohol unit, showed high enantioselectivity.

VII-A-2 Enantioselective Desymmetrization of Meso-Cyclic Anhydrides Catalyzed by Hexahydro-1*H*-pyrrolo[1,2-*c*]imidazolones

UOZUMI, Yasuhiro; YASOSHIMA, Kayo; MIYACHI, Takamasa; NAGAI, Shin-ichi

[*Tetrahedron Lett.* **42**, 411 (2001)]

Enantioselective desymmetrization of meso compounds is a powerful synthetic means of preparing enantiomerically enriched products where plural stereogenic carbon centers are generated in one step. Enantioselective ring opening of meso cyclic anhydrides is one of the cases. Asymmetric methanolysis of meso cyclic carboxylic anhydrides including hexahydrophthalic anhydride proceeded in toluene in the presence of (6*R*,7*aS*)-(2-aryl-6-hydroxy)hexahydro-1*H*-pyrrolo[1,2-*c*]imidazol-1-one to give the corresponding desymmetrized mono ester acids (*e.g.* (1*S*,2*R*)-2-(methoxycarbonyl)-cyclohexane-1-carboxylic acid) with enantiomeric excesses of up to 89%.

VII-B Catalysis in Aqueous Media by Using of Amphiphilic Polymer-Supported Catalysts

Catalytic organic transformations in water using recyclable immobilized catalysts is an important goal in synthetic organic chemistry. We recently reported that several palladium-catalyzed reactions, including π -allylic substitution, carbonylation, the Heck reaction, and Suzuki-Miyaura cross-coupling, took place in water by use of palladium-phosphine complexes bound to an amphiphilic polystyrene-poly(ethylene glycol) graft copolymer (PS-PEG) resin. A chiral palladium complex and a quaternary ammonium salt immobilized on PS-PEG resin were designed and prepared, respectively. Allylic alkylation and Michael addition were investigated by using the resin-supported catalysts in water.^{aa}

VII-B-1 Catalytic Asymmetric Allylic Alkylation in Water with a Recyclable Amphiphilic Resin-Supported *P,N*-Chelating Palladium Complex

UOZUMI, Yasuhiro; SHIBATOMI, Kazutaka

[*J. Am. Chem. Soc.* **123**, 2919 (2001)]

A novel *P,N*-chelate chiral ligand, (3*R*,9*aS*)-(2-aryl-3-(2-diphenylphosphino)phenyl)-tetrahydro-1*H*-imidazo[1,5-*a*]indole-1-one was designed, prepared, and immobilized on an amphiphilic polystyrene–poly(ethylene glycol) graft copolymer (PS–PEG) resin. A palladium complex of the PS–PEG resin-supported *P,N*-ligand catalyzed the allylic substitution of both cyclic and acyclic allylic esters in water with high enantioselectivity. Reactions of cyclopentenyl, cyclohexenyl, and cycloheptenyl carbonates with dialkyl malonate gave the corresponding alkylated products with enantiomeric excess ranging from 89 to 98% ee. The PS-PEG supported Pd complex was readily recovered by simple filtration and reused without loss of catalytic activity or enantioselectivity.

VII-B-2 Michael Reactions in Water Using Amphiphilic Resin-Supported Quaternary Ammonium Hydroxides

SHIBATOMI, Kazutaka; NAKAHASHI, Toshiyuki; UOZUMI, Yasuhiro

[*Synlett* 1643 (2000)]

Quaternary ammonium hydroxides were immobilized on a polystyrene–poly(ethylene glycol) copolymer resin. The amphiphilic polymer-supported ammonium hydroxides catalyzed Michael reaction of cyclic β -keto esters with several Michael acceptors in water to give corresponding adducts in high yields.

VII-C Electrochemical Analysis of Biological Functions of Metalloproteins and Their Mutated Molecules and Its Applications to Coordination Chemistry for Catalysis

Using surface-functionalized electrodes, biological functions and bioelectrochemical properties of metalloproteins and their mutated and redox-center modified molecules have been analyzed electrochemically to develop new bioelectrocatalytic systems and bioelectro-functional devices.

VII-C-1 Simple Methods for Preparation of a Well-Defined 4-Pyridinethiol Modified Surface on Au(111) Electrodes for Cytochrome c Electrochemistry

TANIGUCHI, Isao^{1,2}; YOSHIMOTO, Soichiro¹; YOSHIDA, Masahito¹; KOBAYASHI, Shun-ichi¹; MIYAWAKI, Toshifumi¹; AONO, Yutaka¹; SUNATSUKI, Yukinari¹; TAIRA, Hideo¹
(¹Kumamoto Univ.; ²IMS)

[*Electrochim. Acta* **45**, 2843 (2000)]

A very small amount of sulfide impurity in 4-pyridinethiol (4-PySH) modifier solution was found to interfere with the proper formation of the 4-PySH modified surface for cytochrome c electrochemistry on an Au(111) electrode. When the modification was conducted in an alkaline (*e.g.*, 0.1 M KOH) solution, in aqueous solutions under applying a potential more positive than 0.3 V vs. Ag/AgCl, or at a low modifier concentration (*e.g.*, 20 μ M), the proper 4-PySH modified surface was obtained even using 4-PySH as received, which contained a small amount of sulfide. The selective adsorption of 4-PySH in the presence of a small amount of sulfide under these conditions was due to the rapid formation of proper 4-PySH modified surface, which prevented the sulfide from reacting with the electrode surface.

VII-C-2 Voltammetric and In Situ STM Studies on Self-Assembled Monolayers of 4- and 2-Mercaptopyridines and Thiophenol on Au(111) Electrodes

SAWAGUCHI, Takahiro¹; YOSHIMOTO, Soichiro²; MIZUTANI, Fumio¹; TANIGUCHI, Isao^{2,3}
(¹Natl. Inst. Bioscience and Human Tech.; ²Kumamoto Univ.; ³IMS)

[*Electrochim. Acta* **45**, 2861 (2000)]

Voltammetric and in situ STM studies were carried out for self-assembled monolayers of 4-mercaptopyridine (4-PySH), 2-mercaptopyridine (2-PySH) and thiophenol (PhSH) on well-defined single-crystal Au(111) electrodes in aqueous solutions. A reversible voltammetric response for cytochrome c was clearly observed only at the 4-PyS/Au(111) electrode, showing that only the 4-pyridinethiolate monolayer promotes facial electron transfer reaction between the Au(111)

and cytochrome c. On the basis of reductive desorption, the surface coverages of the three aromatic thiolate monolayers were found to be similar to each other; 4.6×10^{-10} mol/cm² for 4-PyS/Au(111), 4.7×10^{-10} mol/cm² for 2-PyS/Au(111), and 4.4×10^{-10} mol/cm² for PhS/Au(111). High-resolution STM images in perchloric acid solutions revealed *p* ($5 \times \sqrt{3R-30^\circ}$) and *p* ($4 \times \sqrt{7R-40.9^\circ}$) structures for the 4- and 2-pyridinethiolate monolayers on Au(111), respectively. No structure order was observed for the PhSH monolayers. While the pyridine units of both 4- and 2-pyridinethiolate monolayers were found to be oriented normal to the surface, 2-pyridinethiolates adsorbed through not only sulfur but also nitrogen atom of the pyridine ring. From these STM images, the orientation of the N atom of the pyridine moiety must face to the bulk solution, as in the case of 4-PyS/Au(111), in order to obtain a facile electrochemical reaction for cytochrome c.

VII-C-3 Formation of the "Nanotube" Structure of β -Cyclodextrin on Au(111) Surfaces Induced by Potential Controlled Adsorption

OHIRA, Akihiro¹; ISHIZAKI, Takahiro¹; SAKATA, Masayo¹; TANIGUCHI, Isao^{1,2}; HIRAYAMA, Chuichi¹; KUNITAKE, Masashi¹
(¹Kumamoto Univ.; ²IMS)

[*Colloids Surf., A* **169**, 27 (2000)]

The self-organization of β -cyclodextrin (β -CyD) into a nanotube structure, similar to that of CyD-polyrotaxane, was found to be induced by potential controlled adsorption on Au(111) surfaces in sodium perchlorate solution without a threaded polymer. In situ scanning tunneling microscopy (STM) revealed that the cavities of β -CyD faced side ward not upward in the tube. This ordered structure can form only under conditions where the potential is controlled (-0.45 V to -0.25 V vs. SCE). β -CyD molecules were in a disordered state on bare Au(111) surfaces without potential control ($+0$ V vs. SCE). In addition, the desorption of β -CyD from Au surfaces was observed at a negative potential of less than -0.60 V. In the range -0.45 to -0.25 V, β -CyD molecules formed ordered array on Au(111) surfaces. Furthermore, the discontinuity of potential control led to disordered phases and the destruction of the tube structure. This indicates that by controlling the electrode potential a delicate balance of various interactions can be achieved, resulting in the self-organization of molecules on the surface.

VII-C-4 Direct Observation of Perchlorate Induced by Redox Reaction of Ferrocene Terminated Self-Assembled Monolayer Studied by in situ FT-Surface Enhanced Raman Spectroscopy

NISHIYAMA, Katsuhiko¹; UEDA, Akihiro¹;
TANOUE, Shotaro¹; KOGA, Tesshu¹;
TANIGUCHI, Isao^{1,2}
(¹Kumamoto Univ.; ²IMS)

[*Chem. Lett.* 930 (2000)]

The incorporation of perchlorate anion into 8-ferrocenyloctanethiol (8FT) self-assembled monolayer (SAM) induced by the redox reaction at a gold wire electrode was demonstrated using in situ FT Raman spectroelectrochemistry. Upon oxidation of 8FT SAM, a band attributed to perchlorate anion was clearly observed and the band disappeared in its reduced state. On the other hand, when nitric acid was used as a supporting electrolyte, the band attributed to nitrate anion was not observed in the oxidized form of 8FT.

VII-C-5 Novel "Wet Process" Technique Based on Electrochemical Replacement for the Preparation of Fullerene Epitaxial Adlayers

UEMURA, Shinobu¹; SAKATA, Masayo¹;
TANIGUCHI, Isao^{1,2}; KUNITAKE, Masashi¹;
HIRAYAMA, Chuichi¹
(¹Kumamoto Univ.; ²IMS)

[*Langmuir* 17, 5 (2001)]

The electrochemical replacement method to form epitaxial adlayers of fullerene on Au(111) surfaces was proposed and demonstrated by in situ electrochemical STM. The new "wet process" method consists of the transfer of Langmuir film of fullerene onto iodine-modified Au(111) surfaces at an air-water interface followed by the electrochemical removal and replacement of iodine adlayers with fullerene adlayers in solution. The fullerene adlayers prepared by this method showed excellent quality and uniformity, and they were essentially the same as epitaxial adlayers prepared by sublimation.

VII-C-6 Electrochemical and Spectroelectrochemical Studies on Cobalt Myoglobin

LI, Chen-zhong¹; NISHIYAMA, Katsuhiko¹;
TANIGUCHI, Isao^{1,2}
(¹Kumamoto Univ.; ²IMS)

[*Electrochim. Acta* 45, 2883 (2000)]

The cobalt protoporphyrin-IX reconstituted myoglobin (Co-Mb) was prepared and its electrochemical and spectroelectrochemical properties were studied in comparison with native myoglobin. Unlike native myoglobin, a slow electron transfer reaction for Co(III)-Mb/Co(II)-Mb was detected by

cyclic voltammogram and spectroelectrochemical methods. The chemical reduction rate of Co(III)-Mb with dithionite was also slow compared with that of native myoglobin. Direct electron transfer between Co-Mb and an In₂O₃ electrode was observed, with spectroscopic verification of different redox states of Co-Mb using an optically transparent thin layer electrode (OTTLE) cell. The reversible electrochemical redox reaction of Co(III)-Mb/Co(II)-Mb was observed using azure A, 3-amino-7-dimethylaminophenazathionium chloride, as an electron transfer mediator for the first time. The Nernst plot was obtained for Co-Mb with E⁰ of -100 mV vs. Ag|AgCl (sat. KCl) and n = 1 at 25 °C.

VII-C-7 Effect of Rapid Heme Rotation on Electrochemistry of Myoglobin

MIE, Yasuhiro¹; SONODA, Kumiko¹; KISHITA, Midori¹; KRESTYN, Emil¹; NEYA, Saburo²;
FUNASAKI, Noriaki²; TANIGUCHI, Isao^{1,3}
(¹Kumamoto Univ.; ²Kyoto Pharmaceutical Univ.; ³IMS)

[*Electrochim. Acta* 45(18), 2903 (2000)]

Myoglobins (Mbs) reconstituted with rotatable octamethylheme and non-rotatable etioheme were prepared and their electrochemical behavior was studied. The redox potential of octamethylheme reconstituted Mb (OMe-Mb), of which heme rotates around iron-histidine (F8-His) bond, shifted negatively by ca. 30 mV compared with non-rotatable etioheme reconstituted Mb (Etio-Mb). On the other hand, the redox potentials of octamethylheme and etioheme themselves were very similar to each other. Due to the similarity of the distal histidine side of the heme of these two reconstituted Mbs, the shifts of the redox potential would be attributable to the drastic change of the orientation of proximal histidine imidazole ring to the heme plane by heme rotation. The dissociation rate constant of cyanide ion from the ferrous heme iron (II) for OMe-Mb form at 5 °C and pH 7.5 was three times faster than that of Etio-Mb. The electron transfer kinetics of these Mbs showed that the heme rotation causes faster electron transfer rates in both electrode reaction and chemical reduction in solution with dithionite. The obtained heterogeneous electron transfer rate constants at an In₂O₃ electrode and first-order rate constants of the chemical reduction were 12 (± 0.5) × 10⁻⁴ cm s⁻¹, 9.8 (± 1.0) s⁻¹ for OMe-Mb and 6.0 (± 0.5) × 10⁻⁴ cm s⁻¹, 4.5 (± 1.0) s⁻¹ for Etio-Mb under the present experimental conditions.

VII-D Unusual Reactivities of N-Heterocycles

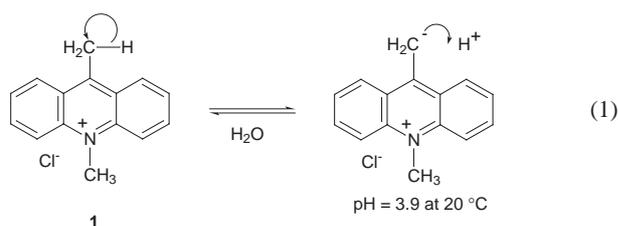
Among aromatic nuclei, acridines and their derivatives are still attracting considerable attention because of the many functions which they possess, including biomimetic redox reactivities, chemiluminescence, and the interaction with DNA as an intercalator. In particular the 9 position, the para position from acridine nitrogen, in acridinium exhibits strong electrophilicity and reacts with alcohols giving rise to 9-alkoxyacridanes. 9-methyl substituted acridinium exhibited a slightly different reactivity with basic alcohol, affording the corresponding 9-alkoxyacridanes followed by an olefinic species, 9-methyleneacridane, through the 9-methyl proton abstraction by an alkoxide. Therefore, the 9 position in acridinium appears to have different electric and steric conditions as compared to the other positions, giving rise to expectations of more unique reactivity. Here we report on the unusual reactivities of the acridinium skeleton as a N-Heterocycle.

VII-D-1 An Unusually Acidic Methyl Group Directly Bound to Acridinium Cation

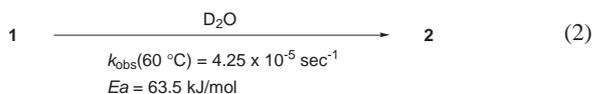
SUZUKI, Hiroshi¹; TANAKA, Yasutaka^{1,2}
(¹Shizuoka Univ.; ²IMS)

[*J. Org. Chem.* **66**, 2227 (2001)]

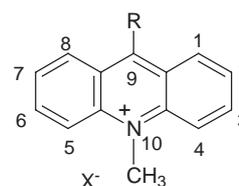
9,10-dimethylacridinium chloride (**1**: X = Cl) exhibited strong acidity of pH 3.90 (3.4×10^{-3} M, 20 °C) in an aqueous solution. H–D exchange reaction of **1** in D₂O indicated that protons in the 9-methyl group dissociated to generated H⁺ ions (equation 1). This is an



unique example of a methyl proton functioning as an acid. The conversion of **1** into **2** followed first-order kinetics with respect to the concentration of **1** over the temperature range studied (equation 2). The acidity



derives from the wider π face in acridinium capable of delocalizing the newly formed negative charge upon proton dissociation. PM3 calculations provided stabilization factors ($\delta\Delta H_f^\circ$) between proton dissociated and undissociated forms of several N-heterocycles and also confirmed the acidity observed in acridinium.



- 1:** R=CH₃, X=Cl, I, CH₃SO₄
2: R=CD₃, X=Cl, I, CH₃SO₄

Figure 1. Chemical Structures of **1** and **2**.

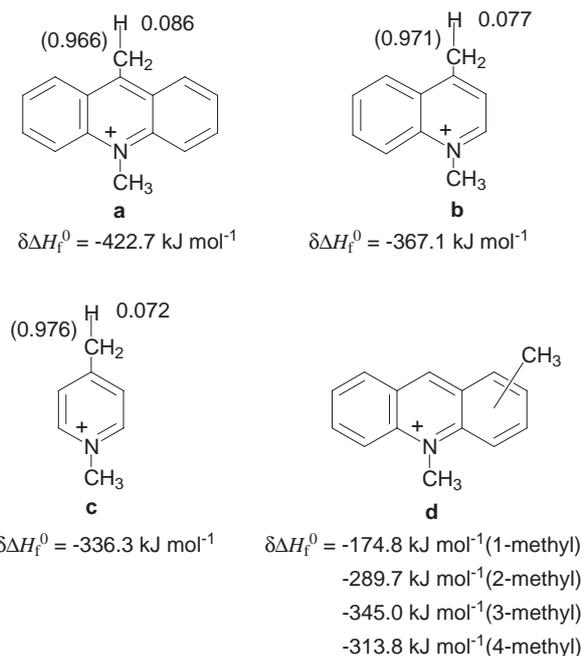


Figure 2. Model Structures for the PM3 calculation. The numbers in the structures refer to the partial charges of the dissociating proton. The numbers in parentheses refer to the bond orders between the proton and an atom bound to the proton. The difference in heat of formation ($\delta\Delta H_f^\circ$) was calculated from ΔH_f° (undissociated form) + ΔH_f° (H₂O) – ΔH_f° (dissociated form) – ΔH_f° (H₃O⁺).

VII-E Reductive Activation of Carbon Dioxide and Oxidative Activation of Water Aimed at Energy Conversion

Free energy required in the reduction of CO₂ continuously decreases with an increase of the number of electrons participated in the reduction. Accordingly, multi-electron reduction of CO₂ is much favorable compared with two-electron reduction of CO₂. An electrophilic attack of CO₂ to low valent coordinatively unsaturated metals complexes gives metal-η¹-CO₂ complexes, which can be easily converted to M-CO ones. A major problem of reduction of CO₂ in homogeneous systems is reductive cleavages of M-CO bonds (CO evolution) under the reaction condition due to accumulation of too much electrons in the central metals. A catalytic system, in which electrons required in the reduction of CO₂ are provided by ligand localized redox reactions not but metal centered ones, therefore, may open a new methodology for the reduction of CO₂. Based on the facts that naphthylidene works as not only monodentate, bidentate and bridging ligand between metals and carbonyl carbon but also electron source in the reduction of CO₂, we have been preparing a variety of meta-naphthylidene complexes to aim at multi-electron reduction of CO₂.

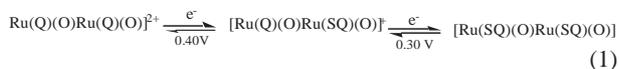
Much attention has been paid to high valent oxo-metal complexes from the view points of the fact that metal proteins participating in oxidation of various organic molecules contain one or multi oxo-metal centers. Among various synthetic route of metal-oxo complexes reported so far, metal aqua-complexes are reasonable precursors, since they undergo acid-base equilibrium among aqua-, hydroxo- and oxo-complexes. The distribution of those complexes can be controlled by selection of bases and pH. Polymerization of aqua-metal complexes upon deprotonation of aqua ligands would depress by introduction of appropriate ligands which can accept electrons generated in the hydroxy and oxo groups. Along the line, we have prepared a series of metal-aqua complexes with dioxolene and dithiolene ligands to decrease basicity of the hydroxy and oxo ligands.

VII-E-1 Syntheses and Redox Properties of Bis(hydroxoruthenium) Complexes with Quinone and Bipyridine Ligands. Water-Oxidation Catalysis

WADA, Tohru; TSUGE, Kiyoshi; TANAKA, Koji

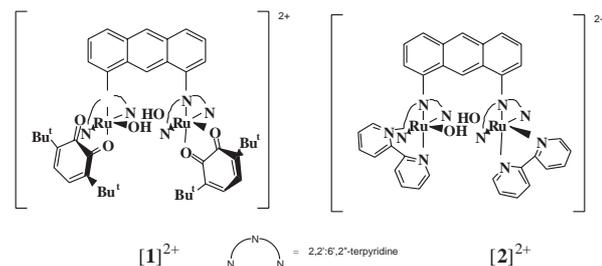
[*Inorg. Chem.* **40**, 329 (2001)]

A novel dimerizing ligand 1,8-bis(2,2':6',2''-terpyridyl)anthracene (btpyan) was prepared by three reactions from 1,8-diformylanthracene. Bis(ruthenium-hydroxo)complex with two 3,6-di(*tert*-butyl)-1,2-benzoquinone ligands (3,6-tBu₂qui), [Ru^{II}₂(OH)₂(3,6-tBu₂qui)₂(btpyan)](SbF₆)₂ (**[1]**)(SbF₆)₂ and with two 2,2'-bipyridine ligands (bpy), [Ru^{II}₂(OH)₂(bpy)₂(btpyan)](SbF₆)₂ (**[2]**)(SbF₆)₂ were synthesized by using btpyan ligand. **[1]**²⁺ easily eliminated two protons by the addition of *t*-BuOK (2.0 equiv.) coupled with the reduction of quinone ligands in the MeOH solution, and converted to the [Ru^{II}₂(O)₂(3,6-tBu₂sq)₂(btpyan)]⁰ (3,6-tBu₂sq = 3,6-di(*tert*-butyl)-1,2-semiquinone), while **[2]**(SbF₆)₂ was not changed by the addition of large excess of *t*-BuOK. Electrochemical and Spectroelectrochemical measurements revealed that the [Ru^{II}₂(O)₂(3,6-tBu₂sq)₂(btpyan)]⁰ derived from **[1]**²⁺ oxidized to [Ru^{III}₂(O)₂(3,6-t-Bu₂qui)₂(btpyan)]⁴⁺ at +1.2 V via the [Ru^{II}₂(O)₂(3,6-tBu₂qui)₂(btpyan)]²⁺ in the MeOH solution. **[1]**²⁺ showed higher catalytic activity for the water-oxidation in a CF₃CH₂OH/ether solution containing water and in pH controlled-water (pH 4.0) by using modified ITO electrode, and the turnover number was 35000. The role



of the equilibrium of equation 1 in the O₂ evolution is evidenced by the fact that the analogous **[2]**(SbF₆)₂ has

no ability to catalyze the oxidation of water under the same conditions.



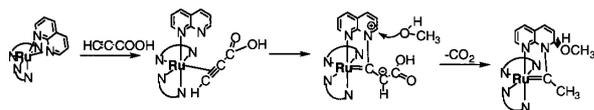
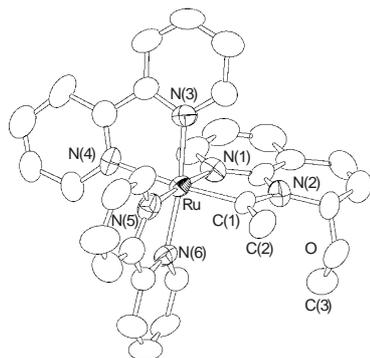
VII-E-2 A Ru-Carbene Complex with a Metallacycle Involving a 1,8-naphthylidene Framework

TOMON, Takashi; OYAMA, Dai; WADA, Tohru; SHIREN, Kazushi; TANAKA, Koji

[*Chem. Commun.* 1100 (2001)]

The reaction of [Ru(bpy)₂(CO)(napy)](PF₆)₂ with HCCC(O)OH in CH₃OH/H₂O (3:2 V/V) gave **[1]**(PF₆)₂. The molecular structure of **1**²⁺ determined by X-ray diffraction analysis. The characteristic feature of **1**²⁺ is the C-N bond formation between the CCH₃ group and one nitrogen of napy, and a unique five-membered metallacycle consisting of Ru-N-C-N-C(O) atoms. The metallacycle ring and the napy moiety form a coplane despite that aromaticity of the napy ligand substantially decreased due to the attachment of CH₃OH to the carbon atom of 2-position of napy. The ¹H-NMR spectrum of the complex **1**²⁺ in CD₃CN/CD₃OD (1:1 v/v) showed the equilibrium between the carbene species and the corresponding vinylidene species. The CH₃O group of **1**²⁺ was substituted by C₂H₅O in C₂H₅OH/CH₃CN. In addition, treatments of **1**²⁺ with the

equivalent amount of OH^- at room temperature in CD_2Cl_2 gave the corresponding vinyl complex with a framework of the five membered metallacycle. The most likely path for the formation of $\mathbf{1}^{2+}$ is depicted in Scheme. The reaction of $\mathbf{1}^{2+}$ with propiolic acid would produce a vinylidene complex through π alkyne complex with monodentate napy. An intra-molecular attack of non-bonded nitrogen of napy to the α carbon of the vinylidene group must increase in acidity of the vicinal carbon of the bonded nitrogen of napy, which will induce a nucleophilic attack of CH_3OH to the C_2 carbon.



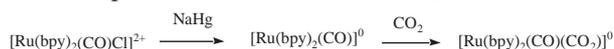
VII-E-3 Characterization of $\text{Ru}(\text{bpy})_2(\text{CO})(\text{COO})$ Prepared by CO_2 Addition to $\text{Ru}(\text{bpy})_2(\text{CO})$ in Acetonitrile

FUJITA, Etsuko; CHOU, M.; TANAKA, Koji

[*Appl. Organomet. Chem.* **14**, 844 (2000)]

DMF solutions containing $[\text{Ru}(\text{bpy})_3]^{2+}$, $[\text{Ru}(\text{bpy})_2(\text{CO})\text{X}]^{n+}$ ($\text{X} = \text{Cl}, \text{H}, n = 1$ or $\text{X} = \text{CO}, n = 2$), and triethanolamine (TEOA) as an electron donor have been used for photochemical CO_2 reduction. These homogeneous systems produce HCOO^- and CO as the major and a minor products with a total quantum yield of approximately 15%. The CO_2 reduction system involves a photochemical cycle for $[\text{Ru}(\text{bpy})_3]^{2+}$ and a thermal cycle for $[\text{Ru}(\text{bpy})_2(\text{CO})\text{X}]^{n+}$. The proposed mechanism involves reductive quenching of the $[\text{Ru}(\text{bpy})_3]^{2+}$ excited state by TEOA to form $[\text{Ru}(\text{bpy})_3]^+$ and reduction of $[\text{Ru}(\text{bpy})_2(\text{CO})\text{X}]^{n+}$ by two $[\text{Ru}(\text{bpy})_3]^+$ molecules to produce $[\text{Ru}(\text{bpy})_2(\text{CO})]^0$. The latter reacts with CO_2 to form $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{COO})]^0$ as a common intermediate for formate and CO production. $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{COO})]^0$ and $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{COOH})]^+$ have been previously prepared by addition of two and one equivalent of OH^- , respectively, to $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$. An alternative preparation of $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{COO})]^0$ from $[\text{Ru}(\text{bpy})_2(\text{CO})]^0$ is the reaction of CO_2 with a doubly reduced species generated from $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}]^+$ in acetonitrile, and the reaction is the key process of CO_2 reduction in the photochemical system.

The CV of $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ in acetonitrile indicates that the two-electron reduction wave at -1.0 V vs. SCE is not affected by CO_2 . Na-Hg reduction of $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ produces a very intense blue solution of $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^0$ which does not react with CO_2 . The CV of $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}]^+$ indicates three reduction wave between -1.3 V and -1.9 V. The catalytic current observed under CO_2 depends on the electrolytes. The first reduction seems to be the bpy-centered reduction. Within a few minute, two tiny peaks at 395 and 510 nm disappear, indicating that intra-molecular electron transfer is taking place to form $[\text{Ru}(\text{bpy})_2(\text{CO})]$ with loss of a Cl ligand. The mono-reduced species does not react with CO_2 .

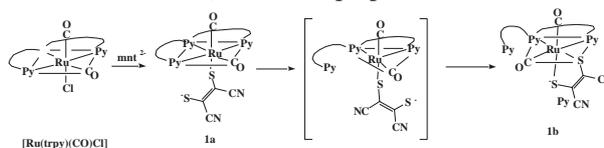


VII-E-4 Ruthenium Terpyridine Complexes with mono- and bi-Dentate Dithiolene Ligands

SUGIMOTO, Hideki; TSUGE, Kiyoshi; TANAKA, Koji

[*J. Chem. Soc., Dalton Trans.* 57 (2001)]

The reaction of $[\text{Ru}(\text{CO})_2\text{Cl}(\text{trpy})]\text{PF}_6$ ($\text{trpy} =$ terpyridine) with Na_2mnt ($\text{mnt} = \text{S}_2\text{C}_2(\text{CN})_2$) initially produced $[\text{Ru}(\text{CO})_2(\text{mnt}-\kappa\text{S})(\text{trpy}-\kappa^3\text{NN}'\text{N}'')]$ (**1a**), which rearranged to $[\text{Ru}(\text{CO})_2(\text{mnt}-\kappa^2\text{S})(\text{trpy}-\kappa^2\text{NN}'\text{N}'')]$ (**1b**) in solutions. The rearrangement from **1a** to **1b** proceeds via the penta-coordinated complex with monodentate mnt and bidentate trpy . The reaction of $[\text{Ru}(\text{CO})_2\text{Cl}(\text{trpy})]\text{PF}_6$ with 3,4-toluenedithiol (H_2tdt) gave $[\text{Ru}(\text{CO})_2(\text{tdt}-\kappa^2\text{S})(\text{trpy}-\kappa^2\text{NN}'\text{N}'')]$ (**2b**) but $[\text{Ru}(\text{CO})_2(\text{tdt}-\kappa\text{S})(\text{trpy}-\kappa^3\text{NN}'\text{N}'')]$ (**2a**) was not identified in the reaction. Thus, ruthenium complexes with bidentate dithiolene and bidentate terpyridine seem to be more stable than those with monodentate dithiolene and tridentate terpyridine. Neither $[\text{Ru}(\text{CO})_2(\text{pdt}-\kappa\text{S})(\text{trpy}-\kappa^3\text{NN}'\text{N}'')]$ (**3a**) nor $[\text{Ru}(\text{CO})_2(\text{pdt}-\kappa^2\text{S})(\text{trpy}-\kappa^2\text{NN}'\text{N}'')]$ (**3b**) ($\text{pdt} = \text{PhC}(\text{S})\text{C}(\text{S})\text{Ph}$) was obtained in the reaction of $[\text{Ru}(\text{CO})_2\text{Cl}(\text{trpy})]\text{PF}_6$ with Cs^+ salt of 4,5-diphenyldithiolate in CH_3OH under N_2 . The same reaction conducted under aerobic conditions afforded $[\text{Ru}(\text{CO})(\text{C}(\text{O})\text{OCH}_3)(\text{SC}(\text{Ph})\text{C}(\text{Ph})(\text{SC}(\text{O})\text{OH})(\text{trpy}-\kappa^2\text{NN}'\text{N}'')]$ (**3**) resulting from double addition of CO_2 and CH_3OH to terminal sulfur of pdt and a carbonyl carbon of **3a**, respectively, followed by esterification of the resultant $[\text{Ru}(\text{CO})(\text{C}(\text{O})\text{OCH}_3)(\text{SC}(\text{Ph})\text{C}(\text{Ph})(\text{SC}(\text{O})\text{OH})(\text{trpy}-\kappa^2\text{NN}'\text{N}'')]$ in CH_3OH . The addition of CO_2 to sulfur of **3a** is ascribed to the strong basicity and weak chelating ability of pdt compared with those of mnt and tdt . A series of $[\text{RuX}(\text{dithiolene})(\text{trpy})]^{n+}$ ($\text{X} = \text{dmsO}, \text{Cl}, \text{OSO}_2\text{CF}_3; n = 0, 1$) were also prepared.



VII-E-5 Syntheses of New Ruthenium Carbonyl Terpyridine *o*-Phenylene Complexes: Strong Interaction Between Carbonyl and *o*-Phenylene Ligands

SUGIMOTO, Hideki; TANAKA, Koji

[*J. Organomet. Chem.* **622**, 280 (2001)]

Ruthenium carbonyl *o*-phenylene complexes, Ru(CO)(3,6-Bu₂seq)(trpy)]PF₆ (**1**)]PF₆) and [Ru(CO)(*o*-monothioat)(trpy)] (**2**), were prepared by the reaction of [Ru(CO)Cl₂(trpy)] with the corresponding *o*-phenylenes in 2-methoxyethanol. X-ray crystallographic study of **1**]BF₄ indicated that the ruthenium center is coordinated by carbonyl, three nitrogens of trpy and two oxygens of 3,6-Bu₂seq. ESR of **1**]PF₆ and **2** indicated that the electronic structures of ruthenium-*o*-phenylene unit of the complexes have Ru(II)-3,6-Bu₂seq and Ru(II)-*o*-monothioat forms, respectively. Significant differences in the redox behavior and the spectroscopical properties between **1**]PF₆ and **2** and [RuCl(3,5-Bu₂seq)(trpy)] were ascribed to the strong interaction between *o*-phenylene and carbonyl ligands through Ru(II).

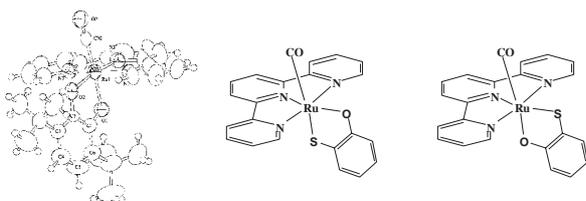


Figure 1. X-ray analysis of [Ru(CO)(*o*-monothioat)(trpy)]⁺.

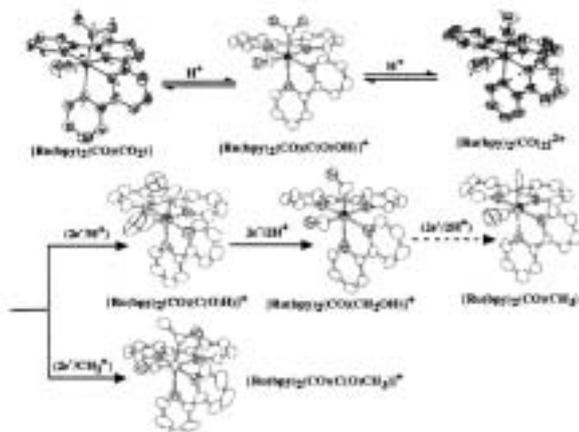
VII-E-6 Structural and Spectroscopic Characterization of Ruthenium(II) Complexes with Methyl, Formyl and Acetyl Groups as Model Species in Multi-Step CO₂ Reduction

OOYAMA, Dai¹; TOMON, Takashi; TSUGE, Kiyoshi; TANAKA, Koji
(¹Fukushima Univ.)

[*J. Organomet. Chem.* **619**, 299 (2001)]

The molecular structures of Ru(II) complexes with methyl, formyl and acetyl groups [Ru(bpy)₂(CO)L]⁺ (L = CH₃, C(O)H and C(O)CH₃) were examined from the view point of active species in multi-step reduction of CO₂ on Ru. The methyl complex was prepared by the reaction of [Ru(bpy)₂(OH₂)₂]²⁺ with trimethylsilyl acetylene and fully characterized by infrared, Raman, ¹³C NMR and single-crystal X-ray crystallography. Disorder of the Ru–CO and Ru–C(O)H bonds in the crystal structure of the formyl complex made it difficult to determine the bond parameters of the two groups accurately, but the molecular structure of the analogous acetyl complex, which was obtained by the reaction of [Ru(bpy)₂(CO₃)] with propiolic acid, was determined by X-ray analysis. The ruthenium–carbonyl (Ru–C–O) bond angles of the methyl and acetyl complex with 174(1) and 175.5(5)°, respectively, are in the ranges of

those of previously characterized [Ru(bpy)₂(CO)L]ⁿ⁺ (L = CO₂, C(O)OH, CO and CH₂OH). On the other hand, the Ru–CH₃ and Ru–C(O)CH₃ bond distances showed unusual relationship against the stretching frequency in the raman spectra.



VII-F Synthesis of Transition-Metal Chalcogenido Complexes and Their Cluster-Forming Reactions

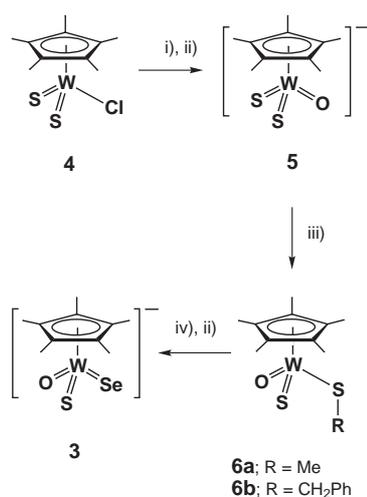
Transition-metal chalcogenido aggregates are of well-documented importance in biological systems and industrial processes such as hydrodesulfurization. A wide variety of metal chalcogenido clusters have been synthesized, in which the tetrathiometalato anions have been widely used as a building block. In this project, we are focusing on preparation of chalcogenido/chalcogenolato and silanechalcogenolato complexes as a precursor for cluster syntheses and their cluster-forming reactions.

VII-F-1 Synthesis of a Pentamethylcyclopentadienyl Complex of Tungsten with Three Different Chalcogenido (O^{2-} , S^{2-} , Se^{2-}) Ligands

KAWAGUCHI, Hiroyuki; TATSUMI, Kazuyuki¹
(¹Nagoya Univ.)

[*Angew. Chem., Int. Ed. Engl.* **113**, 1306 (2001)]

We have synthesized a pentamethylcyclopentadienyl complex of tungsten, $[PPh_4][Cp^*W(O)(S)(Se)]$ (**3**, $Cp^* = \eta^5-C_5Me_5$), in which three different chalcogenido ligands (O^{2-} , S^{2-} , Se^{2-}) are bound to the metal center. This unique mixed-chalcogenido complex is thermodynamically stable, and does not exhibit chalcogen-exchange reactions in solution. The successful route to **3** begins with the high yield synthesis of $[Cp^*W(S)_2Cl]$ (**4**) attained by the reaction between $[Cp^*WCl_4]$ and 1 equiv of $Me_3SiSCH_2CH_2SSiMe_3$. Addition of a small amount of H_2O to a THF solution of **4** under the presence of NEt_3 produced $[Cp^*WS_2O]^-$ (**5**), which was then alkylated by CH_3I or $PhCH_2Br$ to give $[Cp^*W(O)(S)(SR)]$ ($R = CH_3$ (**6a**), CH_2Ph (**6b**)). Finally, a terminal selenide was introduced by the reaction of **6a** or **6b** with Li_2Se_2 and PPh_4Br leading to the desired oxo/thio/seleno complex $[PPh_4][Cp^*W(O)(S)(Se)]$ (**3**).



- i) H_2O/Et_3N / THF, ii) PPh_4Br / CH_3CN
 iii) $PhCH_2Br$ or CH_3I / THF
 iv) Li_2Se_2 / THF

Figure 1.

VII-F-2 Synthesis and Reactions of Triphenylsilanethiolato Complexes of Manganese(II), Iron(II), Cobalt(II), and Nickel(II)

KOMURO, Takashi¹; KAWAGUCHI, Hiroyuki;
TATSUMI, Kazuyuki¹
(¹Nagoya Univ.)

Treatment of $Fe[N(SiMe_3)_2]_2$ with 1 and 2 equiv of Ph_3SiSH in hexane afforded $[Fe\{N(SiMe_3)_2\}(\mu_3-SSiPh_3)]_2$ **1** and $[Fe(SSiPh_3)(\mu_3-SSiPh_3)]_2$ **2**, respectively. Complex **2** reacted with Lewis bases to form the adducts $Fe(SSiPh_3)_2(L)_2$ [$L = CH_3CN$ **3a**, $4-tBuC_5H_4N$ **3b**, PEt_3 **3c**, $(L)_2 = tmeda$ **3d**]. The reactions of $M[N(SiMe_3)_2]_2$ ($M = Mn, Co$) with Ph_3SiSH in the presence of TMEDA gave rise to the corresponding silanethiolato complexes $M(SSiPh_3)_2(tmeda)$ ($M = Mn$ **4**, Co **5**). The analogous reaction using $[Ni(NPh_2)_2]_2$ generated $Ni(SSiPh_3)_2(tmeda)$ **6**. The reaction of **3a** with $(PPh_4)_2[MoS_4]$ produced the linear trinuclear complex $(PPh_4)_2[MoS_4\{Fe(SSiPh_3)_2\}_2]$ **7**, while **3a** reacted with $(NEt_4)_2[FeCl_4]$ to afford $(NEt_4)_2[Fe_2(SSiPh_3)_2Cl_4]$ **8**. The reaction of **3a** with $[Cu(CH_3CN)_4](PF_6)$ gave the cyclic tetranuclear complex $Cu_4(SSiPh_3)_4$ **9**, in which a ligand transfer reaction occurred. Finally, when **5** was treated with $(NBu_4)F$ in THF containing PPh_3 , silicon-sulfur bond cleavage took place to produce the cobalt-sulfido cluster $Co_6(\mu_3-S)_8(PPh_3)_6$ **10**.

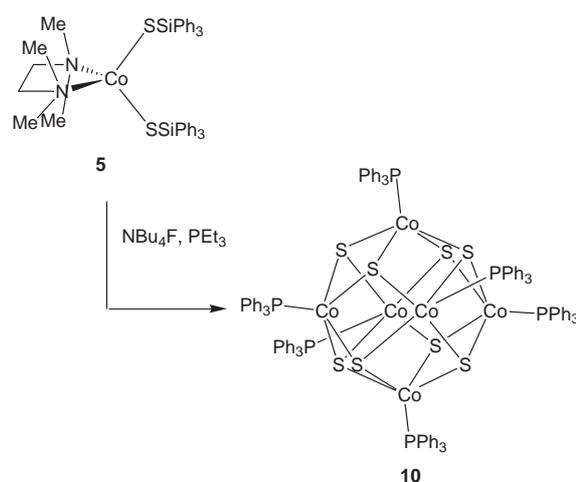


Figure 1.

VII-G Synthesis of Compounds Having a Novel Bonding Containing Heavier Main Group Element

Low-coordinate species of main group elements of the second row such as carbenes, olefins, carbonyl compounds, aromatic compounds, and azo compounds play very important roles in organic chemistry. However, the chemistry of their heavier element homologues has been undeveloped most probably due to their high reactivity and instability under ambient conditions. Since the first isolation of stable diphosphene (P=P), silene (Si=C), and disilene (Si=Si) in 1981 by taking advantage of steric protection, various double-bond compounds containing heavier main group elements have been synthesized and characterized.

On the other hand, we have developed an extremely bulky aromatic substituent, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt hereafter) and 2,6-bis[bis(trimethylsilyl)methyl]-4-tris(trimethylsilyl)methylphenyl (denoted as Bbt hereafter). These substituents were found to be very effective steric protection groups for a variety of reactive species containing a heavier main group element. We have synthesized a variety of unprecedented low-coordinate compounds of heavier main group elements as stable compounds by taking advantage of kinetic stabilization using a new type of steric protection groups, Tbt and Bbt, and elucidated their properties.

VII-G-1 Separation of Orientational Disorder in the X-Ray Analysis of the Kinetically Stabilized 2-Silanaphthalene

WAKITA, Keiji¹; TOKITOH, Norihiro²;
OKAZAKI, Renji¹
(¹Univ. Tokyo; ²IMS and Kyoto Univ.)

[*Bull. Chem. Soc. Jpn.* **73**, 2157 (2000)]

Cyclic electron delocalization of aromatic compounds distinctly appeared in their structure as bond length equalization. In view of the proximity in the periodic table, silicon analogues of aromatic compounds are expected to show similar structural features. However, sila-aromatic compounds are highly reactive and have been observed only in low-temperature matrices or in the gas phase, except for charged systems. During the course of our study on neutral sila-aromatic compounds, we have succeeded in the synthesis of the first stable 2-silanaphthalene **1** by taking advantage of an extremely bulky Tbt group. The structure of **1** was determined by X-ray crystallographic analysis, however, the severe disorder around the 2-silanaphthalene ring of **1** prevented us from discussing the detailed structure of **1** based on the X-ray analysis. Here, we report the refined crystallographic structural analysis of **1**.

The crystal structure of the stable 2-silanaphthalene **1** was refined more adequately by the separation of the disorder of overlapped two 2-silanaphthalene moieties. The bond lengths of the 2-silanaphthalene ring were in fairly good agreement with the theoretically calculated values which we previously reported.

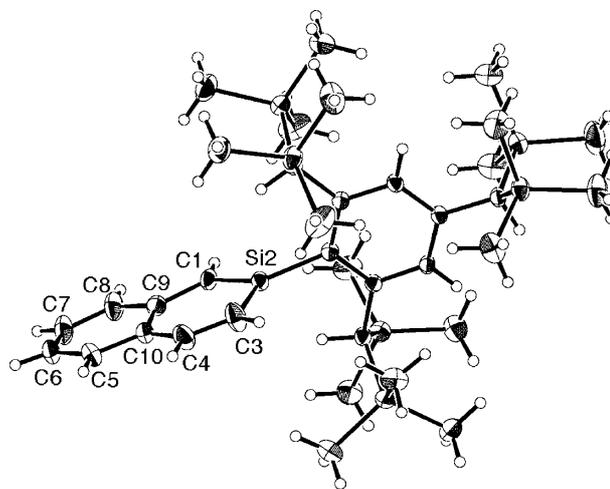


Figure 1. ORTEP drawing of 2-silanaphthalene **1** (major fragment).

VII-G-2 The First Chemical Trapping of Stibinidene, a Monovalent Antimony Compound

SASAMORI, Takahiro¹; ARAI, Yoshimitsu²;
TAKEDA, Nobuhiro³; OKAZAKI, Renji²;
TOKITOH, Norihiro⁴

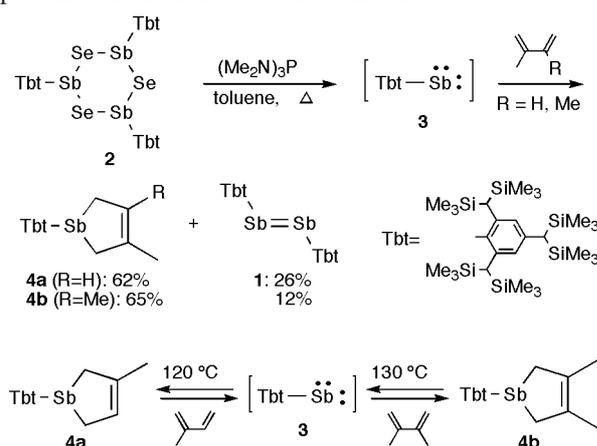
(¹Kyushu Univ.; ²Univ. Tokyo; ³Kyoto Univ.; ⁴IMS and Kyoto Univ.)

[*Chem. Lett.* **42** (2001)]

In recent decades, there has been much interest in the chemistry of monovalent species of heavier group 15 elements. Phosphinidenes (R-P:), phosphorus analogues of nitrenes, have long been postulated as reactive intermediates. Stibinidenes (R-Sb:) are also interesting monovalent species of group 15 elements, but no stibinidene has been detected or trapped so far probably due to its extremely high reactivity. On the other hand, we have recently succeeded in the synthesis and characterization of the first stable distibene (TbtSb=SbTbt, **1**) and dibismuthene (TbtBi=BiTbt) by taking advantage of an efficient steric protection group, Tbt. In the final step for the synthesis of distibene **1**, that

is, deselenation reaction of (TbtSbSe)₃ (**2**) with hexamethylphosphorous triamide (HMPT), it is rational to postulate the initial formation of a stibinidene (Tbt-Sb:, **3**) as an intermediate. In this paper we wish to present the first successful trapping reaction of the intermediary stibinidene.

Deselenation of 1,3,5-triseleno-2,4,6-tristibane **2** in the presence of 1,3-butadienes resulted in the formation of the corresponding [1+4]cycloadducts **4a,b** of a sterically hindered stibinidene **3**, a monovalent species of antimony. Thermal generation of **3** from **4a,b** via retro [1+4]cycloaddition reaction was suggested by the diene-exchange reaction in thermolysis of **4a,b** in the presence of another butadiene derivative.



VII-G-3 Formation of Antimony-Sulfur Double-Bond Compounds and Their Trapping with Nitrile Oxides

TOKITOH, Norihiro¹; ARAI, Yoshimitsu²;
SASAMORI, Takahiro³; TAKEDA, Nobuhiro⁴;
OKAZAKI, Renji²

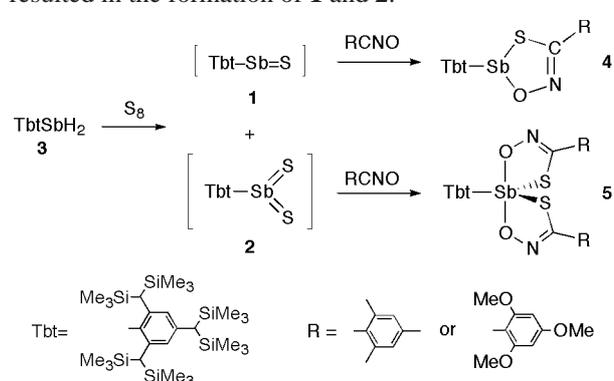
¹IMS and Kyoto Univ.; ²Univ. Tokyo; ³Kyushu Univ.;
⁴Kyoto Univ.)

[*Heteroatom Chem.* **12**, 244 (2001)]

The chemistry of compounds featuring double-bond containing heavier group 15 elements has attracted attention in recent years. As for the low-coordinated double-bond compounds between group 15 and group 16 elements, dithioxophosphorane [RP(S)=S] and diselenoxophosphorane [RP(Se)=Se] have been synthesized as stable compounds, and thioxophosphines [RP=S] and selenoxophosphines [RP=Se] stabilized by the coordination of an amino group have been observed in solution by NMR spectroscopy. However, there are no reports about the double bond of antimony with sulfur. In this paper, we describe the formation of thioxostibine [TbtSb=S (**1**)] and dithioxostiborane [TbtSb(S)=S (**2**)] intermediates, which is confirmed by trapping reactions with nitrile oxides.

The reaction of a highly crowded dihydrostibine **3** with elemental sulfur in the presence of nitrile oxides resulted in the formation of [2+3]cycloaddition reaction products of a thioxostibine [TbtSb=S (**1**)] and a dithioxostiborane [TbtSb(S)=S (**2**)], which are among a novel class of antimony-sulfur double bond

compounds. The structures of the [2+3]cycloadducts of dithioxostiborane **2** with nitrile oxides were determined by X-ray structural analysis. Desulfurization of highly crowded antimony-containing cyclic polysulfides [TbtSbS_x (x = 5 or 7)] with phosphine reagents also resulted in the formation of **1** and **2**.



VII-G-4 Synthesis, Structures, and Reactivities of Novel Silacyclic Systems: The First Stable Silabenzene and Silacyclopropabenzene

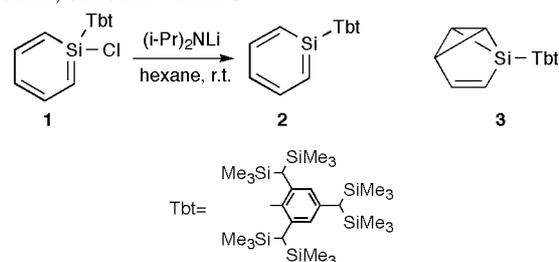
TOKITOH, Norihiro¹

(¹IMS and Kyoto Univ.)

[*Phosphorus, Sulfur Silicon Relat. Elem.* **168**, 31 (2001)]

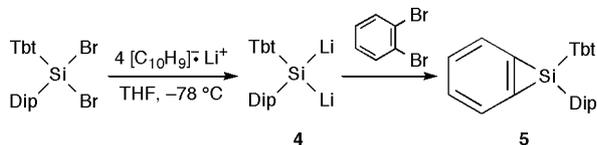
In the last two decades, kinetic stabilization has played an important role in the synthesis and isolation of a variety of heavier main group element compounds having an exotic structure and novel bonding. We have developed an extremely bulky and efficient steric protection group, Tbt, and applied it to the kinetic stabilization of highly reactive species of heavier main group elements. In this paper, the synthesis and isolation of the first stable silabenzene and siacyclopropabenzene are described as further application of Tbt group to the kinetic stabilization of novel conjugated ring systems containing a silicon atom.

The first stable silabenzene **2** was synthesized by the reaction of the corresponding chlorosilane **1** with (*i*-Pr)₂NLi. The crystal structure and spectroscopic properties of **2** indicated that silabenzene **2** has a completely planar, delocalized 6π-electron ring system as in the case of benzene. Interestingly, irradiation of a benzene solution of **2** with the light of 290–350 nm resulted in the formation of an unprecedented valence isomer, silabenzvalene **3**.



On the other hand, an overcrowded diaryldithiosilane **4** was allowed to react with *o*-dibromobenzene to give the first stable silacyclopropabenzene **5**, which was

fully characterized by NMR spectra, FAB-MS, and X-ray structural analysis. The silacyclopropabenzene **5** thus obtained was found to be thermally very stable and have a completely planar geometry but a slightly squashed benzene ring. The crystallographic analysis revealed that no distinct bond localization is observed for the benzene moiety in contrast to its carbon analogue, *i.e.* cyclopropabenzene.



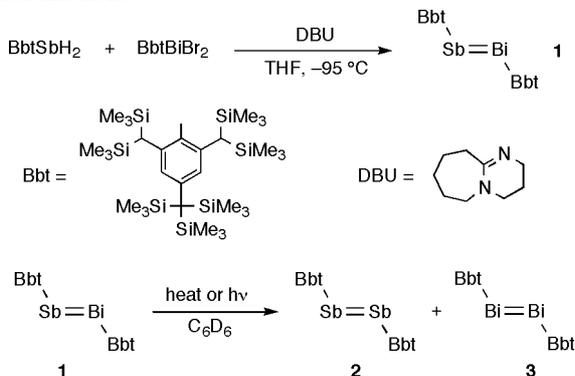
VII-G-5 Synthesis and Reactivities of the First Stable Stibabismuthene

SASAMORI, Takahiro¹; TAKEDA, Nobuhiro²; TOKITOH, Norihiro³
(¹Kyushu Univ.; ²Kyoto Univ.; ³IMS and Kyoto Univ.)

[*Phosphorus, Sulfur Silicon Relat. Elem.* **169**, 89 (2001)]

In recent years there has been much interest in compounds with a double bond between heavier group 15 elements. As for the case of heteronuclear double-bond compounds between heavier group 15 elements, several phospharsenes [RP=AsR] and phosphastibenes [RP=SbR] have been synthesized as stable compounds. However, there is no example of a heteronuclear doubly bonded system between antimony and bismuth, *i.e.* stibabismuthene. Recently, we have succeeded in the synthesis and characterization of the first stable distibene and dibismuthene [Ar-E=E-Ar (E = Sb, Bi; Ar = Tbt, Bbt)] by taking advantage of an efficient steric protection group, Tbt or Bbt group. We now report the successful application of the Bbt group to the synthesis of the first stable stibabismuthene, BbtSb=BiBbt (**1**).

The condensation reaction of an overcrowded dihydrostibine with dibromobismuthine using 1,8-diazabicyclo[5.4.0]undec-7-ene as a base afforded the first stable stibabismuthene **1**, the formation of which was evidenced by UV-vis and Raman spectra and its chemical reactivity. Thermolysis or photolysis of **1** resulted in the disproportionation reaction into the homonuclear double-bond species, distibene **2** and dibismuthene **3**.



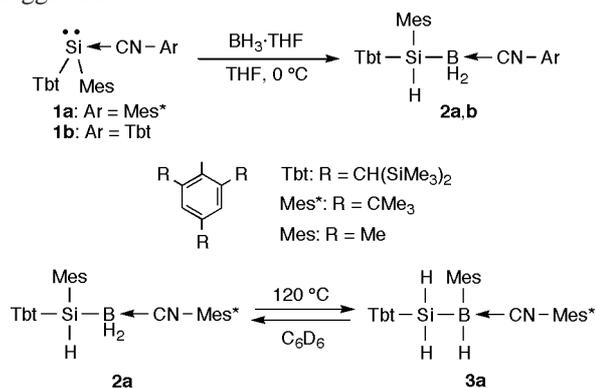
VII-G-6 Reaction of Stable Silylene–Isocyanide Complexes with BH₃·THF

TAKEDA, Nobuhiro¹; KAJIWARA, Takashi¹; TOKITOH, Norihiro²
(¹Kyoto Univ.; ²IMS and Kyoto Univ.)

[*Chem. Lett.* 1076 (2001)]

In recent decades, much attention has been paid to the chemistry of silylenes (silicon analogues of carbenes). Also, silylene complexes with Lewis bases have been extensively studied and some complexes have been synthesized in low temperature matrices so far. However, their properties have not been fully disclosed yet due to their instability at ambient temperature. On the other hand, we have recently succeeded in the synthesis of the first stable silylene–Lewis base complexes **1a,b** by taking advantage of an efficient steric protection group, Tbt group. In this paper, we describe the reactivity of **1a,b** with BH₃·THF.

Stable silylene–isocyanide complexes **1a,b** reacted with BH₃·THF to give the first stable silylborane–isocyanide complexes **2a,b**. The structures of **2a,b** were determined by NMR, IR, and mass spectrometry, elemental analysis, and X-ray crystallographic analysis. Thermolysis of **2a** at 120 °C gave a 1:5 mixture of **2a** and the corresponding migration product **3a** in contrast to the previously reported intermediary silylborane–isocyanide complexes [PhMe₂SiBX₂ ← CNR], which is known to give the corresponding (boryl)(silyl)imino-methanes [(PhMe₂Si)(X₂B)C=NR] as final products. Since the isolated compound **3a** also affords the 1:5 mixture of **2a** and **3a** by heating at 120 °C, the existence of an equilibrium between **2a** and **3a** is strongly suggested.



VII-G-7 Synthesis and Properties of the First Stable Germanaphthalene

NAKATA, Norio¹; TAKEDA, Nobuhiro¹; TOKITOH, Norihiro²
(¹Kyoto Univ.; ²IMS and Kyoto Univ.)

[*Organometallics* in press]

In recent years much attention has been focused on germaaromatic compounds, since they are among heavier congeners of aromatic hydrocarbons which play

very important roles in organic chemistry. Some ionic germaaromatic compounds have been successfully synthesized as stable compounds, while no isolation of a neutral germaaromatic compound has been reported probably due to its high reactivity. On the other hand, we have recently succeeded in the synthesis of kinetically stabilized silabenzene and 2-silanaphthalene, the first examples of stable neutral silaaromatic compounds, by taking advantage of an efficient steric protection group, Tbt group. Here, we report the synthesis and structure of 2-germanaphthalene **1** kinetically stabilized by the Tbt group, the first stable neutral germaaromatic compound.

The first stable 2-germanaphthalene **1** was synthesized by the dehydrobromination of bromogermane **2** with $(i\text{-Pr})_2\text{NLi}$ in THF at room temperature. The molecular structure of **1** was fully characterized by its ^1H and ^{13}C NMR spectra, which indicate the delocalized π -electronic structure of **1**. Moreover, the low-temperature X-ray crystallographic analysis of **1** revealed that 2-germanaphthalene ring was almost planar and the benzene ring of Tbt group was almost perpendicular to the 2-germanaphthalene ring. In addition, all the ^1H and ^{13}C NMR chemical shifts and the structural parameters of **1** experimentally obtained are in good agreement with the values theoretically calculated for some model compounds. UV-vis and Raman spectra of **1** also supported the aromatic character of the 2-germanaphthalene ring system.

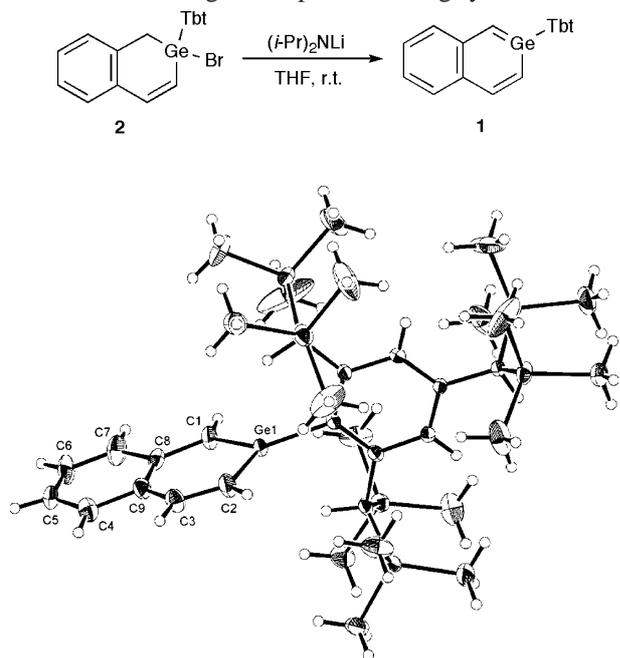


Figure 1. ORTEP drawing of 2-germanaphthalene **1**.

VII-H Development of Coordination Chemistry-based Strategies for Structural and Functional Modulation of Naturally Occurring Proteins or Enzymes

New methodologies based on coordination chemistry are actively developed which one can modulate or switch a structure and a function of naturally occurring proteins and enzymes. Using coordination chemistry on a specific site of a protein or peptide, we aim to explore a new functional molecules or chemistry-based strategy that can selectively recognize a specific surface of a protein and/or modulate its characteristic structure. Such molecules and methodologies would be expected to lead to functional change and regulation of complicated bio-macromolecules.

VII-H-1 Guest-Induced Umpolung on a Protein Surface: A Strategy for Regulation of Enzymatic Activity

HAMACHI, Itaru^{1,2}; EBOSHI, Ryoji¹;
WATANABE, Jun-ichi; SHINKAI, Seiji¹
(¹Kyushu Univ.; ²IMS)

[*J. Am. Chem. Soc.* **122**, 4530 (2000)]

This manuscript describes a new strategy to introduce an on-off switch to an engineered enzyme. We successfully demonstrated that the transition metal ion-induced charge inversion (*i.e.*, guest-induced Umpolung) occurred on a surface of semisynthetic ribonuclease S' efficiently causes sharp on-off switching of enzymatic activity. Semisynthetic ribonuclease S' (RNase S'), an RNA hydrolyzing enzyme, was employed as a suitable model. As a surface charge modulator, an unnatural amino acid bearing iminodiacetic acid group (Ida⁴) was incorporated into the S-peptide region of RNase S' by solid phase peptide synthesis. The mutant S-peptides were combined to S-protein by a self-assemble manner. The charge of the side chain of Ida⁴ is a monoanion at neutral pH and it is inverted to a monocation upon complexation with a trivalent metal cation such as Fe(III) at its iminodiacetic acid moiety. Based on the kinetic assay using single mutants, it is clear that the response to metal ions greatly depends on the charge of the original amino acid, that is, the Fe(III)-induced activity enhancement occurs at positively charged Lys or Arg site and the activity suppression occurs at negatively charged Glu or Asp site. A rationally designed double mutant displayed the sharp on-off switching (10–20 fold) of enzymatic activity which is sensitive to iron(III) concentration.

VII-H-2 Pd(en) as a Sequence-Selective Molecular Pinch for α -Helical Peptides

HAMACHI, Itaru^{1,2}; KASAGI, Noriyuki¹;
KIYONAKA, Shigeki¹; NAGASE, Tsuyoshi¹;
MITO-OKA, Yasuko¹; SHINKAI, Seiji¹
(¹Kyushu Univ.; ²IMS)

[*Chem. Lett.* **16** (2001)]

A palladium(II) ethylenediamine complex was found to selectively stabilize α -helix conformation of peptides having two histidine (His) residues at *i* and *i* + 3 or 4

positions, whereas the helix conformation of the other peptides having one or two His at different positions is destabilized. Based on CD titration, NMR spectral observation and molecular modeling calculation, we established that Pd(en) is a versatile molecular unit for binding to peptides bearing two His at a specific pattern in aqueous solution. The ethylenediamine moiety in this organometallic receptor can be chemically modified with the combination to other binding interactions, so as to facilitate the more selective binding and modulation of a protein surface. This is sharply distinguished from the simple metal ions previously reported by other researchers.

VII-H-3 Zn(II) Dipicolylamine-Based Artificial Receptor as a New Entry for Surface Recognition of α -Helical Peptides in Aqueous Solution

MITO-OKA, Yasuko¹; TSUKIJI, Shinya¹;
HIRAOKA, Takashi¹; KASAGI, Noriyuki¹;
SHINKAI, Seiji¹; HAMACHI, Itaru^{1,2}
(¹Kyushu Univ.; ²IMS)

[*Tetrahedron Lett.* **42**, 7059 (2001)]

Artificial receptors for bioactive peptides are actively developed in the field of the recent molecular recognition chemistry, because of their importance for the peptide sensing and pharmaceutical application. However, the recognition events have been exploited in organic solvents in the most cases, which are still far from the biological prospects. For the development of artificial receptors that can selectively bind a peptide/protein surface so as to inhibit or enhance the function, it is desirable to establish a design strategy for artificial receptors toward a peptide surface in aqueous solution. We describe herein that zinc(II) dipicolylamine (Zn(Dpa))-based coordination chemistry is promising for design of artificial receptors in aqueous solution toward α -helical peptides displaying two Histidine(His) on their surface ($H - i$ and $i + 4$, or $H - i$ and $i + 7$, or $H - i$ and $i + 11$). The spatial juxtaposition by a modular connector greatly influences the affinity to these peptides. To the best of our knowledge, this is the first example for the artificial receptors that can selectively bind peptides bearing two His in the distance of two or three helix pitches in perfectly aqueous solution. This motif can be readily combined with other binding motifs, so that one can design the more selective and

efficient artificial receptors toward a peptide or protein.

VII-I Synthesis and Functionality of Organometallic Dendrimers

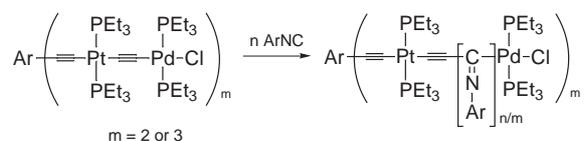
Dendrimers are three-dimensional macromolecules with regularly hyperbranched structures, and have a wide range of potentials applicable to new functional materials. Organometallic dendrimers have attracted much attention due to their unique functions based on photochemical, redox and catalytic behaviors. This project focuses on the development of new synthetic routes toward the dendrimers that consist of organometallic species in every generation. We also examine the physical and chemical properties of these organometallic dendrimers.

VII-I-1 Living Polymerization of Aryl Isocyanides by Multifunctional Initiators Containing Pd–Pt μ -Ethyne-diyl Units

OHSIRO, Nobuaki¹; SHIMIZU, Atsushi¹;
OKUMURA, Reiko¹; TAKEI, Fumie¹; ONITSUKA,
Kiyotaka²; TAKAHASHI, Shigetoshi¹
(¹Osaka Univ.; ²Osaka Univ. and IMS)

[Chem. Lett. 786 (2000)]

Multinuclear acetylide complexes containing two or three Pd–Pt μ -ethyne-diyl units have been prepared and successfully applied to a multifunctional initiator for the living polymerization of aryl isocyanides, which gives two- or three-armed poly(isocyanide)s with a narrow polydispersity index in good yields.



VII-I-2 Synthesis of Hyperbranched Platinum-Poly(yne) Polymers by Self Polycondensation

ONITSUKA, Kiyotaka²; OHSIRO, Nobuaki¹;
FUJIMOTO, Masanori¹; TAKEI, Fumie¹;
TAKAHASHI, Shigetoshi¹
(¹Osaka Univ.; ²Osaka Univ. and IMS)

[Mol. Cryst. Liq. Cryst. 342, 159 (2000)]

A hyperbranched polymer constructed by platinum-acetylide units has been synthesized by self polycondensation of a dinuclear platinum complex having one terminal acetylene and two platinum-chloride groups as an AB₂ monomer in the presence of a copper catalyst in amine. The hyperbranched polymer is soluble in common organic solvents and characterized by means of spectral analyses and GPC.

VII-I-3 Synthesis of Organometallic Dendrimers by Ligand Exchange Reactions: Reversible Bonding of Dendrons to a Core in Transition Metal Acetylide Dendrimers

ONITSUKA, Kiyotaka²; IUCHI, Asako¹;
FUJIMOTO, Masanori¹; TAKAHASHI, Shigetoshi¹
(¹Osaka Univ.; ²Osaka Univ. and IMS)

[Chem. Commun. 741 (2001)]

Ligand exchange reactions of chloride ligands on a trinuclear palladium acetylide core with platinum acetylide dendrons having a 4-pyridyl group at a focal point result in the quantitative formation of novel organometallic dendrimers, which easily revert to the core and the dendrons by treatment with Bu₄NCl.

