RESEARCH ACTIVITIES VII
Coordination Chemistry Laboratories

Prof. Masahito Yamashita, Prof. Naoto Chatani took the position of Laboratory of Synthetic Coordination Chemistry from April 2002. Prof. Isao Taniguchi (Kumamoto University) and Assoc. Prof. Yasutaka Tanaka (Shizuoka University) finished their term as Adjunct Prof. of the Synthetic Coordination Chemistry in March 2002. Their effort during their term is gratefully appreciated. Prof. Nobuhiro Tokito (Kyoto University) and Assoc. Prof. Kiyotaka Onizuka (Osaka University) continue the position of the Coordination Bond.

VII-A Development of Novel Transition Metal Complex Catalysts Having MOP Ligands

Transition metal-mediated organic transformations have emerged as a powerful tool in the domain of synthetic organic chemistry. 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 chiral ligands. Recently, we have designed and prepared a series of homochiral monophosphine ligands bearling axially chiral binaphthyl backbone, so-called MOP, which were identified as effective chiral ligands in various asymmetric catalysis, in particular hydrosilylation of olefins.

VII-A-1 Asymmetric Hydrosilylation of Styrenes Catalyzed by Palladium-MOP Complexes: Ligand Modification and Mechanistic Studies

HAYASHI, Tamio; HIRATE, Seiji; KITAYAMA, Kenji; TSUJI, Hayato; TORII, Akira; UOZUMI, Yasuhiro

[*J. Org. Chem.* **66**, 1441 (2001)]

In the palladium-catalyzed asymmetric hydrosilylation of styrene with trichlorosilane, several chiral monophosphine ligands, (*R*)-2-diarylphosphino-1,1’-binaphthyls, were examined for their enantioselectivity. The highest enantioselectivity was observed in the reaction with (*R*)-2-bis[3,5-bis(trifluoromethyl)phenyl]-phosphino-1,1’-binaphthyl, which gave (*S*)-1-phenylethanol of 98% ee after oxidation of the hydrosilylation product, 1-phenyl-1-(trichlorosilyl)ethane. The palladium complex of (*R*)-2-bis[3,5-bis(trifluoromethyl)phenyl]phosphino-1,1’-binaphthyl also efficiently catalyzed the asymmetric hydrosilylation of substituted styrenes on the phenyl ring or at the β position to give the corresponding chiral benzylic alcohols of over 96% ee. Deuterium-labeling studies on the hydrosilylation of regiospecifically deuteriated styrene revealed that β-hydrogen elimination from 1-phenylethyl(silyl)-palladium intermediate is very fast compared with reductive elimination giving hydrosilylation product when (*R*)-2-bis[3,5-bis(trifluoromethyl)phenyl]-phosphino-1,1’-binaphthyl is used. The reaction of *o*-allylstyrene with trichlorosilane gave (1*S*,2*R*)-1-methyl-2-(trichlorosilylmethyl)indan (91% ee) and (*S*)-1-(2-(propenyl)phenyl)-1-trichlorosilylethanes (95% ee). Based on their opposite configurations at the benzylic position, a rationale for the high enantioselectivity of (*R*)-2-bis[3,5-bis(trifluoromethyl)phenyl]phosphino-1,1’-binaphthyl is proposed.

VII-A-2 Modification of Chiral Monodentate Phosphine Ligands (MOP) for Palladium-Catalyzed Asymmetric Hydrosilylation of Cyclic 1,3-Dienes

HAYASHI, Tamio; HAN, Jin Wook; TAKEDA, Akira; TANG, Jun; NOHMI, Kenji; MUKAIDE, Kotaro; TSUJI, Hayato; TORII, Akira; UOZUMI, Yasuhiro

[*Adv. Synth. Catal.* **343**, 279 (2001)]

Several MOP ligands containing aryl groups at 2’ position of (*R*)-2-(diphenylphosphino)-1,1’-binaphthyl skeleton were prepared and used for palladium-catalyzed asymmetric hydrosilylation of cyclic 1,3-dienes with trichlorosilane. Highest enantioselectivity was observed in the reaction of 1,3-cyclopentadiene catalyzed by a palladium complex (0.25 mol%) coordinated with (*R*)-2-(diphenylphosphino)-2’-(3,5-dimethyl-4-methoxyphenyl)-1,1’-binaphthyl, which gave (*S*)-3-(trichlorosilyl)cyclopentene of 90% ee.

VII-A-3 (*R*)-2-Diphenylphosphino-2’-methoxy-1,1’-binaphthyl

UOZUMI, Yasuhiro; KAWATSURA, Motoi; HAYASHI, Tamio

[*Org. Syn.* **78**, 1 (2002)]

There exist transition metal-catalyzed reactions where the bisphosphine-metal complexes can not be used because of their low catalytic activity and/or low selectivity towards a desired reaction pathway and therefore chiral monodentate phosphine ligands are required for the realization of new types of catalytic asymmetric rreactions. Unfortunately, there have been reported only a limited number of monodentate chiral phosphine ligands, which are not so useful as bisphosphine ligands with few exceptions. Recently, the monodentate optically active phosphine ligand, 2-diphenylphosphino-2'-methoxy-1,1'-binaphthyl (MeO-MOP) and its analogs have been demonstrated to provide high enantioselectivity in palladium-catalyzed hydrosilylation of olefins and palladium-catalyzed reduction of allylic esters by formic acid. The procedures described here allow the convenient preparation of MOP and has advantages over previously published sequences. MeO-MOP can be prepared through 5 steps from binaphthol without racemization and the over all yield is 90%.

VII-B Green and Risk-Free Catalysis

Catalytic organic transformations under mild, safe, and green conditions 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. PS-PEG resin-supported rhodium complexes was designed and prepared with a view toward using them in water. Rhodium-catalyzed hydroformylation, cyclotrimerization of alkynes, and Michael-type addition of arylboronic acids were found to proceed smoothly in water. Palladium-Catalyzed doublecarbonylation under very mild and safe conditions using Pd/PPh_3/DABCO/THF system was also investigated.

VII-B-1 Amphiphilic Resin-Supported Rhodium –Phosphine Catalysts for C–C Bond Forming Reactions in Water

UOZUMI, Yasuhiro; NAKAZONO, Maki

[*Adv. Synth. Catal.* **344**, 274 (2002)]

Amphiphilic resin-supported rhodium-phosphine complexes were prepared on polystyrene-poly(ethylene glycol) graft co-polymer (1% DVB cross-linked) beads. The immobilized rhodium complexes exhibited high catalytic activity in water to promote hydroformylation of 1-alkenes, [2+2+2] cyclotrimerization of internal alkynes forming benzene rings, and 1,4-addition of arylboronic acids.

VII-B-2 Double Carbonylation of Aryl Iodides with Primary Amines under Atmospheric Pressure Conditions Using Pd/PPh_3/DABCO/THF System

UOZUMI, Yasuhiro; ARII, Taro; WATANABE, Toshihiro

[*J. Org. Chem.* **66**, 5272 (2001)]

Double carbonylation of iodobenzene, *p*-iodoanisole, *p*-iodotoluene, and *m*-iodotoluene with primary alkylamines was catalyzed by a Pd-PPh_3 complex in THF in the presence of DABCO as base at 25 °C under atmospheric pressure of carbon monoxide to give phenyl, anisyl, *p*-tolyl, and *m*-tolyl glyoxamides, respectively, with selectivity greater than 90%.

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.

Surface structures and properties of functional modified electrodes have also been examined at molecular level using STM, electrochemical and other spectroscopic techniques.

VII-C-1 Effects of Alkyl Chain as a Spacer on Electrochemical Reaction and SEIRA Spectra for Self-Assembled Monolayer Having Anthraquinone Redox Center

NISHIYAMA, Katsuhiko[1]; KUBO, Atsushi[1]; TANIGUCHI, Isao[2]; YAMADA, Mami[3]; NISHIHARA, Hiroshi[3]
([1]Kumamoto Univ.; [2]IMS and Kumamoto Univ.; [3]Univ. Tokyo)

[*Electrochemistry* **69**, 980 (2001)]

Self-assembled monolayers (SAMs) of 1-mercaptoanthraquinone (AQSC0), bis(3-(1-anthraquinonylthio)-propyl)disulfide (AQSC3) and bis(6-(1-anthraquinononylthio)hexyl)disulfide (AQSC6), on a gold electrode were investigated by cyclic voltammetry and surface enhanced infrared absorption spectroscopy (SEIRAS). A redox wave was observed for all the anthraquinone (AQ) derivatives and the redox potential shifted *ca.* –60 mV/pH in the pH region from 1 to 7. The peak separation of the voltammograms depended on the spacer length of the AQ derivatives, and the heterogeneous electron transfer rates of AQSC0, AQSC3 and AQSC6 at pH 1 were 7.5, 2.3×10^{-1}, and 3.1×10^{-3} s^{-1}, respectively. For the SEIRA spectra of AQSC0 and AQSC3, the C=O stretching and C–C stretching bands of AQ ring were clearly observed, suggesting that the AQ ring plane is perpendicular or tilted to the electrode surface. The SEIRA signal of the AQ derivatives decreased with an increase in the alkyl chain length, indicating taht the AQSC3 and AQSC6 molecules were adsorbed on the electrode not by the sulfide S atoms but by the thiolate S atoms.

VII-C-2 Analysis of Biological Functions of Metalloproteins Using Biocompatible Modified Electrodes

TANIGUCHI, Isao
(IMS and Kumamoto Univ.)

[*Anal. Sci.* **17**, 1355 (2001)]

Recent developments on bioelectroanalytical chemistry of metalloproteins have been discussed for the following subjects. 1) Surface structures for the rapid electron transfer of metalloproteins (in particular for cytochrome *c*) have been discussed and 3-mercaptopyridine has been shown as a new surface modifier for cytochrome c electrochemistry. 2) Biological functions and electron transfer kinetics of myoglobin have been analyzed by comparing electrochemical properties of native molecule with those of artificially designed molecules. For electron transfer kinetics, the re-organization energy due to the structural change at the redox center during electron transfer reaction has been shown to play an important role. 3) Use of ferredoxin as an electron-donating mediator, bioelectrocatalytic reactions have been demonstrated. These results suggest that electrochemical techniques using functional electrodes are useful for analysis and use of biological functions of metalloproteins.

VII-C-3 Interfacial Structures of Self-Assembled Monolayers of 2-Pyridinethiol on Au(111) Studied by In Situ Tunneling Microscopy

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([1]Natl. Inst. Biosci. Human Tech.; [2]IMS and Kumamoto Univ.)

[*Anal. Sci.* **17**, 1383 (2001)]

In situ Scanning Tunneling Microscope (STM) operating under electrochemical condition was used to study self-assembled monolayers of 2-pyridinethiol (2-PySH) on Au(111) in perchloric acid solution. Each molecule appeared as two spots, presumably originated from adsorption through S and N atoms of 2-pyridinethiolate with a vertical orientation on the Au(111) surface. The ordered 2-pyridinethiolate monolayers exhibited a $p\ (4 \times \sqrt{7}R\text{–}40.9^\circ)$ structure, which was constructed by alternative arrangements of two types of molecular rows with differently rotated molecules. In situ STM also revealed that the monolayer consisted of molecularly ordered domains with the $p\ (4 \times \sqrt{7}R\text{–}40.9^\circ)$ structure, its mirror structure defined as $p\ (4 \times \sqrt{7}R\text{–}19.1^\circ)$, and their rotational structures. Detailed interfacial structures and molecularly ordered domains of 2-pyridinethiolate monolayer have been elcidated by in situ STM imaging in aqueous solution.

VII-C-4 NADP$^+$ Sensor on Chrorella Ferredoxin/Ferredoxin-NADP$^+$-Reductase Modified Indium Oxides

NISHIYAMA, Katsuhiko[1]**; IKEBE, Hisami**[1]**; HOSHIDE, Yasuhiro**[1]**; NAGAI, Hidenori**[1]**; TANIGUCHI, Isao**[2]
([1]Kumamoto Univ.; [2]IMS and Kumamoto Univ.)

[*Chem. Sens.* **17**, 92 (2001)]

Chlorella ferredoxin (ChFd) was immobilized electrostatically with the aid of cationic polypeptides such as poly-L-lysine (PLL) or poly-L-ornithine onto indium oxide electrodes. Clear redox waves of the immobilized ChFd was observed. In the presence of ferredoxin-NADP$^+$-reductase (FNR) and NADP$^+$, NADP$^+$ was reduced to NADPH electrocatalytically at the modified electrode. Also, both ChFd and FNR were immobilized on the electrode, and the prepared ChFd/FNR modified electrode was applied to the NADP$^+$ sensor.

VII-C-5 Surface pKa of Amine-Terminated Self-Assembled Monolayers Evaluated by Direct Observation of Counter Anion by FT-Surface Enhanced Raman Spectroscopy

NISHIYAMA, Katsuhiko[1]**; KUBO, Atsushi**[1]**; UEDA, Akihiro**[1]**; TANIGUCHI, Isao**[2]
([1]Kumamoto Univ.; [2]IMS and Kumamoto Univ.)

[*Chem. Lett.* 80 (2002)]

The acid-base reaction of aminothanethol (2-AT) and 6-amino-1hexanethiol (6AT) self-assembled monolayers (SAMs) on a gold electrode was monitored by fourier-transform surface enhanced Raman spectroscopy (FT-SERS). A band attributed to counter anion, such as ClO_4^- or NO_3^- for NH_3^+ , was clearly observed during protonation of the amino group of 2AT or 6AT. The nband intensity decreased with increasing solution pH. The surface pKa's of 2AT and 6AT SAMs on a gold electrode at 0 V *vs.* Ag/AgCl (saturated KCl) were 5.0 ± 0.2 and 3.8 ± 0.3, as evaluated from the intensity-pH curve.

VII-C-6 Ion Selectivity for Electrode Reactions on Functionalized Monolayer Modified Electrode

TANIGUCHI, Isao[1]**; HARA, Kazunori**[2]**; ISHIMOTO, Hitoshi**[2]**; IWAI, Mitsuru**[2]**; RANGARAJAN, Srinivasan**[2]
([1]IMS and Kumamoto Univ.; [2]Kumamoto Univ.)

[*Chem. Sens.* **18**, 133 (2002)]

Electrode reactions of various ionic species on pyridine-, pyrimidine-, benzene- and related thiolate modified Au(111) and Au(100) single crystal surfaces were carried out. Clear selectivity of the electrode reaction for a given ionic species depending on the modified surface was seen. Charge of the ionic species was not so important. In particular, on the benzenethiolate modified electrode surface, the electrode reaction of ferri-/ferro- redox couple in acidic solution was clearly inhibited, but no inhibition was observed for the electrode reaction of ferri-/ferro-cyanide redox couple. On the other hand, by increasing the number of –SH group in the benzene ring (1,4-dithiol < 1,3,5 trithiol < 1,2,4,5 tetrathiol), ferri-/ferro redox couple showed an increased enhancement of the electrochemical responses, but ferri-/ferro-cyanide redox couple showed an inhibition on the electrode reaction. On the bases of the properties of the modified electrode surfaces obtained by STM image, impedance analysis, contact angle and other data, the surface hyrophilicity (or hydration/dehydration of the ionic species) of the modified electrodes was concluded to play an important role on the electrode reaction of ferri-/ferro- redox couple.

VII-C-7 In-Situ STM Observation of Coronene Epitaxial Adlayers on Au(111) Surfaces Prepared by the Transfer of Langmuir Films

UEMURA, Shinobu[1]**; SAKATA, Masayo**[1]**; TANIGUCHI, Isao**[2]**; HIRAYAMA, Chuichi**[1]**; KUNITAKE, Masashi**[1]
([1]Kumamoto Univ.; [2]IMS and Kumamoto Univ.)

[*Thin Solid Films* **409**, 206 (2002)]

A highly ordered epitaxial adlayer of coronene on an Au(111) surface was prepared by a wet process technique, which consisted of the simple transfer of Langmuir films. The structure and dependence on potential of the adlayer were then investigated by in situ scanning tunneling microscopy (STM). The adlayer processed a (4×4)-Au(111) superlattice structure, and each coronene molecule was visualized as an individual hexagon on high-resolution STM images. The multilayer portion was present without any potential control, probably due to the excess generated by the transfer. The adsorption behavior of coronene, including the formation of the multilayers, showed dependence on the potential. A flawless adlayer without the presence of any multilayers was achieved by the application of nagative potential, in which the multilayer-substrate interaction was adequately weakened.

VII-C-8 New Route to Protoporphyrins III and XIII from Common Starting Pyrroles

HAREAU, G. P. -J[1]**; NEYA, Saburo**[2]**; FUNASAKI, Noriaki**[2]**; TANIGUCHI, Isao**[3]
([1]Kumamoto Univ.; [2]Kyoto Pharmaceutical Univ.; [3]IMS and Kumamoto Univ.)

[*Tetrahedron Lett.* **43**, 3109 (2002)]

A new approach to protoporphyrins III (2') and XIII (3') has been developed based on a single set of starting materials, namely, 2,4-dimethyl-3-(2-chloroethyl)-carbethoxypyrrole (4) and 3,3'-di(2-methoxycarbonylethyl)-4,4'-dimethyldipyrromethane-5,5'dicarboxylic acid (5) for both targets. The biladiene route was adopted for the preparation of 2' (five steps, 18% overall yield) while the coupling of two pyrromethenes was used to synthesize 3' (four steps, 11% overall yield).

VII-D Nano-Sciences of Advanced Metal Complexes

Recently, nano-sciences or nano-technologies have been attracting much attention because they show very interesting physical properties based on the non-linearity and quantum effect. There are two methods to obtain the nano-size materials, that is, “top-down” and “bottom-up.” The top-down method such as laser abrasion has a limitation to make particles with less than 100 nm. On the other hand, the bottom-up method is promising to control the nano-size since the chemical reactions are available. However, the researches based on the bottom-up methods are rare and such methods have not been accomplished so far. There are three types of the target materials such as inorganic compounds, organic compounds, and metal complexes. The inorganic compounds easily take three-dimensional bulk structures. The organic compounds easily take 0- and 1-dimesional bulk materials. Therefore, neither inorganic nor organic compounds are suitable for the nano-sciences. On the other hand, the metal complexes easily take nano-size clusters where they are surrounded with the organic ligands. Therefore, the nano-sciences of the advanced metal complexes are most promising. As for the non-linearity, we focus on the gigantic third-order optical non-linearity. As for the quantum effect, we focus on the single-molecule magnets, nano-wire molecule-magnets, and nano-network molecule-magnets.

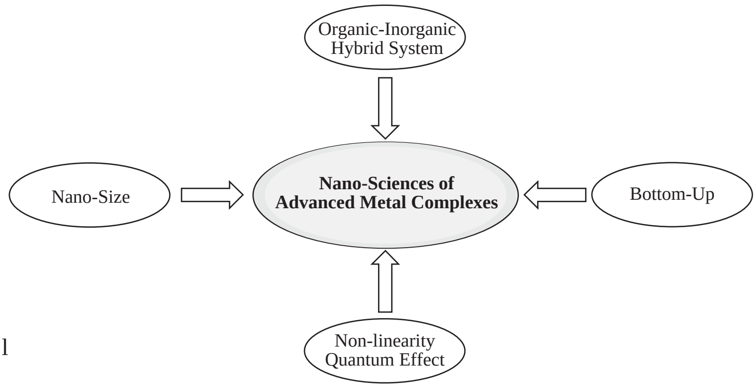


Figure 1. Nano-sciences of advanced metal complexes.

VII-D-1 Tuning of Electronic Structures of Quasi-One-Dimensional Bromo-Bridged Ni(III) Complexes with Strong Electron-Correlation by Doping of Co(III) Ions, $[Ni_{1-x}Co_x(chxn)_2Br]Br_2$

YAMASHITA, Masahiro[1]; **YOKOYAMA, Kohei**[2]; **FURUKAWA, Sachie**[2]; **MANABE, Toshio**[2]; **ONO, Takashi**[2]; **NAKATA, Kazuya**[2]; **KACHI-TERAJIMA, Chihiro**[2]; **IWAHORI, Fumiyasu**[2]; **ISHII, Tomohiko**[2]; **MIYASAKA, Hitoshi**[2]; **SUGIURA, Ken-ichi**[2]; **MATSUZAKI, Hiroyuki**[3]; **KISHIDA, Hideo**[3]; **OKAMOTO, Hiroshi**[3]; **TANAKA, Hisaaki**[4]; **MARUMOTO, Kazuhiro**[4]; **ITO, Hiroshi**[4]; **KURODA, Shin-ichi**[4]
([1]IMS and Tokyo Metropolitan Univ.; [2]Tokyo Metropolitan Univ.; [3]Univ. Tokyo; [4]Nagoya Univ.)

[*Inorg. Chem.* **41**, 1998 (2002)]

The Ni(III) complexes doped by Co(III) ions, $[Ni_{1-x}Co_x(chxn)_2Br]Br_2$ have been synthesized by electrochemical oxidation methods. The single crystal reflectance spectrum of $x = 0.118$ shows an intense CT band about 0.5 eV, which is lower than that of $[Ni(chxn)_2Br]Br_2$ (1.3 eV). The single-crystal electrical conductivities at room temperature of these compounds increase with increase of the amounts of doping of Co(III) ions. In the ESR spectra, peak-to-peak line widths at room temperature change about 600 G in $[Ni(chxn)_2Br]Br_2$ to 200 G in $x = 0.118$. Such a large x dependence of line widths seems to be ascribed to the increasing contribution from the increasing Curie spins which have smaller line width. Therefore, we have succeeded in tuning the electronic structures of quasi-one-dimensional bromo-bridged Ni(III) complexes with strong electron-correlations by doping Co(III) ions.

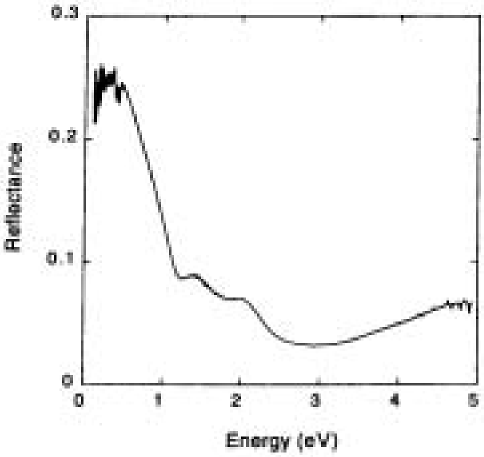


Figure 1. Single-crystal reflectance spectrum of $[Ni_{0.882}Co_{0.118}(chxn)_2Br]Br_2$.

VII-D-2 Angle-Resolved Photoemission Study of the MX-Chain Compound $[Ni(chxn)_2Br]Br_2$: Spin-Charge Separation in Hybridized *d-p* Chains

FUJIMORI, Shin-ichi[1]; **INO, Akihiro**[1]; **OKANE, Tetsuo**[1]; **FUJIMORI, Atsushi**[1]; **OKADA, Kozo**[2]; **MANABE, Toshio**[3]; **YAMASHITA, Masahiro**[4];

KISHIDA, Hideo[5]**; OKAMOTO, Hiroshi**[5]
([1]SPring-8; [2]Okayama Univ.; [3]Tokyo Metropolitan Univ.; [4]IMS and Tokyo Metropolitan Univ.; [5]Univ. Tokyo)

[*Phys. Rev. Lett.* **88**, 247601-1 (2002)]

Angle-resolved photoemission experiments have been carried out for a quasi-one-dimensional (1D) MX-chain compound $[Ni(chxn)_2Br]Br_2$, which shows a gigantic nonlinear optical effect. A “band” having about 500 meV energy dispersion is found in the first half of the Brillouin zone, but disappears at kb/π ~ 1/2. These spectral features are well reproduced by the *d-p* chain model with a small charge-transfer energy Δ compared with that in 1D Cu–O compounds. It is proposed that this smaller Δ is the origin of the absence of clear spin-charge separation in the photoemission spectra and the strong nonlinear optical effect.

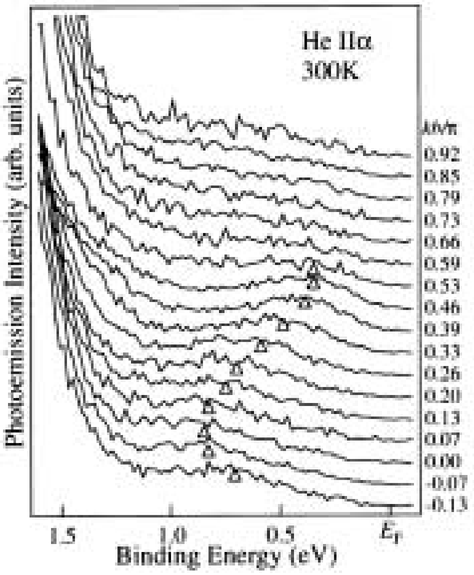


Figure 1. ARPES spectra of $[Ni(chxn)_2Br]Br_2$.

VII-D-3 ESR Detection of Induced Spin Moments in Halogen-Bridged Mixed-Metal Complexes $Ni_{1-x}Pd_x(chxn)_2Br_3$

TANAKA, Hisaaki[1]**; MARUMOTO, Kazuhiro**[1]**; KURODA, Shin-ichi**[1]**; MANABE, Toshio**[2]**; YAMASHITA, Masahiro**[3]
([1]Nagoya Univ.; [2]Tokyo Metropolitan Univ.; [3]IMS and Tokyo Metropolitan Univ.)

[*J. Phys. Soc. Jpn.* **71**, 1370 (2002)]

ESR measurements have been performed on single crystals of the quasi-one-dimensional halogen-bridged mixed-metal complexes, $Ni_{1-x}Pd_x(chxn)_2Br_3$, where on-site Coulomb interaction (Ni^{3+} case) and electron-phonon interaction (Pd^{2+}–Pd^{4+} case) are competing with each other. Monotonic decrease of principal *g*-values from $g(Ni)_{max} = 2.118$ to $g(Pd)_{max} = 2.113$ was observed as *x* increases. This indicates that the magnetic Pd^{3+} ions with smaller *g*-value than that of Ni^{3+} are induced from non-magnetic Pd^{2+}–Pd^{4+} chain, which is consistent with the previous observed spin susceptibility enhancement in this system. In addition, monotonic decrease of the ESR linewidth is observed as *x* increases indicating the contribution of Pd^{3+} ions with longer spin-lattice relaxation time T_{1D}, which is supported by using isomorphic chlorine complexes $Ni(chxn)_2Cl_3$ and $Pd(chxn)_2Cl_3$.

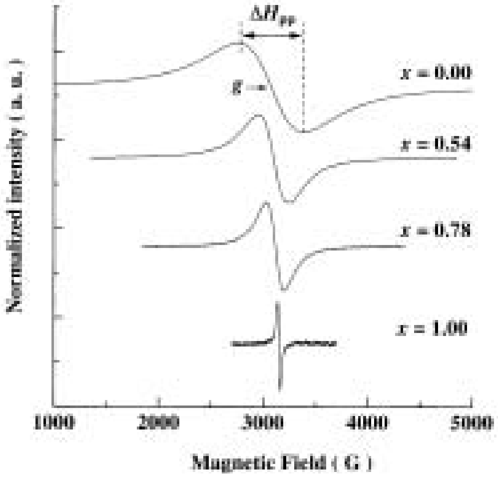


Figure 1. First derivative ESR spectra of single crystalline $Ni_{1-x}Pd_x(chxn)_2Br_3$.

VII-D-4 A Chemical Modification of a Mn_{12} Single-Molecule Magnet by Replacing Carboxylate Anions with Diphenylphosphate Anions

KURODA-SOWA, Takayoshi[1]**; FUKUDA, Satoshi**[1]**; MAEKAWA, Masahiko**[1]**; MUNAKATA, Megumu**[1]**; MIYASAKA, Hitoshi**[2]**; YAMASHITA, Masahiro**[3]
([1]Kinki Univ.; [2]Tokyo Metropolitan Univ.; [3]IMS and Tokyo Metropolitan Univ.)

[*Chem. Lett.* 682 (2002)]

Diphenylphosphate anion can replace with benzoate anions of $[Mn_{12}O_{12}(O_2CPh)_{16}(H_2O)_4]$ to afford a novel Mn_{12} single-molecule magnet (SMM) with mixed bridging ligands.

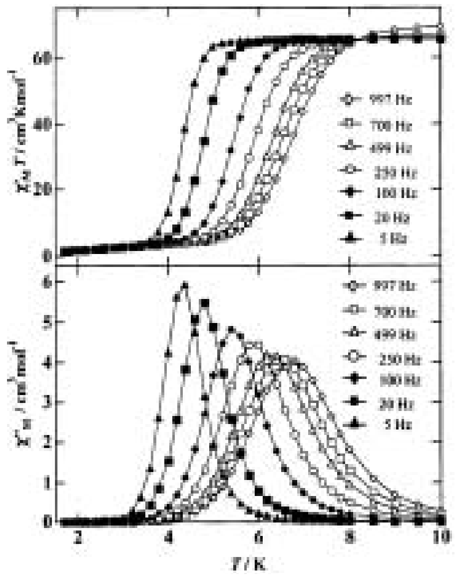


Figure 1. AC magnetic susceptibility data in the form of χ'_MT–T (top) and χ''_M–T(bottom) plots.

VII-D-5 Construction of a One-Dimensional Chain Composed of Mn_6 Clusters and 4,4'-Bipyridine Linker: The First Step for Creation of "Nano-Dots-Wires"

NAKATA, Kazuya[1]; SUGIMOTO, Kunihisa[2]; ISHII, Tomohiko[1]; SUGIURA, Ken-ichi[1]; YAMASHITA, Masahiro[3]
([1]Tokyo Metropolitan Univ.; [2]Rigaku Co. Ltd.; [3]IMS and Tokyo Metropolitan Univ.)

[*Chem. Lett.* 658 (2002)]

Treatment of a mixed-valence Mn_6 cluster, [Mn_6O_2-(t-$BuCO_2$)$_{10}$(t-$BuCO_2H$)$_4$] (1), with 4,4'-bipyridine (bpy) in dichloromethne/1,2-dichloroethane solution gave a one-dimensional polymer chain compounds, [Mn_6O_2(t-$BuCO_2$)$_{10}$(t-$BuCO_2H$)$_2$(bpy)] (2), in which the present cluster core was maintained as a building block.

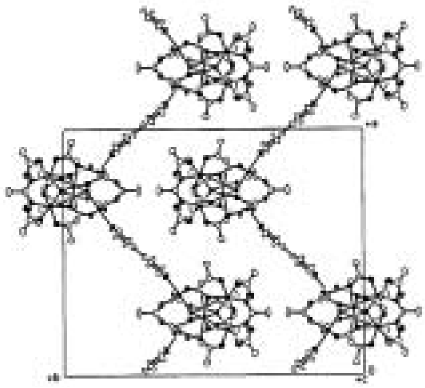


Figure 1. Packing diagram of the 1D chain compound projected along the *c* axis.

VII-D-6 Framework Engineering by Anions and Porous Functionalities Cu(II)/4,4'-bpy Coordination Polymers

NORO, Shin-ichiro[1]; KITAURA, Ryo[1]; KONDO, Mitusru[1]; KITAGAWA, Susumu[1]; ISHII, Tomohiko[2]; MATSUZAKA, Hiroyuki[2]; YAMASHITA, Masahiro[3]
([1]Kyoto Univ.; [2]Tokyo Metropolitan Univ.; [3]IMS and Tokyo Metropolitan Univ.)

[*J. Am. Chem. Soc.* **124**, 2568 (2002)]

A combination of framework-builder (Cu(II) ion and 4,4'-bipyridine (4,4'-byp) ligand) and framework regulator (AF_6 type anions; A = Si, Ge, and P) provides a series of novel porous coordination polymers. The highly porous coordination polymers {[Cu(AF_6)(4,4'-bpy)$_2$]$_8H_2O$}$_n$ (A = Si (1a.8H_2O), Ge (2a.8H_2O) afford robust 3-dimensional (3-D), microporous networks (3D Regular Grid) by using AF_6^{2-} anions. The channel size of these complexes is *ca.* 8 × 8 Å^2 along the *c*-axis and 6 × 2 Å^2 along the *a*-axis or *b*-axis. When compounds 1a.8H_2O or 2a.8H_2O were immersed in water, a conversion of 3-D networks (1a.8H_2O or 2a.8H_2O) to interpenetrated network {[Cu(4,4'-bpy)$_2$(H_2O)$_2$]·AF_6}$_n$ (A = Si(1b) and Ge(2b)) (2D-interpenetration) took place. The 2-D interpenetrated network 1b shows unique dynamic anion-exchange properties, which accompany drastic structural conversions. When a PF_6^- monoanion instead of AF_6^{2-} dianion was used as the framework-regulator with another co-counteranion (coexistent anions), porous coordination polymer with various types of frameworks. Interestingly, these Cu(II) frameworks are rationally controlled by counteranions and selectively converted to other frameworks.

VII-D-7 New Microporous Coordination Polymer Affording Guest-Coordination Sites at Channel Walls

NORO, Shin-ichiro[1]; KITAGAWA, Susumu[1]; YAMASHITA, Masahiro[2]; WADA, Tatsuo[3]
([1]Kyoto Univ.; [2]IMS and Tokyo Metropolitan Univ.; [3]RIKEN)

[*Chem. Commun.* 222 (2002)]

Utilization of a metalloligand, {[Cu(2,4-pydca)$_2$-(H_2O)]·2Et_3NH} (1) (2,4-pydca = pyridine-2,4-dicarboxylate), as a building unit provides a novel porous coordination polymer, {[ZnCu(2,4-pydca)$_2$(H_2O)$_3$-(DMF)]·DMF}$_n$ (2), in which the Zn(II) ion at the node of the network acts as a linker and the Cu(II) ion in the channel wall is available for guest-coordination.

VII-E Large Macrocycle Formation Assisted by Coordination Bonds

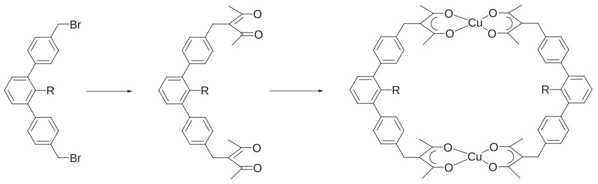
There has been still continuous interest in large macrocyclic molecules due to their cavities formed inside the macrocycle capable of accommodating second molecules as a substrate. The macrocycles often exhibit size and/or shape selectivity, so-called molecular recognition, when binding to the substrate. However, the synthetic complexity of large maclocycles, *e.g.*, the multi-step reactions and the low yield in the ring-closure step, impedes progress in molecular recognition of rather large substrates. Coordination bonds which are slightly weaker than covalent bonds but are easy to form and sensitive to angle seem the most likely candidate for the bond in the ring-closure step. Here we report on a large macrocycle formation from a pair of ligand and metal through coordination bonds. The ligand is bidentate but impossible to be coordinated to a metal simultaneously due to the structure. A 2:2 metal-ligand complex possessing the macrocyclic cavity was thus selectively formed although an infinite ligand-metal arry was also possible.

VII-E-1 Solution and Solid-State Characterization of a Dicopper Receptor for Large Substrates

DAVIDSON, Gerg J. E.[1]**; BAER, Andrew J.**[1]**;**
CÔTE, Adrien P.[1]**; TAYLOR, Nicholas J.**[1]**;**
HANAN, Gerry S.[1]**; TANAKA, Yasutaka**[3]**;**
WATANABE, Masashi[2]
([1]Univ. Waterloo; [2]Shizuoka Univ.; [3]IMS and Shizuoka Univ.)

[*Can. J. Chem.* **80**, 496 (2002)]

Ligand **2** contains two metal-bindigng domains separated by a rigid speacer and assembles into a dicopper receptor **3** with a large central cavity with no evidence of catenation.



2

3

VII-F Development of New Carbonylation Reactions

Carbonylation is recognized as one of useful, reliable, and powerful synthetic methods of carbonyl compounds, such as aldehydes, ketones, esters, lactones, and so on. Our research effort is directed towards the discovery of *novel* type of the catalytic carbonylation reactions; (i) direct carbonylation at C–H bonds and (ii) cycloaddition reaction using carbon monoxide as a one-atom assembling unit (carbonylative cycloaddition reaction).

VII-F-1 $Ru_3(CO)_{12}$-Catalyzed Coupling Reaction of *sp*^{3} C–H Bonds Adjacent to a Nitrogen Atom in Alkylamines with Alkenes

CHATANI, Naoto[1]; ASAUMI, Taku[2]; YORIMITSU, Shuhei[2]; IKEDA, Tsutomu[2]; KAKIUCHI, Fumitoshi[2]; MURAI, Shinji[2]
([1]Osaka Univ. and IMS; [2]Osaka Univ.)

[*J. Am. Chem. Soc.* **123**, 10935 (2001)]

Catalytic reactions which involve the cleavage of an *sp*^{3} C–H bond adjacent to a nitrogen atom in *N*-2-pyridynyl alkylamines are described. The use of $Ru_3(CO)_{12}$ as the catalyst results in the addition of the *sp*^{3} C–H bond across alkene bond to give the coupling products. A variety of alkenes, including terminal, internal, and cyclic alkenes, can be used for the coupling reaction. The presence of directing groups, such as pyridine, pyrimidine, and an oxazoline ring, on the nitrogen of the amine is critical for a successful reaction. This result indicates the importance of the coordination of the nitrogen atom to the ruthenium catalyst. In addition, the nature of the substituents on the pyridine ring has a significant effect on the efficiency of the reaction. Thus, the substitution of an electron-withdrawing group on the pyridine ring as well as a substitution adjacent to the *sp*^{2} nitrogen in the pyridine ring dramatically retards the reaction. Cyclic amines are more reactive than acyclic ones. The choice of solvent is also very important. Of the solvents examined, 2-propanol is the solvent of choice.

VII-F-2 Catalytic Carbonylation Reactions of Benzyne Derivatives

CHATANI, Naoto[1]; KAMITANI, Akihito[2]; OSHITA, Masayuki[2]; FUKUMOTO, Yoshiya[2]; MURAI, Shinji[2]
([1]Osaka Univ. and IMS; [2]Osaka Univ.)

[*J. Am. Chem. Soc.* **123**, 12686 (2001)]

Carbonylation reactions of benzyne are described. The treatment of 2-trimethylsilylphenyl trifluoromethansulfonate (**1**) with CsF and a catalytic amount of $Co_4(CO)_{12}$ in CH_3CN at 10 atm of CO at 60 ˚C gives anthraquinone (**2**). The product **2** consists of two molecules of benzyne, which is generated from the reaction of **1** with CsF, and two molecules of CO. The use of substituted benzyne precursors gives a nearly 1:1 mixture of regioisomers, indicating that a benzyne mechanism is operating. The reaction of 1a with allyl acetate under CO (1 atm) in CH_3CN in the presence of $[(\pi\text{-}C_3H_5)PdCl]_2$, dppe, and CsF at 80 ˚C gives 2-methyleneindanone (**3**). The results on the reaction of substituted benzyne precursors clearly support the intervention of a free benzyne or similar species. The present reaction demonstrates the first example of the catalytic carbonylation of benzyne.

VII-G Development of Cycloisomerization Reactions

Cycloisomerization of enynes is useful methods for the construction of various ring systems form structurally simple acyclic starting materials. An issue critical to the synthetic utility of the cycloisomerization is whether complete conversion with formation of only one product can be attained, because difficulty in separation of the unreacted starting material from the product is foreseen. Simple metal halides, such as $[RuCl_2(CO)_2]_2$, $PtCl_2$, $[IrCl(CO)_3]_n$, and $AuCl_3$ was found to be the effective catalyst for the skeletal reorganization of enynes. The catalysis is initiated by the electrophilic addition of these metal halides to alkynes. This project focuses on the development of new catalytic reaction that consists of the new activation method of C–C triple bonds by metal halides.

VII-G-1 Cycloisomerization of ω-Aryl-1-Alkynes: $GaCl_3$ as a Highly Electrophilic Catalyst for Alkyne Activation

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([1]Osaka Univ. and IMS; [2]Osaka Univ.)

[*J. Org. Chem.* **67**, 1414 (2002)]

Cycloisomerization of a variety of ω-aryl-1-alkynes, where ω = 5 or 6, in the presence of a catalytic amount of $GaCl_3$ provided dihydronaphthalene derivatives or dihydrobenzocycloheptenes, respectively, in high yields. The reactions of the substrates containing electron-withdrawing groups on the aromatic ring were significantly improved with $GaCl_3$ catalyst, compared with the previously reported catalytic system.

VII-H Multi-Electron Reduction of Carbon Dioxide through Metal-Carbonyl and Oxidative Activation of Water *via* Metal-Oxo Complexes

An electrophilic attack of CO_2 to coordinatively unsaturated low valent metal complexes affords M-η^1-CO_2 complexes, which are smoothly converted to *M*-CO ones in protic and aprotic media. Organic synthesis through *M*-CO complexes derived from CO_2, therefore, is highly desired in the viewpoint of C1 chemistry. A major problem to make multi-electron reduction of CO_2 is reductive cleavages of *M*–CO bonds (CO evolution). This problem may be overcome by the construction of a catalytic system, which can supply electrons to carbonyl group of *M*–CO bonds with depressing of an increase in the electron density at the central metal. Such requirements would be fulfilled by the metal complexes with a structurally flexible ligand having an ability to not only open and close a chelate ring for CO_2 binding but also to form a metallacycle including metal and carbon atoms of *M*–CO bonds for inhibition of the bond cleavage.

High valent metal-oxo complexes are feasible candidates for oxidation and hydroxylation of non-activated hydrocarbons from the viewpoints of the enzymatic activity of P-450 enzymes. Mechanistic understandings of the reactivity of high-valent metal-oxo complexes have, however, been limited because no reasonable synthetic route for metal-oxo complex from dioxygen has been proposed so far in artificial systems. On the other hand, Ru–OH_2 complexes are smoothly converted to high-valent Ru=O ones by sequential electron and proton loss, and the latter has attracted much attention in the viepoint of the elucidation of reactivity of metal-oxo frameworks. Taking into account that quinone undergoes stepwise reduction to yield semiquinone and catecholate, introduction of quinone ligands into the Ru–OH_2 framework would assist smooth conversion from aqua to oxo ligands without changing of the oxidation states of the central Ru.

VII-H-1 Syntheses of New Ruthenium Carbonyl Terpyridine *o*-Phenylene Complexes: Strong Interaction between Carbonyl and *o*-Phenylene Ligands

SUGIMOTO, Hideki[1]; TANAKA, Koji
([1]Osaka City Univ.)

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

Ruthenium carbonyl *o*-phenylene complexes, $Ru(CO)(3,6\text{-}Bu_2seq)(trpy)]PF_6$ ([**1**]PF_6) and [Ru(CO)(*o*-monothiocat)(trpy)] (**2**) were prepared by the reaction of $[Ru(CO)C1_2(trpy)]$ with the corresponding *o*-phenylenes in 2-methoxyethanol. X-ray crystallographic study of [**1**]BF_4 indicated that the ruthenium center is coordinated by carbonyl, three nitrogens of trpy and two oxygens of 3,6-Bu_2seq. ESR of [**1**]PF_6 and **2** indicated that the electronic structures of ruthenium-*o*-phenylene unit of the complexes have Ru(II)-3,6-Bu_2seq and Ru(II)-*o*-monothiocat forms, respectively. Significant differences in the redox behavior and the spectroscopical properties between [**1**]PF_6 and **2** and [RuCl(3,5-Bu_2seq)(trpy)] were ascribed to the strong interaction between *o*-phenylene and carbonyl ligands through Ru(II).

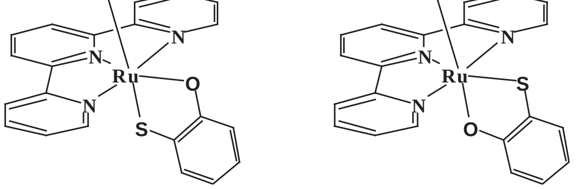


Figure 1. Two isomers of **2**.

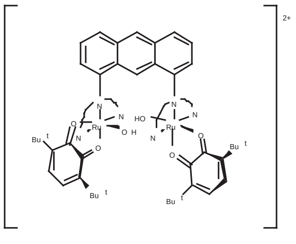
VII-H-2 Synthesis and Redox Properties of Bis(ruthenium-hydroxo)complexes with Quinone and Bipyridine Ligand as a Water-Oxidation Catalysts

WADA, Tohru; TSUGE, Kiyoshi; TANAKA, Koji

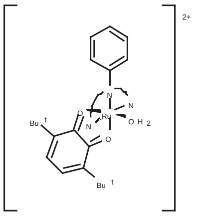
[*Inorg. Chem.* **40**, 329 (2001)]

The novel bridging ligand 1,8-bis(2,2’:6’,2”-terpyridyl)anthracene (btpyan) is synthesized by three reactions from 1,8-diformylanthracene to connect two $[Ru(L)(OH)]^+$ units (*L* = 3,6-*di-tert*-butyl-1,2-benzoquinone (3,6-tBu_2qui) and 2,2’-bipyridine (bpy)). An addition of *t*BuOK (2.0 equiv) to a methanolic solution of $[Ru^{II}_2(OH)_2(3,6\text{-}tBu_2qui)_2(btpyan)](SbF_6)_2$ ([**1**]$(SbF_6)_2$) results in the generation of $[Ru^{II}_2(O)_2(3,6\text{-}tBu_2sq)_2(btpyan)]^0$ (3,6-tBu_2sq = 3,6-*di-tert*-butyl-1,2-semiquinone) due to the reduction of quinone coupled with the dissociation of the hydroxo protons. The resultant complex $[Ru^{II}_2(O)_2(3,6\text{-}tBu_2sq)_2(btpyan)]^0$ undergoes ligand-localized oxidation at $E_{1/2}$ = +0.40 V (*vs* Ag/AgCl) to give $[Ru^{II}_2(O)_2(3,6\text{-}tBu_2qui)_2(btpyan)]^{2+}$ in MeOH solution. Furthermore, metal-localized oxidation of $[Ru^{II}_2(O)_2(3,6\text{-}tBu_2qui)_2(btpyan)]^{2+}$ at E_p = +1.2 V in CF_3CH_2OH/ether or water gives $[Ru^{III}_2(O)_2(3,6\text{-}tBu_2qui)_2(btpyan)]^{4+}$, which catalyzes water oxidation. Controlled-potential electrolysis of [**1**]$(SbF_6)_2$ at +1.70 V in the presence of H_2O in CF_3CH_2OH evolves dioxygen with a current efficiency of 91% (21 turnovers). The turnover number of O_2 evolution increases to 33 500 when the electrolysis is conducted in water (pH 4.0) by using a [**1**]$(SbF_6)_2$-modified ITO electrode. On the other hand, the analogous complex $[Ru^{II}_2(OH)_2(bpy)_2(btpyan)](SbF_6)_2$ ([**2**]$(SbF_6)_2$) shows neither dissociation of the hydroxo protons, even in the presence of a large excess of *t*Bu-

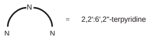
OK, nor activity for the oxidation of H_2O under similar conditions.



$[\mathbf{1}]^{2+}$



$[\mathbf{2}]^{2+}$

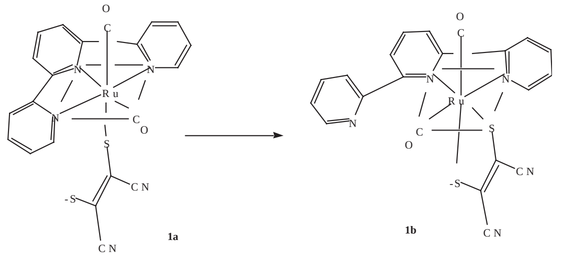


VII-H-3 Ruthenium Terpyridine Complexes with Mono- and Bi-Dentate Dithiolene Ligands

SUGIMOTO, Hideki[1]; TSUGE, Kiyoshi; TANAKA, Koji
([1]Osaka City Univ.)

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

The reaction of $[Ru(CO)_2Cl(terpy)]PF_6$ (terpy = 2,2':6':2"-terpyridine) with Na_2mnt (mnt = $S_2C_2(CN)_2$) initially produced $[Ru(CO)_2(mnt)(terpy\text{-}\kappa^3NN'N'')]$ **1a**, which rearranged to $[Ru(CO)_2(mnt\text{-}\kappa^2SS')(terpy\text{-}\kappa^2NN')]$ **1b** in solution. The molecular structures of **1a** and **1b** indicate that the rearrangement proceeds *via* a five-coordinated complex with monodentate mnt and bidentate terpy. The reaction of $[Ru(CO)_2Cl(terpy)]PF_6$ with 3,4-toluenedithiol (H_2tdt) gave $[Ru(CO)_2(tdt\text{-}\kappa^2SS')(terpy\text{-}\kappa^2NN')]$ **2b** but $[Ru(CO)_2(tdt\text{-}\kappa S)(terpy\text{-}\kappa^3NN'N'')]$ **2a** was not identified. Thus, ruthenium complexes with bidentate dithiolene and bidentate terpyridine seem to be more stable than those with monodentate dithiolene and tridentate terpyridine. Neither $[Ru(CO)_2(pdt\text{-}\kappa S)(terpy\text{-}\kappa^3NN'N'')]$ **3a** nor $[Ru(CO)_2(pdt\text{-}\kappa^2S)(terpy\text{-}\kappa^2NN')]$ **3b** (pdt = PhC(S)-C(S)Ph) was obtained in the reaction of $[Ru(CO)_2Cl\text{-}(terpy)]PF_6$ with the Cs^+ salt of pdt^{2-} in CH_3OH under N_2. The same reaction conducted under aerobic conditions afforded $[Ru(CO)(C(O)OCH_3)(SC(Ph)C(Ph)\text{-}SC(O)OMe)(terpy\text{-}\kappa^3NN'N'')]$ **3a** resulting from double addition of CO_2 and CH_3OH to the terminal sulfur of pdt and a carbonyl carbon of **3a**, respectively, followed by esterification of the resultant $[Ru(CO)(C(O)OCH_3)\text{-}(SC(Ph)C(Ph)SC(O)OH)(terpy\text{-}\kappa^3NN'N'')]$ in CH_3OH. The addition of CO_2 to the 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 $[RuX\text{-}(dithiolene)(terpy)]^{n+}$ (X = dmso, Cl or OSO_2CF_3; n =0 or 1) were also prepared.



1a

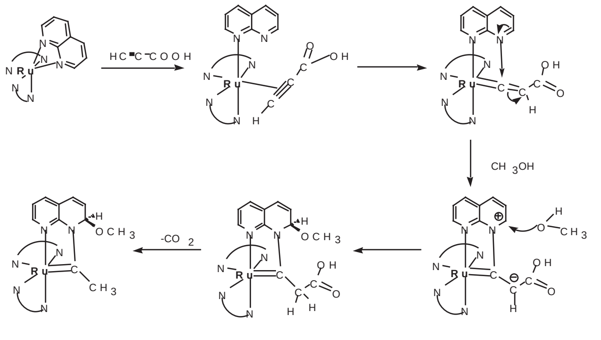
1b

VII-H-4 A Ru-Carbene Complex with a Metallacycle Involving a 1,8-Naphthylidine Framework

TOMON, Takashi; OOYAMA, Dai[1]; WADA, Tohru; SHIREN, Kazushi; TANAKA, Koji
([1]Fukushima Univ.)

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

A CH_3OH/H_2O solution containing $[\mathbf{1}](PF_6)_2$ and HCCC(O)OH was refluxed for 2 h, and $[\mathbf{2a}](PF_6)_2$ was obtained from the solution. Recrystallization of the crude product from CH_3CN/CH_3OH gave single crystals of $[\mathbf{2a}](PF_6)_2\cdot CH_3CN$ in 64% yield. The similar reaction between $[\mathbf{1}](SbF_6)_2$ and HCCC(O)OH in $C_2H_5\text{-}OH/H_2O$ under similar reaction conditions afforded $[\mathbf{2b}](SbF_6)_2$ in 56% yield. The ruthenium atom of $\mathbf{2a}^{2+}$ has octahedral geometry with four nitrogen atoms of two bpy ligands, one nitrogen from napy and one carbon of the CCH_3 group. The characteristic features of $\mathbf{2a}^{2+}$ are the C–N bond formation between the CCH_3 group and one nitrogen of napy, and the attachment of the CH_3O group to the 2-position of the napy moiety. The resultant five-membered metallacycle consisting of Ru, N(1), C(11), N(2), and C(2) atoms in an almost planar structure, and the sum of the bond angles around the five-membered ring is almost 360. Despite the attachment of CH_3O to the 2-positon of the napy moiety, the resultant ligand still maintains the planar structure in $\mathbf{2a}^{2+}$. As a result, the napy moiety and the five-membered metallacycle are co-planar. The Ru–N(4) (2.156(9) Å) bond trans to Ru–C(2) is substantially longer than the other Ru–N bonds of $\mathbf{2a}^{2+}$ (2.03(1)–2.08(1) Å), suggesting a strong trans effect of the carbene ligand. The Ru–C(2) bond distance (1.93(1) Å) is in the expected range of hexa-coordinated ruthenium carbene bonds (1.941–1.98 Å), and the bond length is longer than those expected for penta-coordinated ruthenium carbene complexes (1.810–1.861 Å). The ^{13}C NMR spectrum of $\mathbf{2a}^{2+}$ also showed the carbon signal of the Ru–CCH_3 group at 293 ppm as a singlet, similar to most Ru carbene complexes.



Scheme

VII-H-5 Ruthenium Oxyl Radical Complex Containing *o*-Quinone Ligand Detected by ESR Measurements of Spin Trapping Technique

KOBAYASHI, Katsuaki; OHTSU, Hideki; WADA, Tohru; TANAKA, Koji

[*Chem. Lett.* 868 (2002)]

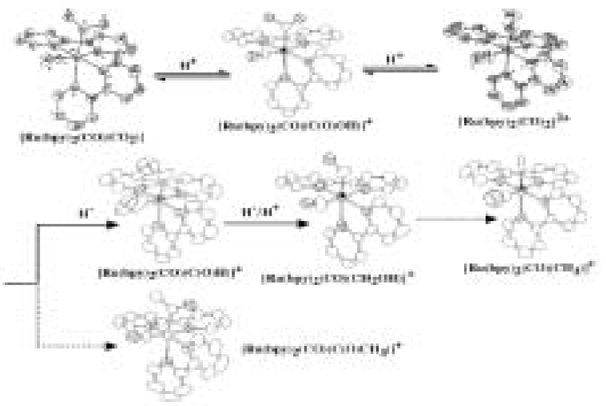
The ESR spectrum obtained upon an addition of a 3 equiv of *t*BuOK and DMPO to a CH_2C1_2 solution of $[Ru(trpy)(3,5\text{-}dbQ)(OH_2)]^{2+}$ at 193 K is depicted in Figure 1A and 1B, which shows an isotropic broad signal without hyperfine structure (g = 2.029, ΔH_{msl} = 7.3 mT) together with 12-line sharp signal centered at g = 2.006 (Figure 1B). The pattern of ESR spectrum was not perturbed by a change of modulation amplitude within 0.14 mT. The hyperfine coupling constants values of the characteristic 12-line sharp signal (g = 2.006, $a_N{}^{\alpha}$ = l.32, $a_H{}^{\beta}$ = 0.63 and $a_H{}^{\gamma}$ = 0.20 mT) are determined by the computer simulation. The ESR signal centered at g = 2.029 is very close to those of the Ru^{II}-semiquinone complex, $[Ru^{II}(trpy)(35tBu_2SQ)AcO^-]$ (g = 2.030, ΔH_{msl} = 8.0 mT), thus, the isotropic broad signal (g = 2.029) can be assigned to the Ru^{II}-SQ moiety. The signal intensity resulted from the Ru^{II}-SQ moiety linearly increased with increasing amounts of *t*BuOK, when more than 1 eq of *t*BuOK was added to the solution. The other ESR signal centered at g = 2.006 can be assigned to the DMPO spin adduct, $[Ru^{II}(trpy)\text{-}(35tBu_2SQ)(O)(DMPO)]l^0$.

Formation of the DMPO spin adduct is further confirmed by ESI mass spectrum which exhibited a signal at m/z 684. The observed mass and isotope patterns corresponded to $[Ru^{II}(trpy)(35tBu_2SQ)(^{16}O)\text{-}(DMPO)]^+$. The labeling experiment using $H_2{}^{18}O$ showed an expected signal at m/z 686 corresponding to $[Ru^{II}(trpy)(35tBu_2SQ)(^{18}O)(DMPO)]^+$ suggesting that an oxyl radical ligand was generated by the deprotonation of an aqua ligand. Thus, oxyl radical is induced by the acid-base equilibrium of the aqua ligand coupled with the reduction of the quinone ligand.

VII-H-6 Multi-Electron Reduction of CO_2 *via* Ru-CO_2 -C(O)OH, -CO, -CHO, and -CH_2OH Species

TANAKA, Koji; OOYAMA, Dai

A series of $[Ru(bpy)_2(CO)L]^{n+}$ (L = CO_2, C(O)OH, CO, CHO, CH_2OH, CH_3, and $C(O)CH_3$; n = 0, l, 2) were prepared and their molecular structures were determined by X-ray analyses. These complexes are reasonable models of reaction intermediates in the multi-electron reduction of CO_2 catalyzed by metal complexes, since reductive cleavage of the Ru–L bonds of the complexes in protic media affords HCOOH, CO, HCHO, CH_3OH, and CH_4 as two-, four-, six- and eight-electron reduction products of CO_2. The free energy required in the reduction of CO_2 progressively decreases with an increase of the number of electrons participating in the reduction of CO_2. The Ru–L bond character of the series of $[Ru(bpy)_2(CO)L]^{n+}$ was assessed by the ν(Ru–L) bands and the Ru–L bond distances from the viewpoint of elucidation of a correlation between free energy changes in the multi-electron reduction of CO_2 catalyzed by metal complexes and the metal–carbon bond strength of each intermediate. The ruthenium–carbon bond distance of $[Ru(bpy)_2(CO)L]^{n+}$ largely depends on the hybrid orbital of the carbon atom bonded to ruthenium and lengthens in the order Ru–C_{sp} < Ru–C_{sp2} < Ru–C_{sp3}. An unusual shift of the ν(Ru–L) bands to higher wavenumber with decrease of the Ru–L bond distances was discussed in terms of σ- and π-character of the ruthenium–carbon bonds.



VII-I Silanechalcogenolato Complexes

Transition metal–chalcogenido clusters have attracted attention in light of their relevance to various active sites of metalloproteins, desulfurization catalysis, and inorganic functional materials. An important and challenging subject in this chemistry is to develop rational methods to synthesize desirable chalcogenido cluster complexes of high nuclearity, by assembling suitable metal–chalcogenido fragments. Compared with complexes containing alkyl(aryl) chalcogenolato ligands, the coordination chemistry of silanechalcogenolates has yet to be explored. However, the use of silanechalcogenolates has the following two advantages in developing rational synthetic routes to transition metal chalcogenido clusters. First, silicon–chacogen (sulfur, selenium, and tellurium) bonds are expected to be more labile and more readily cleaved under a mild condition than corresponding carbon–chalcogen bonds. Secondly, the reactivity of silanetchalcogenolato ligands can be controlled by steric and electronic properties of substituents in the silyl group. In this project, we are studying the chemistry of transition metal silanechalcogenolato complexes and their use as a precursor for cluster synthesis.

VII-I-1 Palladium Dimethylsilanedithiolato Complex: a Precursor for Ti-Pd and Ti-Pd_2 Heterometallic Complexes

KOMURO, Takashi[1]; MATSUO, Tsukasa; KAWAGUCHI, Hiroyuki; TATSUMI, Kazuyuki[1]
([1]Nagoya Univ.)

[*Chem. Commun.* 988 (2002)]

The bis-silylated sulfides $(R_3Si)_2S$ have been widely used to prepare a variety of metal sulfide clusters, because these reagents exploit the strength of the Si–O and Si–Cl bond to replace a halide, alkoxide, acetate or oxide with a sulfido ligand under very mild and controlled conditions. Therefore, a metal-silanethiolato complex (*eg.*, M–$SSiR_3$) would be expected to serve as a synthetic precursor of homo- and hetero-metallic sulfido clusters. However, compounds containing the silanethiolato ligand are less common compared with alkylthiolato complexes. The silanedithiolato complex $Pd(S_2SiMe_2)(PEt_3)_2$ (**1**) reacted with $(C_5H_5)TiCl_3$ and $TiCl_4(thf)_2$ to produce the heterometallic clusters $(C_5H_5)TiCl(\mu\text{–}S)_2Pd(PEt_3)_2$ (**2**) and $TiCl_2(S)(\mu\text{–}S)_2Pd_2(PEt_3)_4$ (**3**) along with silicon–sulfur bond cleavage, respectively.

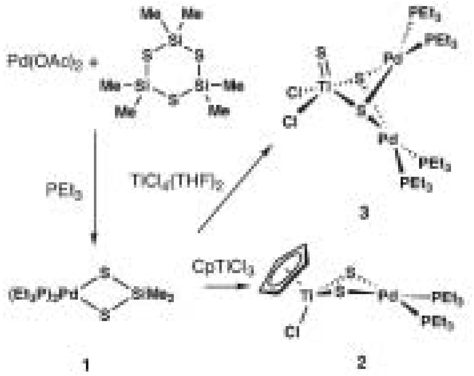


Figure 1.

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

KOMURO, Takashi[1]; KAWAGUCHI, Hiroyuki; TATSUMI, Kazuyuki[1]
([1]Nagoya Univ.)

[*Inorg. Chem.* **41**, 5083 (2002)]

Reactions of $Fe[N(SiMe_3)_2]_2$ with 1 and 2 equiv of Ph_3SiSH in hexane afforded dinuclear silanethiolato complexes, $[Fe\{N(SiMe_3)_2\}(\mu\text{–}SSiPh_3)]_2$ (**1**) and $[Fe(SSiPh_3)(\mu\text{–}SSiPh_3)]_2$ (**2**), respectively. Various Lewis bases were readily added to **2**, generating mononuclear adducts, $Fe(SSiPh_3)_2(L)_2$ [L = CH_3CN (**3a**), 4-$^tBuC_5H_4N$ (**3b**), PEt_3 (**3c**), $(L)_2$ = tmeda (**3d**)]. From the analogous reactions of $M[N(SiMe_3)_2]_2$ (M = Mn, Co) and $[Ni(NPh_2)_2]_2$ with Ph_3SiSH in the presence of TMEDA, the corresponding silanethiolato complexes, $M(SSiPh_3)_2$(tmeda) [M = Mn (**4**), Co (**5**), Ni (**6**)], were isolated. Treatment of **3a** with $(PPh_4)_2[MoS_4]$ or $(NEt_4)_2[FeCl_4]$ resulted in formation of a linear trinuclear Fe–Mo–Fe cluster $(PPh_4)_2[MoS_4\{Fe(SSiPh_3)_2\}_2]$ (**7**) or a dinuclear complex $(NEt_4)_2[Fe_2(SSiPh_3)_2Cl_4]$ (**8**). On the other hand, the reaction of **3a** with $[Cu(CH_3CN)_4](PF_6)$ gave a cyclic tetranuclear copper cluster $Cu_4(SSiPh_3)_4$ (**9**), where silanethiolato ligands were transferred from iron to copper. Silicon–sulfur bond cleavage was found to occur when the cobalt complex **5** was treated with $(NBu_4)F$ in THF, and a cobalt-sulfido cluster $Co_6(\mu_3\text{–}S)_8(PPh_3)_6$ (**10**) was isolated upon addition of PPh_3 to the reaction system. The silanethiolato complexes reported here are expected to serve as convenient precursors for sulfido cluster synthesis.

VII-J Coordination Chemistry of New Multidentate Ligands and Activation of Small Molecules

This project is focused on the design and synthesis of new ligands that are capable of supporting novel structural features and reactivity. Currently, we are investigating multidentate ligands based on aryloxide, thiolate, and amidinate. Our recent efforts have been directed toward activation of small molecules.

VII-J-1 Binuclear Iron(II) Complex from a Linked-bis(amidinate) Ligand: Synthesis and its Reaction with Carbon Monoxide

KAWAGUCHI, Hiroyuki; MATSUO, Tsukasa

[*Chem. Commun.* 958 (2002)]

We synthesized and fully characterized binuclear iron(II) complexes supported by a linked bis(amidinate) ligand. As part of a program aimed at developing new ancillary ligands to support reactive binuclear metal centers, we chose to employ a *trans*-cyclohexane-linked bis(amidinate) ligand L^{2-}. The use of this linked bis(amidinate) ligand leads to isolation of double-stranded binulear complexes of iron(II), in which metal centers are coordinatively unsaturated. According to X-ray analyses, the size of a cage created by the L^{2-} ligands is flexible. Furthermore, another interesting aspect of this system is the ligand self-recognition in the assembly process. Although the recemic L^{2-} ligand is used, the reaction of racemic $Li_2(L)$ with $FeCl_2$ exclusively affords two discrete homochiral metal complexes Λ,Λ-$Fe_2(L^{RR})_2$ and Δ,Δ-$Fe_2(L^{SS})_2$. The robustness of this homochiral binuclear flame is examined in the reaction with CO.

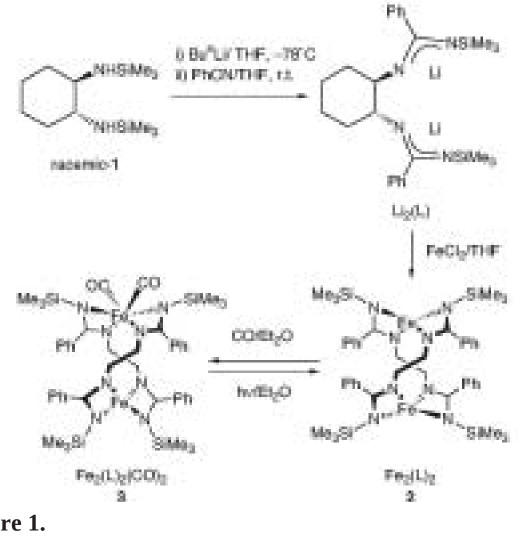


Figure 1.

VII-J-2 Synthesis and Structures of Ti(III) and Ti(IV) Complexes Supported by a Tridentate Aryloxide Ligand

MATSUO, Tsukasa; KAWAGUCHI, Hiroyuki; SAKAI, Masahiro

[*J. Chem. Soc., Dalton Trans.* 2536 (2002)]

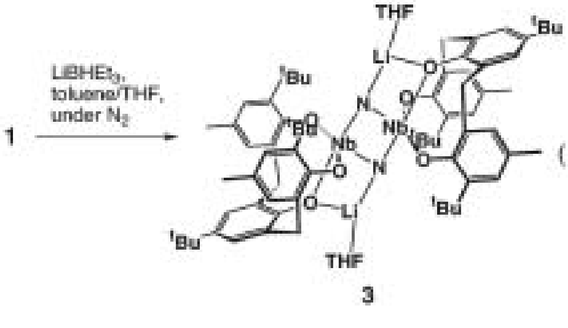
Titanium complexes of the tridentate aryloxide $Me–L^{3-}$ [$H_3(Me–L)$ = 2,6-bis(4,6-dimethylsalicyl)-4-*tert*-butylphenol] have been prepared. Reaction of $TiCl_4$ with 1 equiv of $H_3(Me–L)$ gave $[Ti(Me–L)Cl]_2$ **1**. Recrystallization of **1** from THF resulted in formation of the THF adduct $Ti(Me–L)Cl(THF)_2$ **2**. Treatment of **1** with $[NEt_4]Cl$ in THF quantitatively gave $[NEt_4][Ti_2(Me–L)_2Cl_3]$ **3**. Complex **1** was reduced with 2 equiv of potassium to produce the Ti(III) complex $[Ti(Me–L)(DME)]_2$ **4**. Structures of **1**, **2**, **3**, and **4** have been determined by X-ray analyses. For **1**, **2**, and **4**, the Me–L ligand assumes a U-conformation. In the case of **3**, it is coordinated in an S-conformation.

VII-J-3 Dinitrogen-Bond Cleavage in a Niobium Complex Supported by a Tridentate Aryloxide Ligand

KAWAGUCHI, Hiroyuki; MATSUO, Tsukasa

[*Angew. Chem., Int. Ed. Engl.* **41**, 2792 (2002)]

The N≡N triple bond cleavage took place in the reaction of $[Nb(tBu–L)Cl_2]_2$ (**1**) with $LiBHEt_3$, resulting in the formation of $[Nb(tBu–L)(\mu–N)Li(THF)]_2$ (**3**) [$H_3(tBu–L)$ = 2,6-bis(4,6-methyl-*tert*-butyl-salicyl)-4-*tert*-butylphenol]. On the other hand, the analogous reaction of $[Nb(Me–L)Cl_2]_2$ (**2**) with $LiBHEt_3$ yielded $[Nb_2(Me–L)_2(\mu–H)(\mu–Cl)(THF)_2]Li_4(THF)_4Cl_2$ (**4**) [$H_3(Me–L)$ = 2,6-bis(4,6-dimethylsalicyl)-4-*tert*-butylphenol] concomitant with reduction of the metal center from Nb^V to Nb^{III}. Structures of **3** and **4** have been determined by X-ray diffraction analyses. Repeating the experiment under an atmosphere of $^{15}N_2$ affords $[Nb(tBu–L)(\mu–^{15}N)Li(THF)]_2$ (**3**-^{15}N). The ^{15}N NMR spectrum of **3**-^{15}N shows a single peak at δ 312, thus unambiguously confirming the origin of the bridging ligands in **3** to be N_2. This work clearly shows that each $R–L^{3-}$ ligand behaves in a very distinctive manner with respect to dinitrogen activation and metal–metal interaction.



(1)

Figure 1.

VII-K Synthesis of Compounds Having a Novel Bonding Containing Heavier Main Group Elements

Double-bond compounds of main group elements of the second row such as 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.

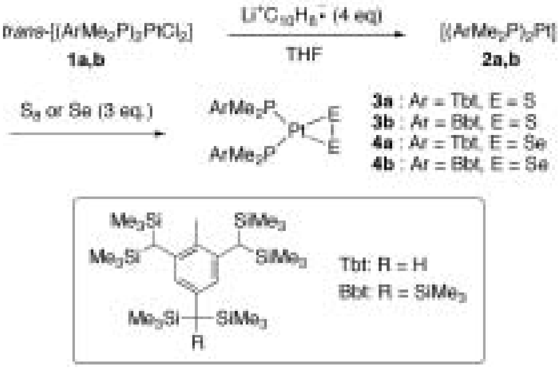
VII-K-1 Syntheses and Crystal Structures of the First Disulfur and Diselenium Complexes of Platinum

NAGATA, Kazuto[1]; TAKEDA, Nobuhiro[1]; TOKITOH, Norihiro[2]
([1]Kyoto Univ.; [2]IMS and Kyoto Univ.)

[*Angew. Chem. Int. Ed. Engl.* **41**, 136 (2002)]

The chemistry of complexes with diatomic chalcogen ligands has attracted much attention due to their unique structure, biological interest, potential for hydrogen-transfer catalysis, and synthetic utility as a precursor of new metal cluster complexes. However, since sulfur and selenium ligands have a strong propensity for bridging metal atoms, it is often difficult to prepare their mononuclear diatomic complexes. To our knowledge, the disulfur and diselenium complexes of platinum remain unknown, although the dioxygen analogues, *e. g.*, [$(Ph_3P)_2PtO_2$], have been extensively studied.

When platinum dichlorides **1a**,**b** were reduced by an excess of lithium naphthalenide in THF and the resulting platinum(0) species [$(ArMe_2P)_2Pt$] (**2a**,**b**) were successively treated with elemental sulfur (3 equiv. as S) and elemental selenium, the first platinum disulfur and diselenium complexes [$(ArMe_2P)_2PtE_2$] (**3a**,**b**: E = S; **4a**,**b**: E = Se) were obtained, respectively. The structures of **3a**,**b** and **4a**,**b** were identified by mass spectrometry, elemental analysis, and multinuclear NMR spectroscopy, and the molecular structures of **3b** and **4b** were finally determined by X-ray crystallographic analysis. The molecular structures of **3a**,**b** and **4a**,**b** are very similar, and these complexes have a square-planar geometry and a three-membered PtE_2 (E = S, Se) ring as well as an analogous dioxygen complex [$(Ph_3P)_2PtO_2$].



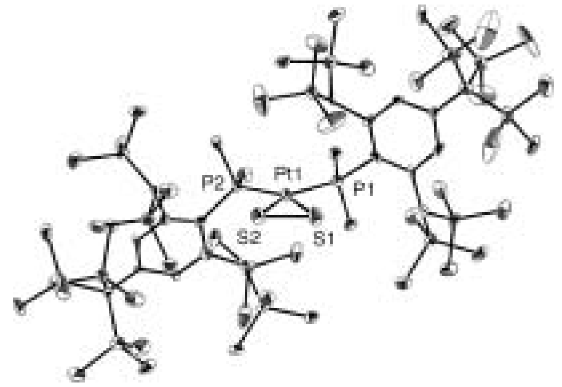


Figure 1. ORTEP drawing of a disulfur complex of platinum **3b**.

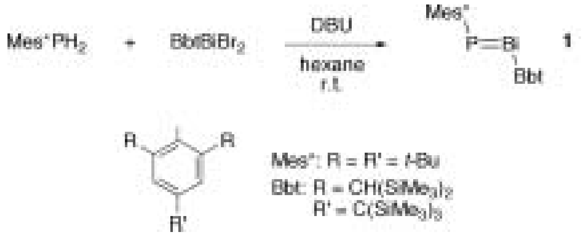
VII-K-2 Synthesis and Structure of the First Stable Phosphabismuthene

SASAMORI, Takahiro[1]; TAKEDA, Nobuhiro[2]; FUJIO, Mizue[1]; KIMURA, Masahiro[3]; NAGASE, Shigeru; TOKITOH, Norihiro[4]
([1]Kyushu Univ.; [2]Kyoto Univ.; [3]Tokyo Metropolitan Univ.; [4]IMS and Kyoto Univ.)

[*Angew. Chem. Int. Ed. Engl.* **41**, 139 (2002)]

Recently, there has been much interest in doubly bonded compounds between group 15 elements, *i. e.*, heavier congeners of azo-compounds. Homonuclear doubly bonded systems between heavier group 15 elements are no more imaginary species even in the case of bismuth, and the next target molecules are heteronuclear doubly bonded systems, which may be key compounds of great importance in the systematic elucidation of the intrinsic nature of low-coordinated compounds of heavier main group elements.

The first stable phosphabismuthene **1** was successfully synthesized by the condensation reaction of $BbtBiBr_2$ with $Mes^{*}PH_2$ in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in hexane at room temperature. It is noteworthy that compound **1** is not only a new member of a novel class of heteronuclear doubly bonded systems between heavier group 15 elements but also the first example of a stable species with a double bond between the third and sixth row main group elements. Phosphabismuthene **1** features a double bond between phosphorus and bismuth atom in the solid state and even in solution, as suggested by the NMR and UV/vis spectra and X-ray crystallographic analysis.



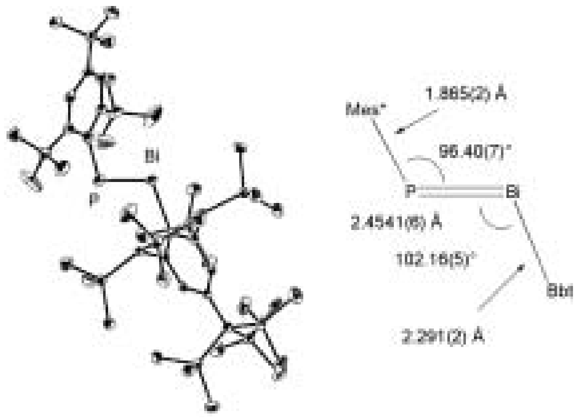


Figure 1. ORTEP drawing of phosphabismuthene **1**.

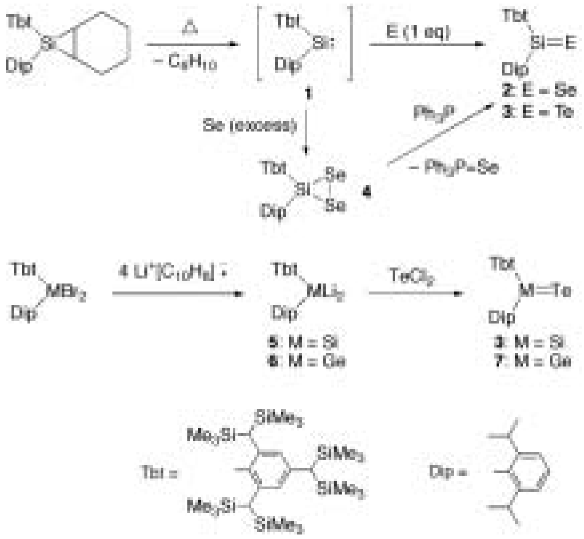
VII-K-3 Synthesis of Kineically Stabilized Silaneselone and Silanetellone

TOKITOH, Norihiro[1]**; SADAHIRO, Tomoyuki**[2]**; HATANO, Ken**[3]**; SASAKI, Takayo**[4]**; TAKEDA, Nobuhiro**[4]**; OKAZAKI, Renji**[2]
([1]IMS and Kyoto Univ.; [2]Univ. Tokyo; [3]Kyushu Univ.; [4]Kyoto Univ.)

[*Chem. Lett.* 34 (2002)]

Since ketones play very important roles in organic chemistry, much interest has been focused on the chemistry of double-bond compounds between heavier group 14 and group 16 elements (we refer to this family of heavier congeners of ketones as “heavy ketones”). As for silicon-containing heavy ketones, only a silanethione bearing 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) and 2,4,6-triisopropylphenyl (Tip) groups [Tbt(Tip)-Si=S] was isolated as a stable compound. Although some examples are known for silaneselones stabilized by the intramolecular coordination of a nitrogen atom and transient silaneselones as reactive intermediates, no coordination-free examples have been synthesized yet for silaneselones and silanetellones so far.

Kinetically stabilized silaneselone **2** and silanetellone **3** were successfully synthesized by direct chalcogenation of silylene **1** with elemental chalcogen. The formation of **2** and **3** was confirmed by multinuclear NMR spectroscopy and trapping experiments. Deselenation of diselenasilirane **4**, which was generated by the reaction of **1** with an excess of selenium, also gave **2**. In addition, metallanetellones, **3** and **7**, were synthesized by a new synthetic method for heavy ketones, *i. e.*, the reaction of dilithiometallane, **5** and **6**, with $TeCl_2$.



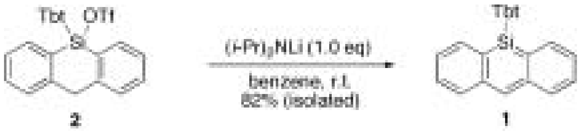
VII-K-4 The First Stable 9-Silaanthracene

TAKEDA, Nobuhiro[1]**; SHINOHARA, Akihiro**[1]**; TOKITOH, Norihiro**[2]
([1]Kyoto Univ.; [2]IMS and Kyoto Univ.)

[*Organometallics* **21**, 256 (2002)]

Since aromatic compounds play very important roles in organic chemistry, much attention has been also paid to silaaromatics. However, there are few reports on the synthesis and isolation of silaaromatic compounds stable at room temperature because of their high reactivity. Recently, we have succeeded in the synthesis of the first stable 2-silanaphthalene and silabenzene by taking advantage of an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt). In contrast, silaanthracenes have never been isolated as stable compounds, although there are some reports of the chemical trapping of intermediary silaanthracenes and of observation by UV/vis spectroscopy of unstable silanathracenes in matrices at low temperature.

The first stable 9-silanathracene **1** was successfully synthesized by the reaction of the corresponding silyl triflate **2** with 1.0 molar amount of lithium diisopropylamide. The aromaticity of **1** is discussed on the basis of the NMR, UV/vis, and Raman spectra, X-ray structural analysis, and theoretical calculations. Although 9-silaanthracene **1** is thermally stable even at 100 °C in solution, treatment of **1** with H_2O at room temperature gave the corresponding silanol (90%) via the 1,4-addition of water to the 9- and 10-positions of 9-silaanthracene ring. Furthermore, 9-silaanthracene **1** reacted with styrene and benzophenone at room temperature to give the corresponding [2 + 4] cycloadduct in good yields.



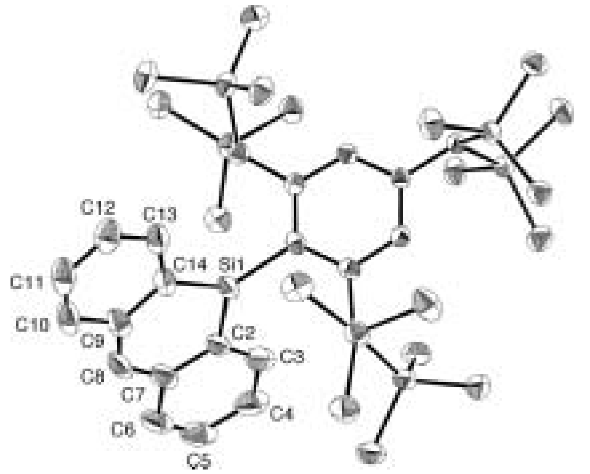


Figure 1. ORTEP drawing of 9-silaanthracene **1**.

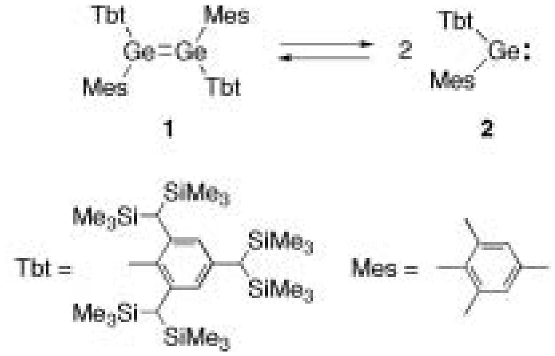
VII-K-5 Synthesis and Characterization of an Extremely Hindered Tetraaryl-Substituted Digermene and its Unique Properties in the Solid State and in Solution

TOKITOH, Norihiro[1]; KISHIKAWA, Kuniyuki[2]; OKAZAKI, Renji[2]; SASAMORI, Takahiro[3]; NAKATA, Norio[3]; TAKEDA, Nobuhiro[3]
([1]IMS and Kyoto Univ.; [2]Univ. Tokyo; [3]Kyoto Univ.)

[*Polyhedron* **21**, 563 (2002)]

During the last two decades remarkable progress has been made in the chemistry of low-coordinate compounds of heavier group 14 elements, especially in those of dimetallenes and metallylenes because of their unique structures and reactivities. In this paper, we present the synthesis and characterization of an extremely hindered digermene **1** bearing 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) group.

Digermene **1** was synthesized by the reaction of Tbt(Mes)$GeCl_2$ with lithium naphthalenide, and its crystal structure was determined by X-ray crystallographic analysis. An equilibrium between the digermene **1** and the corresponding germylene **2** was observed by the UV/vis spectra, and the thermodynamic parameters for the dissociation of digermene **1** to germylene **2** were obtained from temperature dependence of the absorption of **1**. Reactions of the digermene with O_2, $W(CO)_5$(THF), *etc.* in solution proceeded via the germylene, while, in the solid state, the digermene reacts with O_2 without the dissociation into the germylene.



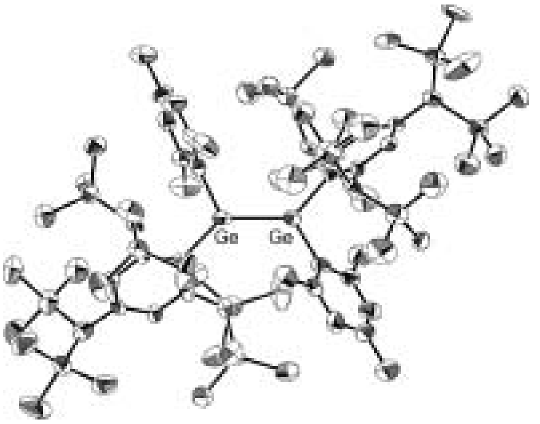


Figure 1. ORTEP drawing of digermene **1**.

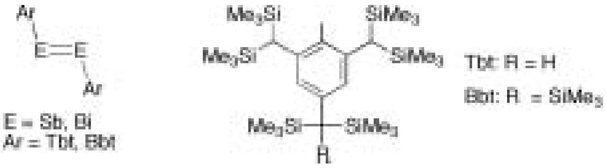
VII-K-6 Syntheses, Structures and Properties of Kinetically Stabilized Distibenes and Dibismuthenes, Novel Doubly Bonded Systems between Heavier Goup 15 Elements

SASAMORI, Takahiro[1]; ARAI, Yoshimitsu[2]; TAKEDA, Nobuhiro[3]; OKAZAKI, Renji[2]; FURUKAWA, Yukio[4]; KIMURA, Masahiro[5]; NAGASE, Shigeru; TOKITOH, Norihiro[6]
([1]Kyushu Univ.; [2]Univ. Tokyo; [3]Kyoto Univ.; [4]Waseda Univ.; [5]Tokyo Metropolitan Univ.; [6]IMS and Kyoto Univ.)

[*Bull. Chem. Soc. Jpn.* **75**, 661 (2002)]

The syntheses of stable compounds containing multiple bonds between heavier main group elements have been among the frontiers of great interest in chemical research. Nowadays, as for the heavier dipnictene series, numerous examples of kinetically stabilized diphosphenes (RP=PR), diarsenes (RAs=AsR), and phosphaarsenes (RP=AsR) have been isolated and fully characterized, and their various chemical properties have been revealed. However, distibene (RSb=SbR) and dibismuthene (RBi=BiR) had not been reported until our successful syntheses of the first stable distibene and dibismuthene utilizing a very effective and bulky substituent, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) group.

Stable distibenes and dibismuthenes were successfully synthesized by taking advantage of an efficient steric protection group, Tbt or 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (Bbt) group. The crystallographic analysis and spectroscopic studies of these stable dipnictenes led to the systematic comparison of structural parameters and physical properties for all homonuclear doubly bonded systems between heavier group 15 elements. In addition to these experimentally obtained results, theoretical calculations for these doubly bonded systems also revealed the intrinsic character of dipnictenes.



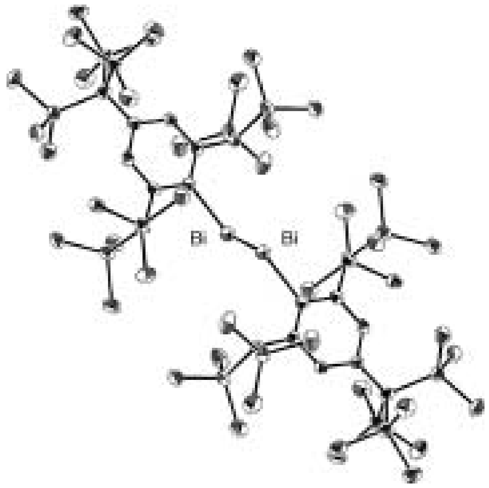


Figure 1. ORTEP drawing of BbtBi=BiBbt.

VII-K-7 Synthesis and Properties of the First Stable Germabenzene

NAKATA, Norio[1]**; TAKEDA, Nobuhiro**[1]**;**
TOKITOH, Norihiro[2]
([1]Kyoto Univ.; [2]IMS and Kyoto Univ.)

[*J. Am. Chem. Soc.* **124**, 6914 (2002)]

Recently, much attention has been focused on the chemistry of [4*n* + 2] π-electron ring systems containing at least one heavier group 14 element. However, no synthesis and isolation of these compounds as stable molecules had been reported until quite recently due to their extremely high reactivity. We have recently succeeded in the synthesis and characterization of the first stable silabenzene, 2-silanaphthalene, 9-silaanthracene, and 2-germanaphthalene by taking advantage of an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt). These successful results in the sila- and germaaromatic systems naturally prompted us to extend this method to the synthesis of a germabenzene, which is the most fundamental germaaromatic compound having a simple 6 π-electron ring system.

The first stable germabenzene **1** was successfully synthesized by the reaction of the corresponding chlorogermane **2** with lithium diisopropylamide in THF. The molecular structure and aromaticity of **1** were discussed on the basis of its NMR, UV-vis, and Raman spectra, X-ray crystallographic analysis, and theoretical calculations. Although the structural and spectroscopic data showed that **1** had aromaticity, in the reaction with various reagents, germabenzene **1** underwent 1,2- and/or 1,4-addition to the 1-germabuta-1,3-diene moiety reflecting the extremely high reactivity of the Ge–C double bond.

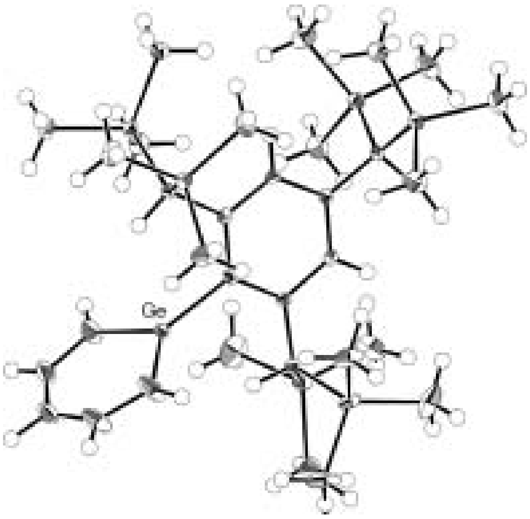


Figure 1. ORTEP drawing of germabenzene **1**.

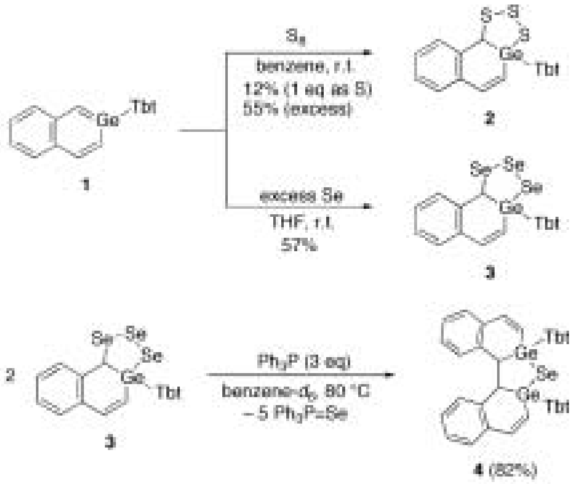
VII-K-8 Reactions of 2-Germanaphthalene with Elemental Sulfur and Selenium: Synthesis of Novel Cyclic Polychalcogenides Containing a Germanium, Trichalcogenagermolanes

NAKATA, Norio[1]**; TAKEDA, Nobuhiro**[1]**;**
TOKITOH, Norihiro[2]
([1]Kyoto Univ.; [2]IMS and Kyoto Univ.)

[*Chem. Lett.* 818 (2002)]

The chemistry of cyclic polychalcogenides has attracted much interest because of their unique structures, reactivities and biological activities. Among them, however, cyclic polychalcogenides containing a germanium atom have been little known. Herein, we present the synthesis of novel Ge-containing cyclic polychalcogenides by the reactions of the first stable 2-germaphthalene **1** bearing 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) with elemental sulfur and selenium.

The reactions of a kinetically stabilized 2-germanaphthalene **1** with elemental sulfur and selenium resulted in the formation of novel five-membered cyclic trichalcogenides, **2** and **3**, containing a germanium, and the molecular structure of the triselenide was determined by X-ray crystallographic analysis. Desulfulization of **2** with 3 equivalent of Ph_3P resulted in the formation of **1** (76%), while deselenation of **3** with 3 equivalent of Ph_3P gave a novel heterocycle, 1-selena-2,5-digermacyclopentane **4** (82%).



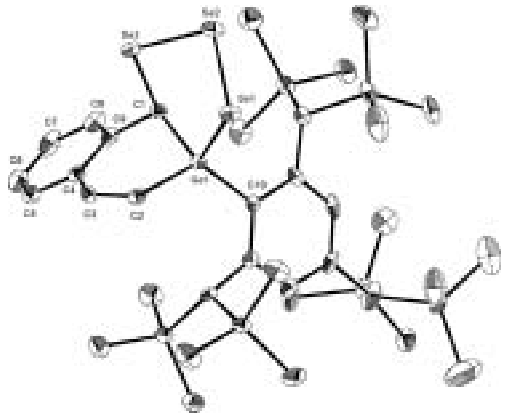


Figure 1. ORTEP drawing of triselenagermolane **3**.

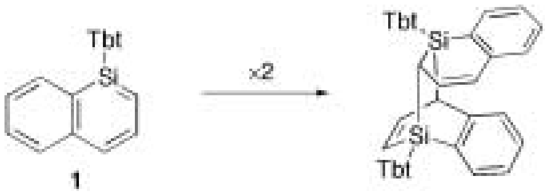
VII-K-9 Synthesis and Properties of the First Stable 1-Silanaphthalene

TAKEDA, Nobuhiro[1]; SHINOHARA, Akihiro[1]; TOKITOH, Norihiro[2]
([1]Kyoto Univ.; [2]IMS and Kyoto Univ.)

[*Organometallics* in press]

In recent decades, much interest has been paid to the chemistry of silicon analogs of aromatic compounds. However, the properties of silaaromatic compounds have not been fully revealed yet because of the extreme instability of the low-coordinated silicon compounds. Very recently, we have succeeded in the synthesis of the first stable silabenzene, 2-silanaphthalene, and 9-silaanthracene by taking advantage of an extremely bulky substituent, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt). On the other hand, there is no report for the synthesis of 1-silanaphthalene, which is a structural isomer of 2-silanaphthalene, although much attention has been focused on the similarities and differences between 1- and 2-silanaphthalenes.

The first 1-silanaphthalene **1** was successfully synthesized as moisture-sensitive, pale yellow crystals by taking advantage of Tbt group. The structure of **1** was determined based on its ^{1}H, ^{13}C, and ^{29}Si NMR, Raman, and UV/vis spectra together with theoretical calculations. These data clearly indicated that **1** has aromaticity comparable with naphthalene as well as Tbt-substituted 2-silanaphthalene. In contrast to the thermal stability of 2-Tbt-2-silanaphthalene, 1-Tbt-1-silanaphthalene (**1**) underwent a ready [2 + 4] dimerization reaction in solution even at room temperature.



VII-K-10 Synthesis and Isolation of the First Germacyclopropabenzene: A Study to Elucidate the Intrinsic Factor for the Ring Deformation of Cyclopropabenzene Skeletons

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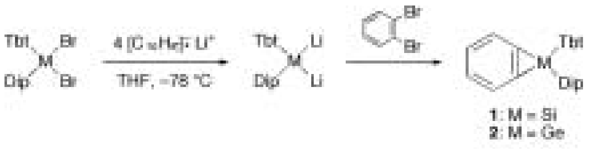
([1]IMS and Kyoto Uniiv.; [2]Kyushu Univ.; [3]Kyoto Univ.)

[*Organometallics* in press]

Since the finding of significant deformation for the fused aromatic rings in the series of benzocycloalkanes, it has been one of the important subjects assigned to organic chemists to solve a riddle for such deformation. Cyclopropabenzene has attracted special attention because of the most severely enforced deformation in this series. Recently, we have synthesized and isolated silacyclopropabenzene **1** as the first example of a stable heteracyclopropabenzene by taking advantage of the characteristic reactivity of the sterically hindered dilithiosilane, $Tbt(Dip)SiLi_2$ (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Dip = 2,6-diisopropylphenyl), towards 1,2-dibromobenzene. This successful isolation of **1** naturally prompted us to examine the synthesis of germacyclopropabenzenes.

The treatment of an overcrowded diaryldilithiogermane, $Tbt(Dip)GeLi_2$, generated by exhaustive reduction of $Tbt(Dip)GeBr_2$, with 1,2-dibromobenzene resulted in the isolation of the first stable germacyclopropabenzene **2**, which was fully characterized by ^{1}H and ^{13}C NMR spectra, FAB-MS, and X-ray structural analysis. As well as the case of silacyclopropabenzene **1**, the structural parameters of **2** indicated that the germacyclopropane ring can enjoy annelation with much less perturbation, in contrast to the severe distortion in cyclopropabenzene rings.



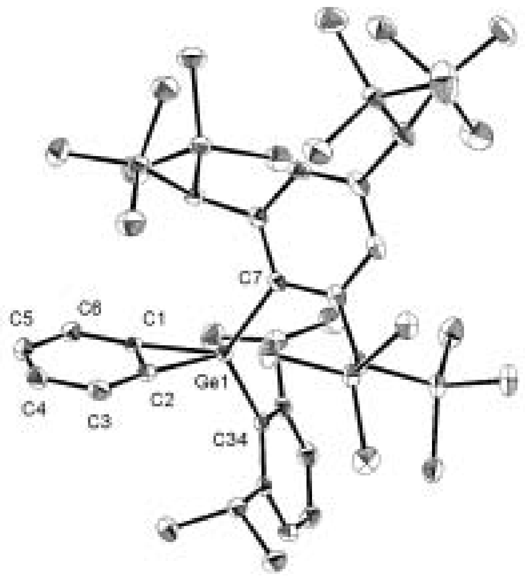


Figure 1. ORTEP drawing of germacyclopropabenzene **1**.

VII-L Precise Synthesis of Functional Macromolecules Using Organometallic Complexes

The helix is one of the most important and fundamental secondary structures of macromolecules and is closely related to the unique functionalities of biomacromolecules. This project focuses on the development of precise polymerization catalyzed by organometallic complexes providing novel functional macromolecules, in which not only molecular weight and sequence but also secondary structures are well controlled. We also examined the physical and chemical properties of the resulting helical polymers.

VII-L-1 Helical Poly(aryl isocyanide)s Possessing Chiral Alkoxycarbonyl Groups

TAKEI, Fumie[1]; HAYASHI, Hiroko[1]; ONITSUKA, Kiyotaka[2]; TAKAHASHI, Shigetoshi[1]
([1]Osaka Univ.; [2]Osaka Univ. and IMS)

[*Polymer J.* **33**, 310 (2001)]

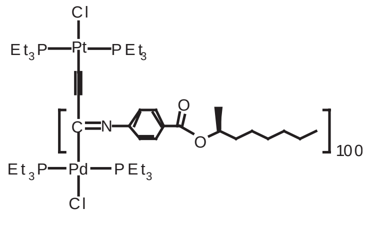
The relation between the structure of chiral monomers and the selectivity of the screw sense of poly(aryl isocyanide)s having several kinds of chiral alkoxycarbonyl groups was determined. The selectivity of screw sense in the poly(aryl isocyanide)s depends on the some structural factors including the position of chiral substituents on aromatic rings, the position of stereogenic center, and the bulkiness of chiral groups.

VII-L-2 Formation of an Optically Active Helical Polyisocyanide Langmuir-Blodgett Film

FENG, Fei[1]; MIYASHITA, Tokuji[1]; TAKEI, Fumie[2]; ONITSUKA, Kiyotaka[3]; TAKAHASHI, Shigetoshi[2]
([1]Tohoku Univ.; [2]Osaka Univ.; [3]Osaka Univ. and IMS)

[*Chem. Lett.* 764 (2001)]

An optically active helical polyisocyanide synthesized with a screw-sense selective living polymerization formed a condensed monolayer on the water surface and was transferred onto a solid support as Y-type LB film with an ordered orientation.



VII-L-3 Helical Chiral Polyisocyanides Possessing Porphyrin Pendants: Determination of Helicity by Exciton Coupled Circular Dichroism

TAKEI, Fumie[1]; HAYASHI, Hiroko[1]; ONITSUKA, Kiyotaka[2]; KOBAYASHI, Nagao[3]; TAKAHASHI, Shigetoshi[1]
([1]Osaka Univ.; [2]Osaka Univ. and IMS; [3]Tohoku Univ.)

[*Angew. Chem., Int. Ed.* **40**, 4092 (2001)]

A novel and practical method for determining the helical sense of poly(aryl isocyanide)s has been developed by using exciton coupled CD of the porphyrin Soret band in triblock copolymers between chiral isocyanide monomers and an achiral tetraphenylporphyrin derivative.