RESEARCH ACTIVITIES VII
Coordination Chemistry Laboratories

Prof. Hiroyuki Matsusaka (Osaka Prefecture Univ.), Assoc. Prof. Keiji Ueno (Gunma Univ.) took the position of Laboratory of Coordination Bond from April 2003. Prof. Nobuhiro Tokito (Kyoto University) and Assoc. Prof. Kiyotaka Onizuka (Osaka University) finished their term as Adjunct Prof. of the Coordination Bond in March 2003. Their effort during their term is gratefully appreciated. Prof. Masahito Yamashita (Tokyo Metropolitan Univ.) and Prof. Naoto Chatani (Osaka Univ.) continue the position of the Laboratory of Synthetic Coordination Chemistry.

VII-A 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 the size 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.

VII-A-1 Out-of-Plane Dimers of Mn(III) Quadridentate Schiff-Base Complexes with Saltmen^{2-} and Naphtmen^{2-} Ligands: Structure Analysis and Ferromagnetic Exchange

MIYASAKA, Hitoshi[1]; CLERAC, Rodolphe[2]; ISHII, Tomohiko[1]; CHANG, Ho-Chol[3]; KITAGAWA, Susumu[3]; YAMASHITA, Masahiro[4]
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[*J. Chem. Soc., Dalton Trans.* **7**, 1528–1534 (2002)]

Six Mn(III) quadridentate Schiff base compounds with N,N’-(1,1,2,2-tetramethylethylene)bis(salicylideneiminato) dianion (saltmen^{2-}) and N,N’-(1,1,2,2-tetramethylethylene)bis(naphthylideneiminato) dianion (naphtmen^{2-}) were prepared and structurally characterized: [Mn(saltmen)(H_2O)]ClO_4 (1), [Mn(naphtmen)(H_2O)]ClO_4 (2), [Mn(saltmen)(NCS)] (3), [Mn(naphtmen)(NCS)] (4), [Mn(saltmen)(Cl)] (5) and [Mn(naphtmen)(Cl)] (6). Among them, 1 and 2 form phenolate-bridged out-of-plane dimers with Mn-Ophenolate bond distances of 2.434(2) and 2.662(3) Å, respectively. X-ray diffraction analyses show that compounds 3, 4 and 6 can also be considered as out-of-plane dimers in spite of long Mn-Ophenolate interacting distances (3.441(2) Å for 3, 3.758(3) Å for 4 and 3.505(5) Å for 6). In contrast with the above compounds, 5 is a discrete Mn(III) mononuclear complex with a square-pyramidal geometry. In the dimer series (compounds 1–4 and 6), the out-of-plane intermolecular distance varies dramatically according to equatorial ligands, saltmen^{2-} or naphtmen^{2-}, and axial ligands, H_2O, NCS^- and Cl^-. The relation between substitution of the ligands and structural parameters of the dimeric molecules are discussed. Magnetic susceptibility studies reveal interesting intra-dimer ferromagnetic interactions between Mn(III) ions. These new $S = 4$ building blocks open new possibilities in the design of magnetic molecule-based materials.

VII-A-2 Electron Spin Resonance Studies of Co(tbp)·C_{60} Single Crystal

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[*J. Phys.: Condens. Matter* **14**, 3993–4000 (2002)]

ESR measurements were made on a newly synthesized cocrystallite of C_{60} with the Co^{II} complex of 5, 10, 15, 20-tetrakis[3, 5-(di-tert-butyl)-phenyl]porphyrin (tbp) single crystal to study the strong intermolecular interactions which are suggested by x-ray structural analyses. A single anisotropic ESR absorption line is observed. At room temperature with the principal g-values ($g_\perp = 2.423$ and $g_\parallel = 2.005$), which are typical values for the low-spin Co^{II} ions ($S = 1/2$). The antiferromagnetic superexchange interaction between Co^{II}

ions *via* C_{60} is confirmed from the observation of the finite Weiss temperature, which is further supported by the absence of the hyperfine splitting due to ^{59}Co (I = 7/2) nuclei. As the temperature is lowered, the $g_\perp$-value decreases monotonically suggesting an increase of the crystal-field splitting energy. This result is consistent with the fact that the intermolecular distance between Co^{II} and C_{60} becomes shorter as the temperature decreases. The peak-to-peak ESR linewidths ΔHpp along both principal axes increase with temperature due to the shorter spin-lattice relaxation time.

VII-A-3 Structure, Magnetic and Electronic Properties of Charge Transfer Complex Containing Hexacyanoferrate Chain and BEDT-TTF Column

NAKATA, Kazuya[1]; YOSHINO, Yuko[1]; HARA, Hatsune[1]; MANABE, Toshio[1]; ISHII, Tomohiko[1]; MIYASAKA, Hitoshi[1]; YAMASHITA, Masahiro[2]; MATSUZAKA, Hiroyuki[1]; KATADA, Motomi[1]
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[*Mol. Cryst. Liq. Cryst.* **380**, 117–122 (2002)]

A novel charge transfer complex containing of hexacyanoferrate ($Fe(CN)_6$) unit, which has been exhibited variety of magnetic topics in prussian blue systems, was synthesized. X-ray analysis of the single crystal obtained by electrolysis of BEDT-TTF (ET) and hexacyanoferrate suggests that this complex contains 1-dimensional magnetic hexacyanoferrate chain perpendicular to the conducting ET column. This significant structure implies that significant properties can be expected caused by the interaction between the spin momentum on *d*-electrons and a conducting π-electrons influenced vertically by the applied magnetic field. From the electronical conducting measurement, it is suggested that is a semiconductor, with the activation energy and the conductivity at room temperature to be 0.113 eV and 0.46 S/cm, respectively. Detailed x-ray analysis suggests that the occupancies of Fe and C elements in the 1-dimensional hexacyanoferrate chain are 0.5, that of N element is 1.0.

VII-A-4 Creations of Solitons and Polarons in MX-Chain Compounds, $\{[Pt(en)_2][PtX_2(en)_2]\}_3(CuX_4)_4$ (X = Cl and Br)

ASO, Hidemitsu[1]; MANABE, Toshio[1]; KAWASHIMA, Takuya[3]; ISHII, Tomohiko[1]; MIYASAKA, Hitoshi[1]; MATSUZAKA, Hiroyuki[1]; YAMASHITA, Masahiro[2]; KURODA, Noritaka[4]; SHIRO, Motoo[5]
([1]Tokyo Metropolitan Univ. and PRESTO(JST); [2]IMS and Tokyo Metropolitan Univ.; [3]Nagoya Univ.; [4]Kumamoto Univ.; [5]Rigaku Co.)

[*Mol. Cryst. Liq. Cryst.* **376**, 7–12 (2002)]

The creations of solitons and polarons in the $\{[Pt(en)_2][PtX_2(en)_2]\}_3(CuX_4)_4$ (X = Cl and Br) which consist of the double linear chain structures of the main one-dimensional halogen-bridged Pt(II)-Pt(IV) mixed-valence units and one-dimensional counteranions of trigonal bipyramidal Cu(I) ions, have been investigated by the absorption spectra, photoinduced absorption spectra, and ESR spectra. The ESR signals of the Pt(III) and Cu(II) species, which were introduced during the synthetic process, are observed in the compound. The relative intensities of *d-d* transitions and ESR spectra of Cu(II) species in counteranions are consistent with each other in the Cl-bridged compounds obtained by pH control. The photoinduced absorption of the Cl-bridged compound is observed in the mid-gap region, which is attributable to the soliton. The doping effect by Br_2 was investigated for the Br-bridged compound. The relative intensities of *d-d* transition and ESR spectra in Cu(II) increase with increasing exposure time. However, the electrical conductivities do not increase. Therefore, the induced Pt(III) species are attributable to neutral solitons.

VII-A-5 Syntheses and Physical Properties of Complexes of Fullerene with Magnetic Metal Porphyrins

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[*Mol. Cryst. Liq. Cryst.* **376**, 13–18 (2002)]

Crystals containing C_{60} and M(OEP) (M^{2+} = Pd, Cu, Ag; OEP^{2-} = octaethylporphinato) were synthesized. Crystal structures were determined for $Cu(OEP)\cdot C_{60}\cdot 2C_6H_6$, $Ag(OEP)\cdot C_{60}\cdot 2C_6H_6$ and $Pd(OEP)\cdot C_{60}\cdot 1.5C_6H_6$. From the x-ray analysis of the cocrystallites, the porphyrin molecules still retain their planar structures without deforming to the fit to the curved surface of the fullerene.

VII-A-6 Crystal and Electronic Structures of Quasi-One-Dimensional Halogen-Bridged Binuclear Platinum Complexes, $\{(C_nH_{2n+1})_2NH_2\}_4[Pt_2(pop)_4I]$ (n = 2–6)

TAKIZAWA, Kouichi[1]; ISHII, Tomohiko[1]; MIYASAKA, Hitoshi[1]; MATSUZAKA, Hiroyuki[1]; YAMASHITA, Masahiro[2]; KAWASHIMA, Takuya[3]; MATSUZAKI, Hiroyuki[4]; KISHIDA, Hideo[4]; OKAMOTO, Hiroshi[4]
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[*Mol. Cryst. Liq. Cryst.* **376**, 159–164 (2002)]

The crystal structures of $\{(C_nH_{2n+1})_2NH_2\}_4[Pt_2(pop)_4I]$ (pop = $O(PO_2H)_2^{2-}$, n = 2–6) were determined. Judging from the results of the x-ray structural analyses and Raman spectra, 1-dimensional electronic structures of these compounds are considered to be $\cdots Pt^{2+}–Pt^{3+}–X\cdots Pt^{2+}–Pt^{3+}–X\cdots$ charge-polarized states.

VII-A-7 Physical Properties of Quasi-One-Dimensional Mixed-Metal and Mixed-Halogen Complexes, $Ni_{1-x}Pd_x(chxn)_2Cl_yBr_{1-y}Y_2$

MANABE, Toshio[1]; YOKOYAMA, Kohei[1]; ISHII, Tomohiko[1]; MIYASAKA, Hitoshi[1]; MATSUZAKA, Hiroyuki[1]; YAMASHITA, Masahiro[2]; KAWASHIMA, Takuya[3]; MATSUZAKI, Hiroyuki[4]; KISHIDA, Hideo[4]; OKAMOTO, Hiroshi[4]; MARUMOTO, Kazuhiro[3]; TANAKA, Hisaaki[3]; ITOH, Hiroshi[3]; KURODA, Shin-ichi[3]
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[*Mol. Cryst. Liq. Cryst.* **376**, 165–170 (2002)]

Single crystals of quasi-one-dimensional Ni-Pd mixed-metal MX-chain compounds, $Ni_{1-x}Pd_x(chxn)_2Br_3$, and mixed-halogen MX-chain compounds, $Ni(chxn)_2Cl_yBr_{1-y}(NO_3)_2$ were obtained by electrochemical oxidation methods. To investigate the electronic states of these compounds, the optical conducting spectra were measured. The electronic states of the Ni compounds can be controlled by forming the mixed-metal or mixed-halogen systems.

VII-A-8 Magnetic/Conducting Hybrid Compound Composed of 1-D Chain $[Mn^{II}_2Cl_5(EtOH)]_\infty^-$ and BEDT-TTF Stacking Layer

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[*J. Solid State Chem.* **168**, 418–426 (2002)]

An assembled compound $(BEDT\text{-}TTF)_2[Mn_2Cl_5(EtOH)]$ (1) consisting of two structural lattices of Mn(II)-Cl 1-dimensional (1-D) chains and bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) stacking layers was synthesized by electrochemical method. Compound 1 crystallized in triclinic space group with a = 13.1628(5), b = 20.3985(9), c = 7.4966(3) Å, α = 98.3498(8), β =104.980(1), γ = 74.602(2)°, and Z = 2. The 1-dimensional chains and the stacking layers are aligned along the c-axis of the unit cell. The 1-dimensional chain is described as $[Mn_2Cl_5(EtOH)]_\infty^-$ in which two Mn(II) ions and four Cl^- ions form a ladder-like chain with Kagome (cuboidal) sublattices, and the remaining Cl^- ion and an EtOH molecule cap the edge-positioned Mn(II) ions of the chains. The BEDT-TTF molecules are packed between the Mn-Cl chains (ac-plane), the intermolecules S···S contacts of which are approximately found in the range 3.440(2)–3.599(2) Å. The packing feature of BEDT-TTF molecule is very similar to that of $(BEDT\text{-}TTF)_2ClO_4(TCE)_{0.5}$ (TCE = 1,1,2-trichloroethane). Regarding the electronic state of each BEDT-TTF molecule, Raman spectroscopic analysis and ESR study revealed half-valence BEDT-TTF molecules (charge delocalization) in 1. Magnetic measurements clearly demonstrated that the paramagnetic spins on the 1-dimensional chain $[Mn_2Cl_5(EtOH)]_\infty^-$ arrange antiferromagnetically in the low-temperature region. Additionally, 1 exhibits metallic conduction in the temperature range 2.0–300 K (σ = 21 S cm^{-1} at 300 K and 1719 S cm^{-1} at 2.0 K), due to the contribution of the stacked BEDT-TTFs. Consequently, these peculiarities that correspond to antiferromagnetic/metallic conduction demonstrate the bifunctionality of 1.

VII-A-9 Structure and Electrochemistry of the Bridging-Ligand Mono-Substituted Diruthenium Compound, $[Ru_2(II,III)(O_2CCH_3)_3(admpym)(Cl)(MeOH)]$ (Hadmpym = 2-amino-4,6-dimethylpyrimidine)

KACHI-TERAJIMA, Chihiro[1]; MIYASAKA, Hitoshi[1]; ISHII, Tomohiko[1]; SUGIURA, Ken-ichi[1]; YAMASHITA, Masahiro[2]
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[*Inorg. Chim. Acta* **332**, 210–215 (2002)]

The ligand substitution reaction of $Ru_2(O_2CCH_3)_4Cl$ with 2-amino-4,6-dimethylpyrimidine (Hadmpym) under gentle refluxing conditions in MeOH gave a bridging-ligand mono-substituted compound, $[Ru_2(O_2CCH_3)_3(admpym)(Cl)(MeOH)]$ (**1**). **1** Crystallized in monoclinic space group $P2_1/n$ with a = 8.3074(8), b = 12.3722(8) Å, c = 18.913(1) Å, β =95.559(3)°, V = 1934.8(3) $Å^3$, and Z = 4. Temperature dependence of the magnetic susceptibility of 1 revealed it to be in a spin ground state S = 3/2 arising from the electronic configuration of $\sigma^2\pi^4\delta^2(\delta^*\pi^*)^3$. Compound 1 undergoes three metal-centered redox reactions in electrochem.: $E_{1/2}$ (ox) = +0.72 V (Ia/Ic < 1, ΔEp = 0.17 V); $E_{1/2}$ (1,red) = –0.65 V (Ia/Ic ≈ 1, ΔEp = 0.10 V); and $E_{1/2}$ (2,red) = –1.80 V (Ia/Ic.mchlt.1, ΔEp = 0.16 V). Then, the redox species produced by electrolysis were characterized by spectroscopic studies.

VII-A-10 Electrical Conduction of Halogen-Bridged Metal Complexes $Ni_{1-x}Pd_x(chxn)_2Br_3$

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[*Mol. Cryst. Liq. Cryst.* **379**, 285–290 (2002)]

The resistance and thermopower of the quasi-one-dimensional halogen-bridged metal complexes $Ni_{1-x}Pd_x(chxn)_2Br_3$ were studied. Pressure dependence of the resistance indicates the crossover from SDW state to CDW state at x = 0.84–0.95. For almost all x region, thermopower is negative. For x < 0.5, thermopower is independent of temperature, while it is semiconducting for x > 0.6.

VII-A-11 Reactions of Mn(III) Quadridentate Schiff Base Compounds with TCNQ Anion to Form Unusual TCNQ Derivatives by Alcoholysis

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[*Mol. Cryst. Liq. Cryst.* **379**, 197–204 (2002)]

The reactions of Mn(III) quadridentate Schiff base compounds, $[\mathrm{Mn(saltmen)(H_2O)}]\mathrm{ClO_4}$ (1; saltmen^{2-} = N,N'-(1,1,2,2-tetramethylethylene)bis(salicylideneiminato)) and $[\mathrm{Mn(naphtmen)(H_2O)}]\mathrm{ClO_4}$ (2; naphtmen^{2-} = N,N'-(1,1,2,2-tetramethylethylene)bis(naphthylideneiminato)), with LiTCNQ gave three types of compounds depending on reaction conditions: [Mn(saltmen)(H_2O)](TCNQ) (3), [Mn(saltmen)(MeOH)(TCNQ-OMe)] (4, TCNQ-OMe$^-$ = p-(α,α-dicyano-α-methoxytolyl)dicyanomethanide), and [Mn(naphtmen)(MeOH)(TCNQA-OMe)] (5, TCNQA-OMe$^-$ = p-(α-cyano-α-methoxy-a-methylamidotolyl)$^-$ dicyanomethanide). Compounds 3·MeOH and 5 were characterized by x-ray crystallography. Compounds 3 and 4 were prepared under anaerobic and aerobic conditions, respectively, in MeOH/H_2O. Compound 5 was synthesized under aerobic conditions analogous to 4. For 4 and 5, unusual additional reactions on the anionic TCNQ molecule occurred to form (TCNQ-OMe)$^-$ for 4 and (TCNQA-OMe)$^-$ for 5. Ferromagnetic and antiferromagnetic interactions in the prepared compounds were investigated.

VII-A-12 Out-of-Plane Dimer Structures and Magnetic Properties of Mn(III) Quadridentate Schiff Base Compounds with N,N'-(1,1,2,2-tetramethylethylene)bis(5-chlorosalicylideneiminato)

MIYASAKA, Hitoshi[1]; MIZUSHIMA, Kaori[1]; FURUKAWA, Sachie[1]; SUGIURA, Ken-ichi[1]; ISHII, Tomohiko[1]; YAMASHITA, Masahiro[2]
([1]Tokyo Metropolitan Univ.; [2]IMS and Tokyo Metropolitan Univ.)

[*Mol. Cryst. Liq. Cryst.* **379**, 171–178 (2002)]

Three Mn(III) quadridentate Schiff base compounds with N,N'-(1,1,2,2-tetramethylethylene)bis(5-chlorosalicylideneiminato) (5-Clsaltmen^{2-}) were prepared and characterized: $[\mathrm{Mn_2(5\text{-}Clsaltmen)_2(H_2O)_2}](\mathrm{ClO_4})_2$ (1), $[\mathrm{Mn_2(5\text{-}Clsaltmen)_2(5\text{-}Clsal)_2}]$ (2, 5-Clsal = phenol-bonded 5-chlorosalicylaldehyde), and $[\mathrm{NEt_4}]_2[\mathrm{Mn_2(5\text{-}Clsaltmen)_2(MeOH)_2}][\mathrm{Fe(CN)_6}]\mathrm{ClO_4\cdot 2MeOH}$ (3). All compounds contain Mn(III) out-of-plane dimer units. The magnetic measurements revealed intra-dimer ferromagnetic exchange interaction between Mn(III) ions via phenolate O, producing a $S = 4$ spin ground state. The structures of 2 and 3 were determined by x-ray crystallography.

VII-A-13 Synthesis, Structure and Magnetic Properties of the Antiferromagnetic Hexamanganese Cluster $[\mathrm{Mn_6(\mu_4\text{-}O)_2(O_2CC_6HF_4)_{10}(HO_2CCH_3)_4}]\cdot(\mathrm{C_7H_8})$

NAKATA, Kazuya[1]; MIYASAKA, Hitoshi[1]; ISHII, Tomohiko[1]; YAMASHITA, Masahiro[2]; AWAGA, Kunio[3]
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[*Mol. Cryst. Liq. Cryst.* **379**, 211–216 (2002)]

A hexanuclear $\mathrm{Mn^{II}\text{-}Mn^{III}}$-cluster, $[\mathrm{Mn_6(O)_2(O_2CC_6HF_4)_{10}(HO_2CCH_3)_4}]\cdot(\mathrm{C_7H_8})$ (1), was synthesized by a typical acetate-substitution reaction of the known $\mathrm{Mn_{12}}$-cluster, $[\mathrm{Mn_{12}(O)_{12}(O_2CCH_3)_{16}(H_2O)_4}]\cdot 2\mathrm{CH_3CO_2H}\cdot 4\mathrm{H_2O}$ in the presence of an excess of 2,3,5,6-tetrafluorobenzoic acid. Each unpaired spin on Mn(II) and Mn(III) ions is promoted as to be antiferromagnetically cancelled to produce an $S = 0$ ground state.

VII-A-14 Evidence for Single-Chain Magnet Behavior in a $\mathrm{Mn^{III}\text{-}Ni^{II}}$ Chain Designed with High Spin Magnetic Units: A Route to High Temperature Metastable Magnets

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([1]Cent. Recherche Paul Pascal; [2]Tokyo Metropolitan Univ.; [3]IMS and Tokyo Metropolitan Univ.)

[*J. Am. Chem. Soc.* **124**, 12837–12844 (2002)]

The authors herein present the synthesis, crystal structure, and magnetic properties of a new heterometallic chain of $\mathrm{Mn^{III}}$ and $\mathrm{Ni^{II}}$ ions, $[\mathrm{Mn_2(saltmen)_2Ni(pao)_2(py)_2}](\mathrm{ClO_4})_2$ (1) (saltmen^{2-} = N,N'-(1,1,2,2-tetramethylethylene)bis(salicylideneiminate) and pao$^-$ = pyridine-2-aldoximate). The crystal structure of 1 was studied by x-ray crystallography analysis: compound 1 crystallized in monoclinic, space group $C2/c$ with $a = 21.140(3)$, $b = 15.975(1)$, $c = 18.6212(4)$ Å, $\beta = 98.0586(4)°$, and $Z = 4$. This compound consists of two fragments, the out-of-plane dimer $[\mathrm{Mn_2(saltmen)_2}]^{2+}$ as a coordination acceptor building block and the neutral mononuclear unit $[\mathrm{Ni(pao)_2(py)_2}]$ as a coordination donor building block, forming an alternating chain having the repeating unit $[\text{–Mn–(O)}_2\text{–Mn–ON–Ni–NO–}]_n$. In the crystal structure, each chain is well separated with a minimum intermetallic distance between Mn and Ni ions of 10.39 Å and with the absence of interchain π overlaps between organic ligands. These features ensure a good magnetic isolation of the chains. The *d.c.* and *a.c.* magnetic measurements were performed on both the polycrystalline sample and the aligned single crystals of 1. Above 30 K, the magnetic susceptibility of this 1-dimensional compound was successfully described in a mean field approximation as an assembly of trimers (Mn···Ni···Mn) with a $\mathrm{Ni^{II}\cdots Mn^{III}}$ antiferromagnetic interaction (J = –21 K) connected through a ferromagnetic $\mathrm{Mn^{III}\cdots Mn^{III}}$ interaction (J'). However, the mean field theory fails to describe the magnetic behavior < 30 K emphasizing the

1-dimensional magnetic character of the title compound. Between 5 and 15 K, the susceptibility in the chain direction was fitted to a 1-dimensional Ising model leading to the same value of *J'*. Hysteresis loops are observed < 3.5 K, indicating a magnet-type behavior. In the same range of temperature, combined *a.c.* and *d.c.* measurements show a slow relaxation of the magnetization. This result indicates a metastable state without magnetic long-range order. This material is the 1st experimental design of a heterometallic chain with S_T = 3 magnetic units showing a single-chain magnet behavior predicted in 1963 by R. J. Glauber for an Ising 1-dimensional system. This work opens new perspectives for 1-dimensional systems to obtain high temperature metastable magnets by combining high spin magnetic units, strong inter-unit interactions, and uniaxial anisotropy.

VII-A-15 Tuning of Spin Density Wave Strengths in Quasi-One-Dimensional Mixed-Halogen-Bridged Ni(III) Complexes with Strong-Electron Correlation, $[Ni^{III}(chxn)_2Cl_{1-x}Br_x](NO_3)_2$

MANABE, Toshio[1]; YOKOYAMA, Kohei[1]; FURUKAWA, Sachie[1]; KACHI-TERAJIMA, Chihiro[1]; NAKATA, Kazuya[1]; IWAHORI, Fumiyasu[1]; MIYASAKA, Hitoshi[1]; SUGIURA, Ken-ichi[1]; YAMASHITA, Masahiro[2]; KISHIDA, Hideo[3]; OKAMOTO, Hiroshi[3]
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[*Inorg. Chem.* **41**, 4993–4995 (2002)]

This communication describes the syntheses of the quasi-one-dimensional mixed-halogen-bridged Ni^{III} complexes with strong electron correlation $[Ni(chxn)_2Cl_{1-x}Br_x](NO_3)_2$ and the tuning of the spin density wave strengths of these compounds. If the Cl 3*p* and Br 4*p* make one band in the compounds, we should observe a single peak in the electronic spectra. As a result, we should observe the single peak from 1.45 to 2.00 eV depending on the mixing ratios of Cl and Br ions. Therefore, the Cl 3*p* and Br 4*p* make one band. Then, we have succeeded in tuning the spin density wave strengths of the Ni^{III} complexes with the strong electron correlation by mixing the bridging halogen ions successively.

VII-A-16 Syntheses and Physical Properties of New Charge-Transfer Salts Consisting of a Conducting BEDT-TTF Column and Magnetic 1D or 2D Fe(III) Networks

KANEHAMA, Ryo[1]; YOSHINO, Yuko[1]; ISHII, Tomohiko[1]; MANABE, Toshio[1]; HARA, Hatsune[1]; MIYASAKA, Hitoshi[1]; MATSUZAKA, Hiroyuki[1]; YAMASHITA, Masahiro[2]; KATADA, Motomi[1]; NISHIKAWA, Hiroyuki[1]; IKEMOTO, Isao[1]
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[*Synth. Met.* **133-134**, 553–554 (2003)]

Two new molecular-based charge-transfer salts of bis(ethylenedithio)tetrathiafulvalene were prepared, that is $(BEDT\text{-}TTF)_3Fe(CN)_6{\cdot}4H_2O$ and $(BEDT\text{-}TTF)_4Fe(C_2O_4)_3K{\cdot}PhCl$. Their crystal structures and physical properties were studied. Their structures consist of conducting columns of BEDT-TTF and magnetic 1-dimensional or 2-dimensional networks containing Fe(III) ions connected by cyano- or oxalate-bridges. The *d*-π interactions are discussed.

VII-A-17 Novel Optical and Magnetic Bistability and Photoinduced Transition in a One-Dimensional Halogen-Bridged Binuclear Pt Complex

MATSUZAKI, Hiroyuki[1]; MATSUOKA, Takashi[1]; KISHIDA, Hideo[1]; TAKIZAWA, Kouichi[2]; MIYASAKA, Hitoshi[2]; SUGIURA, Ken-ichi[2]; YAMASHITA, Masahiro[3]; OKAMOTO, Hiroshi[1]
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[*Phys. Rev. Lett.* **90**, 046401 (4 pages) (2003)]

In I-bridged binuclear Pt compounds, $R_4[Pt_2(pop)_4I]nH_2O$ and $R'_2[Pt_2(pop)_4I]nH_2O$ (pop = $P_2O_5H_2^{2-}$), electronic structures on the PtPtI chains were controlled between a diamagnetic charge-density-wave (CDW) state and a paramagnetic charge-polarization (CP) state by modification of the counterions (R, R') located between chains. In the R = $Et_2NH_2^+$ compound, a pressure-induced CP to CDW transition with a drastic color change is identified. This transition is accompanied by a large hysteresis loop within which photo-induced transition between CDW and CP can be driven by selecting the excitation photon energy.

VII-A-18 Unprecedented Soliton Formation Mechanism in Quasi-One-Dimensional Chloro-Bridged Pt^{II}-Pt^{IV} Mixed-Valence Compound, $\{[Pt(en)_2][PtCl_2(en)_2]\}_3(CuCl_4)_4{\cdot}12H_2O$

YAMASHITA, Masahiro[1]; ASO, Hidemitsu[2]; MATSUNAGA, Satoshi[2]; TAKIZAWA, Kouichi[2]; NAKATA, Kazuya[2]; KACHI-TERAJIMA, Chihiro[2]; IWAHORI, Fumiyasu[2]; ISHII, Tomohiko[2]; MIYASAKA, Hitoshi[2]; SUGIURA, Ken-ichi[2]; KAWASHIMA, Takuya[3]; TAKAI, Kenzi[3]; KURODA, Noritaka[4]; SHIRO, Motoo[5]; KISHIDA, Hideo[6]; OKAMOTO, Hiroshi[6]; TAKAHASHI, Hiroyuki[3]; TANAKA, Hisaaki[3]; MARUMOTO, Kazuhiro[3]; KURODA, Shin-ichi[3]
([1]IMS and Tokyo Metropolitan Univ.; [2]Tokyo Metropolitan Univ.; [3]Nagoya Univ.; [4]Kumamoto Univ.; [5]Rigaku Co.; [6]Univ. Tokyo)

[*Chem. Lett.* **32**, 278–279 (2003)]

A new type of complex consisting of double liner-chain structure $\{[Pt(en)_2][PtCl_2(en)_2]\}_3(CuCl_4)_4{\cdot}12H_2O$ was synthesized. High concentration (*ca.* 200 times larger than the literature) of neutral soliton (Pt^{III} component) formation was found. This unprecedented soliton formation mechanism will be discussed.

VII-A-19 A Series of Ni(II) Pyridyloximato (pao$^-$) Compounds [Ni(pao)$_2$(L)$_2$] (L = Unidentate Ligand): As a Coordination Donor Building Block in the Assembly with Mn(III) Salen Analogues

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[*Synth. Met.* **137**, 1245–1246 (2003)]

A series of mononuclear Ni(II) compounds [Ni(pao)$_2$(L)$_2$] (pao$^-$ = 2-pyridyloximate, L = pyridine (1), 4-picoline (2), 4-ethylpyridine (3), 4-tert-butylpyridine (4), and N-methylimidazole (5)) were synthesized and characterized. The structures of 1–3 were determined by X-ray crystallography and revealed that all compounds have the same structural motif with trans coordination fashion for the identical ligands. For magnetic data, the best-fitting to an S = 1 ground state with the zero-field splitting effect found to have the zero-field splitting parameter |D| of 3 as approximate 4 K in this series. These compounds are good coordination donor building blocks for assembly with Mn(III) salen analogs as coordination acceptor building blocks to form 1-D magnetic chains.

VII-A-20 Pressure Effects on an S = 1 Haldane Compound Ni(C$_5$H$_{14}$N$_2$)$_2$N$_3$(PF$_6$)

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([1]Kyushu Inst. Tech.; [2]Kyushu Univ.; [3]Tokyo Metropolitan Univ.; [4]IMS and Tokyo Metropolitan Univ.; [5]Tohoku Univ.; [6]Hokkaido Univ.)

[*J. Phys. Soc. Jpn.* **72**, 399–404 (2003)]

The pressure effects on an S = 1 Haldane compound Ni(C$_5$H$_{14}$N$_2$)$_2$N$_3$(PF$_6$) (NDMAP) were studied through the magnetic susceptibility (χ) measurements using single crystal samples and the powder x-ray structural analysis experiment under pressure up to 11.5 kbar. The crystal-axis dependence of χ was analyzed with the results of quantum Monte Carlo simulation. Probably both the intrachain interaction (J) and single-ion anisotropy (D) are enhanced by pressure: J = 31.5 K (P = 0 kbar) → 90.0 K (10.0 kbar) and D/J = 0.3 (P = 0 kbar) → 0.4 (9.5 kbar). As for J, there is the linear increase against pressure as dJ/dP = 2.0 K/kbar in the pressure region below P = 8.0 kbar, at around which dJ/dP rapidly changes to dJ/dP = 2.1 × 101 K/kbar. The ratio of D/J changes within 0.3–0.4, and probably D as well as J drastically change at around P = 8.0 kbar. Also, at P = 9.5 kbar, the development of paramagnetic moment on the easy plane is detected, and it is assumed that the interchain interaction may be also enhanced under pressure. The structural analysis shows that the interchain shrinkage is larger than the intrachain one. However, a result concerning the rapid changes of J and D at around P = 8.0 kbar was not observed, and the authors suppose that the changes of bond-angles such as –N–Ni–N– and –N–N–N– as well as interatomic shrinkage probably change under pressure. The authors assume that those bond-angles of NDMAP at around P = 9.0 kbar (J .simeq. 70 K) may become close to those of Ni(C$_5$H$_{14}$N$_2$)$_2$N$_3$(ClO$_4$) (NDMAZ), where the value of J is 71.0 K.

VII-A-21 Platinum(II) Complex with S = 1/2 Organic Radical Ligand

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[*Synth. Met.* **135-136**, 355–356 (2003)]

A platinum(II) complex with organic radical ligand p-NNpy (= 2-(4’-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide) is synthesized. X-ray crystallographic analysis revealed that it has a square-planer four-coordinate anionic structure with formula of [Pt(p-NNpy)Cl$_3$]$^-$. Paramagnetic behavior which corresponds to S = 1/2 was observed with weak intermolecular antiferromagnetic interaction in the temperature range of 2–300 K. The structure, magnetic property and spectroscopic data will be reported.

VII-A-22 Tuning of Spin Density Wave Strength of Ni(III) Complexes with Strong Electron-Correlation

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[*Synth. Met.* **135-136**, 257–258 (2003)]

We have succeeded in synthesizing the Ni^{III} complexes doped by Co^{III} ions, [Ni$_{1-x}$Co$_x$(chxn)$_2$Br]Br$_2$ (x = 0, 0.044, 0.098, 0.118) by using an electrochemical oxidation method. The reflectance spectrum of [Ni$_{1-x}$Co$_x$(chxn)$_2$Br]Br$_2$ shows intense charge transfer bands about 0.5 eV, which are lower than that of [Ni(chxn)$_2$Br]Br$_2$. (1.3 eV).

VII-A-23 New Charge-Transfer Salts (ET)$_8$(Mn^{II}Br$_4$)$_2$(DCE)$_2$ and (ET)$_3$Mn^{II}Br$_4$: Preparations, Structures and Physical Properties (ET = BEDT-TTF, DCE = 1,2-Dichloroethane)

KANEHAMA, Ryo[1]; MIYASAKA, Hitoshi[1];

SUGIURA, Ken-ichi[1]; YAMASHITA, Masahiro[2]; ITOH, Hiroshi[3]; KURODA, Shin-ichi[3]; KISHIDA, Hideo[4]; OKAMOTO, Hiroshi[4]
([1]Tokyo Metropolitan Univ.; [2]IMS and Tokyo Metropolitan Univ.; [3]Nagoya Univ.; [4]Univ. Tokyo)

[*Synth. Met.* **135-136**, 633–634 (2003)]

New charge-transfer salts $(ET)_8(MnBr_4)_2(DCE)_2$ **1** and $(ET)_3MnBr_4$ **2** have been synthesized electrochemically and characterized. In both compounds, the magnetic $MnBr_4^{2-}$ anions exist between the conducting ET-layers. The shortest intermolecular Mn···Mn distances are 7.28 and 10.12 Å, respectively, which are too far to magnetically interact directly. But magnetic susceptibility measurements demonstrated that the antiferromagnetic interactions was observed at low temperature. This aniferromagnetic interactions between Mn ions may be operative *via* the π-electrons of conducting layers, that are so-called *d*-π interactions. The crystal structures and physical properties of these compounds are reported.

VII-A-24 Gigantic Third-Order Optical Nonlinearity in One-Dimensional Mott Insulators

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[*Synth. Met.* **135-136**, 315–316 (2003)]

Third-order optical nonlinearity has been studied in one-dimensional Mott- insulators, Sr_2CuO_3, Ca_2CuO_3, and halogen-bridged Ni compounds $[Ni(chxn)_2X]Y_2$ (X = Br, Cl; Y = Br, Cl, NO_3), by electroreflectance (ER) spectroscopy. In $\chi(3)(-\omega;0,0,\omega)$ (ER) is evaluated to be $\chi(3) \approx 10^{-8}$ to 10^{-5} esu, which is significantly larger than those of conjugated polymers, $10^{-10} \approx 10^{-8}$ esu. An analysis of the ER spectral shape reveals that the strong enhancement of nonlinear optical response originates from the large transition dipole moments between nearly degenerate odd and even states.

VII-A-25 Structure and Magnetic Properties of the Two-Dimensional Ferrimagnet $(NEt_4)[\{Mn(salen)\}_2Fe(CN)_6]$: Investigation of Magnetic Anisotropy on a Single Crystal

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[*Inorg. Chem.* **42**, 3509–3515 (2003)]

The title compound, $(NEt_4)[\{Mn(salen)\}_2Fe(CN)_6]$ (1), was synthesized *via* a 1:1 reaction of $[Mn(salen)(H_2O)]ClO_4$ with $(NEt_4)_3[Fe(CN)_6]$ in a MeOH/EtOH medium ($NEt_4^+ = Et_4N^+$ cation, salen^{2-} = N,N'-ethylenebis(salicylidene)iminate). The two-dimensional layered structure of 1 was revealed by x-ray crystallographic analysis: 1 crystallizes in monoclinic space group $P2_1/c$ with a = 12.3660(8), b = 15.311(1), c = 12.918(1) Å, β = 110.971(4)°, Z = 2 and is isostructural to the previously synthesized compound, $(NEt_4)[\{Mn(5\text{-}Clsalen)\}_2Fe(CN)_6]$ (5-Clsalen^{2-} = N,N'-ethylenebis(5-chlorosalicylidene)iminate). The Mn ion is surrounded by an equatorial salen quadridentate ligand and two axial N atoms from the $[Fe(CN)_6]^{3-}$ unit, the four Fe-CN groups of which coordinate to the Mn ions of $[Mn(salen)]^+$ units, forming a two-dimensional network having $[-Mn-NC-Fe-CN-]_4$ cyclic repeating units. The network is spread over the *bc*-plane of the unit cell, and the layers are stacked along the *a*-axis. The countercation NEt_4^+ is located between the layers. Compound 1 is a ferrimagnet with T_c = 7.7 K and exhibits hysteresis with a remnant magnetization of 13.44 cm^3 mol^{-1} at zero field and a coercivity of 1000 Oe when the powder sample was measured at 1.9 K. Magnetic measurements of a direction-arranged single crystal were also carried out. The orientation of the crystallographic axes of a selected single crystal was determined by x-ray analysis, and magnetization was measured when an external field was applied in the *a**, *b*, and *c* directions. The magnetization in the *a** direction increased more easily than those in the *b* and *c* directions below the critical temperature. No hysteresis was observed only for the measurement in the *a** direction, indicating the presence of strong structural anisotropy with potential anisotropy on Mn(III) ions.

VII-A-26 LESR Studies of Long-Lived Photogenerated Spins in the MX-Chain Complex, $Pd(chxn)_2Br_3$

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([1]Nagoya Univ.; [2]IMS and Tokyo Metropolitan Univ.)

[*Synth. Met.* **135-136**, 317–318 (2003)]

Light-induced ESR (LESR) measurements have been applied on the halogen-bridged metal complex (MX-chain), $Pd(chxn)_2Br_3$, to study the dynamics of the photogenerated spin such as neutral soliton and polaron. The time evolution of the LESR intensity is interpleted in terms of the pair-creation and recombination model of photo-generated spins which are separated by the finite potential barriers on the chain. The LESR intensity showed the same excitation power dependence with the one in the Pt-Cl compound.

VII-A-27 Heterometallic Hexanuclear Cluster with an *S* = 8 Spin Ground State: $Mn^{II}\{Mn^{II}(hfac)_2\}_3\{Ni^{II}(pao)_3\}_2$ (hfac$^-$ = Hexafluoroacetylacetonate, pao$^-$ = Pyridine-2-aldoximate)

MIYASAKA, Hitoshi[1]; NEZU, Tomohiro[1]; IWAHORI, Fumiyasu[1]; FURUKAWA, Sachie[1]; SUGIMOTO, Kunihisa[2]; CLERAC, Rodolphe[3]; SUGIURA, Ken-ichi[1]; YAMASHITA, Masahiro[4]

([1]Tokyo Metropolitan Univ.; [2]Rigaku Co.; [3]Cent. Recherche Paul Pascal; [4]IMS and Tokyo Metropolitan Univ.)

[*Inorg. Chem.* **42**, 4501–4503 (2003)]

The heterometallic $Mn^{II}_4Ni^{II}_2$ title compound has been synthesized and characterized by X-ray crystallography. The compound consists of a Ni–Mn–Ni linear moiety, $[\{Ni\text{-}(\mu\text{-}NO)_3\}_2\text{-}Mn]$, linked by oximate bridges and three Mn(II) hfac terminal units attached by oximate oxygens in a di-μ-oxo fashion, forming a novel heterometallic cluster: $Mn\{Mn(hfac)_2\}_3\{Ni(pao)_3\}_2$ (1). Magnetic measurements reveal the antiferromagnetic nature of the oximate pathway between Mn(II) and Ni(II) metal ions, which imposes an unusual high-spin ground state ($S = 8$) for 1.

VII-B Development of New Carbonylation Reactions

Carbonylation reactions are recognized as useful and reliable transformations for the preparation of a variety of carbonyl compounds, such as aldehydes, ketones, esters, lactones, and lactams. 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-B-1 $Ru_3(CO)_{12}$-Catalyzed C–H/CO/Olefin Coupling of *N*-Pyridylindolines. Direct Carbonylation at a C–H Bond δ to the Pyridine Nitrogen

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[*J. Org. Chem.* **67**, 7557–7560 (2002)]

The reaction of *N*-pyridylindolines with CO and ethylene in the presence of $Ru_3(CO)_{12}$ results in direct carbonylation at a C–H bond δ to the pyridine sp^2 nitrogen, which represents a new type of C–H/CO/olefin coupling. The presence of a pyridine ring as a directing group on the substrates is essential for the reaction to proceed. The choice of *N*,*N*-dimethylacetamide (DMA) as the solvent is crucial for the reaction to proceed efficiently.

VII-B-2 Ruthenium-Catalyzed Reaction of α,β-Unsaturated Imines with Carbon Monoxide and Alkenes Leading to β,γ-Unsaturated γ-Butyrolactams: Involvement of Direct Carbonylation of Olefinic C–H Bonds as a Key Step

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

[*J. Org. Chem.* **67**, 7014–7018 (2002)]

The reaction of α,β-unsaturated imines with CO and alkenes in the presence of $Ru_3(CO)_{12}$ as a catalyst results in a three-component coupling reaction that gives α,α-disubstituted β,γ-unsaturated γ-butyrolactams. The reaction proceeds *via* a two-step sequence involving the initial formation of ketone derivatives by catalytic carbonylation at the β-olefinic C–H bonds of α,β-unsaturated imines, followed by the (uncatalyzed) intramolecular nucleophilic attack of the imine nitrogen on the ketonic carbon to generate a tetrahedral intermediate, which then undergoes a 1,2-ethyl migration. The reaction of a cyclic unsaturated imine, derived from the reaction of (1*R*)-(–)-myrtenal with *tert*-butylamine, gives a β-aminocyclopentene derivative, which is formed by an aldol-type condensation of the initially formed ketone, indicating the initial formation of ethyl ketone.

VII-B-3 Ruthenium-Catalyzed Carbonylative Cycloaddition of α-Keto Lactones with Alkenes or Alkynes: The Participation of an Ester-Carbonyl group in Cycloaddition Reactions as the Two-Atom Assembling Unit

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[*J. Org. Chem.* **68**, 1591–1593 (2003)]

The reaction of benzofuran-2,3-dione derivatives with CO and alkenes (or alkynes) results in a carbonylative [2+2+1] cycloaddition in which the ester-carbonyl group is incorporated into a two-atom assembling unit to give spirolactone derivatives. This reaction provides the first example of an ester-carbonyl group participating in a carbonylative cycloaddition reaction.

VII-B-4 Palladium-Catalyzed Carbonylation of 2-(Propargyl)allyl Phosphates Leading to Highly Unsaturated γ-Lactones

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[*Angew. Chem. Int. Ed.* **42**, 1397–1399 (2003)]

The reaction of 2-(propargyl)allyl phosphates with CO in THF in the presence of $[(\eta^3\text{-allyl})PdCl]_2$ and dicyclohexylmethylamine results in the incorporation of two molecules of CO to give highly unsaturated bicyclic lactones in good to high yields. The reaction proceeds smoothly even under an ambient pressure of CO. The experimental data indicates the formation of π-allyl palladium complexes.

VII-C Development of $GaCl_3$-Catalyzed Reaction

We have interested in the development of new catalytic reactions based on a unique reactivity of $GaCl_3$. $GaCl_3$ is a Lewis acid, however it has higher affinity toward an alkyne than oxygen, unlike common Lewis acids, such as $AlCl_3$ and $TiCl_4$. We have already reported that the skeletal reorganization of enynes leading to 1-vinylcycloalkenes is achieved by the presence of a catalytic amount of $GaCl_3$ by taking advantage of a high affinity of $GaCl_3$ toward an alkyne (*J. Am. Chem. Soc.* **124**, 10294–10295 (2002)). Utilization of its lower oxophilicity would have a new possibility to explore new catalytic reactions.

VII-C-1 A $GaCl_3$-Catalyzed [4+1] Cycloaddition of α,β-Unsaturated Carbonyl Compounds and Isocyanides Leading to Unsaturated γ-Lactone Derivatives

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[*J. Am. Chem. Soc.* **125**, 7812–7813 (2003)]

A $GaCl_3$-catalyzed reaction of α,β-unsaturated ketones with isocycanides leading to the formation of unsaturated lactone derivatives is described. This is the first example of the catalytic [4+1] cycloaddition of α,β-unsaturated ketones and isocycanides. $GaCl_3$ is an excellent catalyst due to its lower oxophilicity, which is desirable for all of the key steps, such as *E*/*Z* isomerization, cyclization, and deattachment from the products.

VII-D Reductive Activation of Carbon Dioxide and Oxidative Activation of Water Aiming at Reversible Conversion between CO_2 and Organic Molecules

Multi-electron reduction of CO_2 aiming at smooth conversion to organics is highly desired in the viewpoints of not only the utilization of C1 resources but also the decrease of the concentration in the air. Carbon dioxide easily reacts with coordinatively unsaturated low-valent metal complexes to form η^1- or η^2-CO_2 adducts, the former of which are easily converted to metal-CO complexes in protic media. Accumulation of much electrons on metal centers usually accelerates not only reduction of CO_2 but also metal-CO bond cleavages. As a result, CO is the main product in photo- and electro-chemical reduction of CO_2 catalyzed by metal complexes. It is, therefore, highly desired to develop new methodologies that can supply electrons to the carbonyl ligand of metal-CO complexes derived from CO_2 without accumulation of electrons at the central metals. Along the line, we are designing new types of metal complexes that have an ability to provide electrons to carbonyl carbon through metallacycle rings involving the CO groups aiming at catalytic generation higher organic molecules by the electro- and photochemical reduction of CO_2.

Oxygenations and oxidations of organic molecules by high valent metal-oxo complexes are of current interest from the viewpoints of the enzymatic activities of P-450. Mechanistic understandings of the reactivity of metal-oxo species derived from O_2, however, have been limited because of the difficulty of selective cleavage of the O–O bond of M–O_2 frameworks in artificial systems. Alternatively, high valent Ru=O complexes can be obtained by sequential electron and proton loss of the Ru–OH_2 frameworks, and some of Ru=O complexes have proven to work as oxidants of organic molecules. Introduction of quinone molecules, which are reduced to semiquinone and catecholate in a wide range of potentials, into M–OH_2 frameworks also induces sequential electron and proton loss of the Ru–OH_2 ones without addition of oxidizing agents. Such acid-base equilibria of the aqua ligands by taking advantages of smooth redox reactions of quinone ligands can be applied for energy conversion from pH gradients to electronic energy.

VII-D-1 Coordination Ability of 1,10-Phenanthroline-5,6-Dione: Syntheses and Redox Behavior of a Ru(II) Complex with an o-Quinoid Moiety and of Bridged Ru(II)-M(II) Complexes (M = Pd, Pt)

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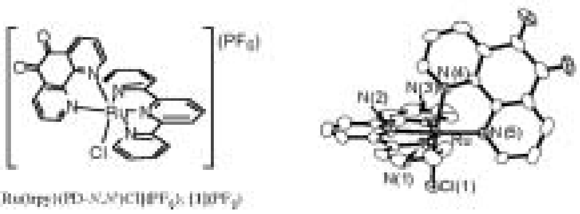
[*Dalton Trans.* 3221–3226 (2003)]

The synthesis and electrochemical properties of Ru(II) complexes having 1,10-phenanthroline-5,6-dione (PD), [Ru(trpy)(PD-N,N')Cl](PF_6) ([**1**](PF_6)), mixed-metal complexes [$(PPh_3)_2$Pd(O,O'-PD-N,N')Ru(trpy)-Cl](PF_6) ([**2**](PF_6)), and [$(PPh_3)_2$Pt(O,O'-PD-N,N')Ru-(trpy)Cl](PF_6) ([**3**](PF_6)) (trpy = 2,2':6',2"-terpyridine) are presented. The PD ligand of $[\mathbf{1}]^+$, which was prepared by the reaction of Ru(trpy)(DMSO)Cl_2 with PD in hot ethanol, existed as the quinoid form and underwent two reversible ligand-based redox reactions. The quinoid group of $[\mathbf{1}]^+$ did not show any interactions with Pd(II) and Pt(II), whereas the ligand was endowed with coordination ability to metals by one- and two-electron reduction of the ligand-based redox reaction. Indeed, the mixed-metal complexes of $[\mathbf{2}]^+$ and $[\mathbf{3}]^+$ prepared by the reactions of $[\mathbf{1}]^+$ with $M(PPh_3)_4$ (M = Pd, Pt) have the $[\mathbf{1}]^-$ core bearing the two-electron reduced form of PD (catecolato form) and M(II) frameworks.



VII-D-2 Characterization of a Stable Ruthenium Complex with an Oxyl Radical

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[*J. Am. Chem. Soc.* **125**, 6729–6739 (2003)]

The ruthenium oxyl radical complex, [Ru^{II}(trpy)-(Bu_2SQ)$O^{-\cdot}$] (trpy = 2,2':6',2"-terpyridine, Bu_2SQ = 3,5-di-tert-butyl-1,2-benzosemiquinone) was prepare for the first time by the double deprotonation of the aqua ligand of [Ru^{III}(trpy)(Bu_2SQ)(OH_2)]$(ClO_4)_2$. [Ru^{III}-(trpy)(Bu_2SQ)(OH_2)]$(ClO_4)_2$ is reversibly converted to $[Ru^{III}(trpy)(Bu_2SQ)(OH^-)]^+$ upon dissociation of the aqua proton (pKa 5.5). Deprotonation of the hydroxo proton gave rise to intramolecular electron transfer from the resultant O^{2-} to the Ru-dioxolene framework. The resultant [Ru^{II}(trpy)(Bu_2SQ)$O^{-\cdot}$] showed antiferromagnetic behavior with a Ru^{II}-semiquinone moiety and oxyl radical, the latter of which was characterized by a spin trapping technique. The most characteristic structural feature of [Ru^{II}(trpy)(Bu_2SQ)$O^{-\cdot}$] is a long Ru–O bond length (2.042(6) Å) as the first terminal metal–O bond with a single bond length. To elucidate the substituent effect of a quinone ligand, we prepared $[Ru^{III}(trpy)(4ClSQ)(OH_2)](ClO_4)_2$ (4ClSQ = 4-chloro-1,2-benzosemiquinone) and compared the deprotonation behavior of the aqua ligand with that of $[Ru^{III}(trpy)(Bu_2SQ)(OH_2)](ClO_4)_2$. Deprotonation of the aqua ligand of $[Ru^{III}(trpy)(4ClSQ)(OH_2)](ClO_4)_2$ induced intramolecular electron transfer from OH^- to the $[Ru^{III}(4ClSQ)]$ moiety affording $[Ru^{II}(trpy)(4ClSQ)(OH\cdot)]^+$, which then probably changed to $[Ru^{II}(trpy)(4ClSQ)O^{-\cdot}]$. The antiferromagnetic interactions (*J* values) between Ru^{II}-semiquinone and the oxyl radical for $[Ru^{II}(trpy)(Bu_2SQ)O^{-\cdot}]$ and for $[Ru^{II}(trpy)(4ClSQ)O\cdot]$ were $2J = -0.67\ cm^{-1}$ and $-1.97\ cm^{-1}$, respectively.

VII-D-3 Terpyridine-Analogous (N,N,C)-Tridentate Ligands: Synthesis, Structures, and Electrochemical Properties of Ruthenium(II) Complexes Bearing Tridentate Pyridinium and Pyridinylidene Ligands

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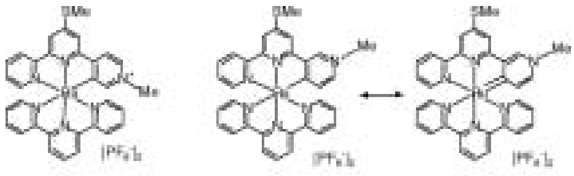
([1]IMS, CREST/JST)

[*Organometallics* **22**, 970–975 (2003)]

The cyclometalated complexes $[RuL(terpy)][PF_6]_2$ (**3**, L = N”-methyl-4’-methylthio-2,2’:6’,4”-terpyridinium; **4**, L = N”-methyl-4’-methylthio-2,2’:6’,3”-terpyridinium) with a (N,N,N)(N,N,C)-coordination mode were synthesized in good yields and fully characterized by x-ray crystallographic, spectroscopic, and electrochemical measurements. $^{13}C\{^1H\}$ NMR and electronic spectra revealed that the Ru–C bond of complex **4**, which has a quaternized N–Me unit at the para-position of the carbon atom bonding to the metal center in the terminal ring of the tridentate ligand, involves carbenic (Ru=C) character in solutions.



3 4

VII-D-4 Syntheses of a 6-(2-pyrrolyl)-2,2’-Bipyridine Derivative and its Ruthenium Complex

NAGATA, Toshi; TANAKA, Koji

[*Bull. Chem. Soc. Jpn.* **75**, 2469–2470 (2002)]

Syntheses of a new planar terdentate ligand, 6-(3,5-diphenyl-2-pyrrolyl)-2,2’-bipyridine (L^1H) and its Ru(II) complex ($[Ru(L^1)_2]$) are reported. The x-ray structure of $[Ru(L^1)_2]$ showed the distorted octahedral Ru(II) center similar to the structures of terpyridine complexes. The cyclic voltammograms revealed that $[Ru(L^1)_2]$ was more easily oxidized than $[Ru(terpy)_2]^{2+}$ by 1.10 V.

VII-D-5 Acid-Base Equilibrium of Aqua-Chromium-Dioxolene Complexes Aimed at Formation of Oxo-Chromium Complexes

SHIREN, Kazushi[1]; TANAKA, Koji
([1]IMS, CREST/JST)

[*Inorg. Chem.* **41**, 5912–5919 (2002)]

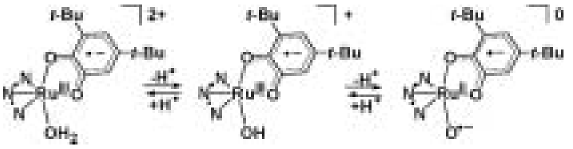
A series of aqua-Cr(III)-dioxolene complexes, $[Cr(OH_2)(3,5\text{-}Bu_2SQ)(trpy)](ClO_4)_2$ (**1s**), $[Cr(OH_2)(3,5\text{-}Bu_2Cat)(trpy)]ClO_4$ (**1c**), $[Cr(OH_2)(3,6\text{-}Bu_2SQ)(trpy)](ClO_4)_2$ (**2**), $[Cr(OH_2)(Cat)(trpy)]ClO_4$ (**3**), $[Cr(OH_2)(Cl_4Cat)(trpy)]ClO_4$ (**4**), $[Cr(OH_2)(3,5\text{-}Bu_2SQ)(Me_3\text{-}tacn)](ClO_4)_2$ (**5**), $[Cr(OH_2)(Cat)(Me_3\text{-}tacn)]ClO_4$ (**6**), and $[Cr(OH_2)(Cl_4Cat)(Me_3\text{-}tacn)]ClO_4$ (**7**) (Bu_2SQ = di-*tert*-butyl-*o*-benzosemiquinonate anion, Bu_2Cat = di-*tert*-butylcatecholate dianion, Cat = catecholate dianion, Cl_4Cat = tetrachlorocatecholate dianion, trpy = 2,2’:6’,2”-terpyridine, and Me_3-tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane), were prepared. On the basis of the crystal structures, redox behavior, and elemental analyses of these complexes, dioxolene in **1c**, **3**, **4**, **6**, and **7** coordinated to Cr(III) as the catechol form, and the ligand in **1s**, **2**, and **5** was linked to Cr(III) with the semiquinone form. All the aqua-Cr(III) complexes reversibly changed to the hydroxo-Cr(III) ones upon dissociation of the aqua proton, and the *pKa* value of the aqua-Cr(III) complexes increased in the order **6** > **3** ≈ **1c** > **7** > **5** ≈ **4** > **1s**. Hydroxo-Cr(III)-catechol complexes derived from **1c**, **3**, **4**, **6**, and **7** did not show any signs of dissociation of their hydroxy proton. On the other hand, hydroxo-Cr(III)-semiquinone complexes were reduced to hydroxo-Cr(III)-catechol in H_2O/THF at pH 11 under illumination of visible light.

VII-D-6 Ruthenium Oxyl Radical Complex Containing *o*-Quinone Ligand Detected by ESR Measurements of Spin Trapping Technique

KOBAYASHI, Katsuaki[1]; OHTSU, Hideki[1]; WADA, Tohru; TANAKA, Koji
([1]IMS, CREST/JST)

[*Chem. Lett.* 868–869 (2002)]

Ru-quinone complex containing an aqua ligand, $[Ru(II)(trpy)(35tBu_2Q)(OH_2)](ClO_4)_2$ (trpy = 2,2’:6’,2”-terpyridine, $35tBu_2Q$ = 3,5-di-tert-butyl-1,2-benzoquinone) underwent deprotonation of an aqua ligand accompanied with intramolecular electron transfer from O^{2-} ligand to quinone ligand generating $O^{\cdot-}$ ligand.



VII-D-7 Multi-Electron Reduction of CO_2 *via* Ru-CO_2, -C(O)OH, -CO, -CHO, and -CH_2OH Species

TANAKA, Koji; OOYAMA, Dai[1]
([1]Fukusima Univ., CREST/JST)

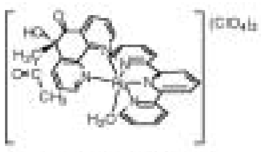
[*Coord. Chem. Rev.* **226**, 211–218 (2002)]

A review about preparations and the molecular structures determined by x-ray analyses 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, 1, 2) were presented. 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. Thermodynamically, 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 $[Ru(bpy)_2(CO)L]^{n+}$ were 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–C bond strength of each intermediate. The Ru–C bond distance of $[Ru(bpy)_2(CO)L]^{n+}$ largely depends on the hybrid orbital of the C atom bonded to Ru and lengthens in the order Ru–C*sp* < Ru–Csp_2 < Ru–Csp_3. An unusual shift of the ν(Ru–L) bands to higher wavenumber with decrease of the Ru–L bond distances is discussed in terms of σ- and π-character of the Ru–C bonds.

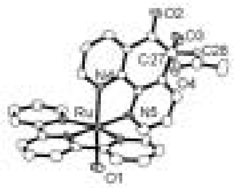
VII-D-8 Acid-Base Equilibria of Various Oxidation States of Aqua-Ruthenium Complexes with 1,10-Phenanthroline-5,6-Dione in Aqueous Media

FUJIHARA, Tetsuaki[1]**; WADA, Tohru; TANAKA, Koji**
([1]IMS, CREST/JST)

Synthesis and electrochemical behavior of aqua-ruthenium(II) complexes, $[Ru(trpy)(PDA\text{-}N,N')(OH_2)](ClO_4)_2$ ($[\mathbf{1}](ClO_4)_2$) and $[Ru(trpy)(PD\text{-}N,N')(OH_2)](ClO_4)_2$ ($[\mathbf{2}](ClO_4)_2$) (trpy = 2,2’:6’,2”-terpyridine, PDA = 6-acetonyl-6-hydroxy-5-oxo-1,10-phenanthroline, PD = 1,10-phenanthroline-5,6-dione) are presented. Treatment of $[Ru(trpy)(PD\text{-}N,N')Cl](PF_6)$ with $AgClO_4$ in a mixed solvent of acetone and H_2O selectively produced the acetonyl-PD complex $[\mathbf{1}](ClO_4)_2$, and the similar treatment in a mixed solvent of 2-methoxyethanol and H_2O gave the PD complex $[\mathbf{2}](ClO_4)_2$. The molecular structures of both complexes were determined by X-ray structural analysis. Simulation of pH dependent redox potentials ($E_{1/2}$) of $[\mathbf{1}]^{2+}$ and $[\mathbf{2}]^{2+}$ in H_2O revealed that the acetonyl-PD complex $[\mathbf{1}]^{2+}$ underwent closely successive Ru(II)/Ru(III) and Ru(III)/Ru(IV) redox reactions. In addition to the similar successive Ru(II)/Ru(III) and Ru(III)/Ru(IV) redox reactions, the aqua complex $[\mathbf{2}]^{2+}$ showed simultaneous two-electron quinone/catechol redox couple of the PD ligand.



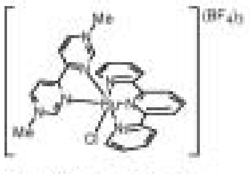
$[Ru(trpy)(PDA\text{-}N,N')(OH_2)](ClO_4)_2$
$[\mathbf{1}](ClO_4)_2$



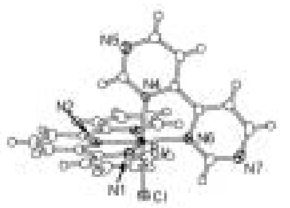
VII-D-9 Syntheses and Electrochemical Properties of Ruthenium(II) Polypyridyl Complexes with 4,4’-Bipyrimidine and Quaternized 4,4’-Bipyrimidinium Ligands

FUJIHARA, Tetsuaki[1]**; WADA, Tohru; TANAKA, Koji**
([1]IMS, CREST/JST)

The synthesis and electrochemical properties of novel ruthenium(II) polypyridyl complexes with 4,4’-bipyrimidine, [Ru(trpy)(bpm)Cl](X) ($[\mathbf{1}]$(X; X = PF_6^-, BF_4^-)), and with a quaternized bipyrimidinium ligand, $[Ru(trpy)(Me_2bpm)Cl](BF_4)_3$ ($[\mathbf{2}](BF_4)_3$) (trpy = 2,2’:6’,2”-terpyridine, bpm = 4,4’-bipyrimidine, Me_2bpm = 1,1’-dimethyl-4,4’-byprimidinium) are presented. The bpm complex of $[\mathbf{1}]^+$ was prepared by the reaction of $Ru(trpy)Cl_3$ with 4,4’-bipyrimidine in $EtOH/H_2O$. The structural characterization of $[\mathbf{1}]^+$ revealed that the bpm ligand was coordinated to the ruthenium atom with the bidentate fashion. Diquaternization of the non-coordinating nitrogen atoms on bpm of $[\mathbf{1}]^+$ by $(CH_3)_3OBF_4$ in CH_3CN gave $[\mathbf{2}](BF_4)_3$. The electrochemical and spectroelectrochemical properties of the complexes are described.



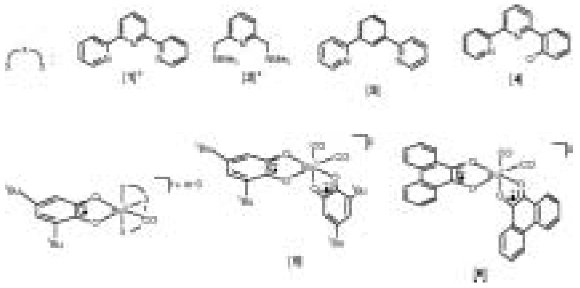
$[Ru(trpy)(Me_2bpm)Cl](BF_4)_3$
$[\mathbf{2}](BF_4)_3$



VII-D-10 Strong Interaction between Carbonyl and Dioxolene Ligands through Charge Distribution of Mono- and Dicarbonyl Ruthenium Complexes with Semiquinone

WADA, Tohru; FUJIHARA, Tetsuaki[1]**; TOMORI, Mizuno**[2] **; OOYAMA, Dai**[2]**; TANAKA, Koji**
([1]IMS, CREST/JST; [2]Fukushima Univ., CREST/JST)

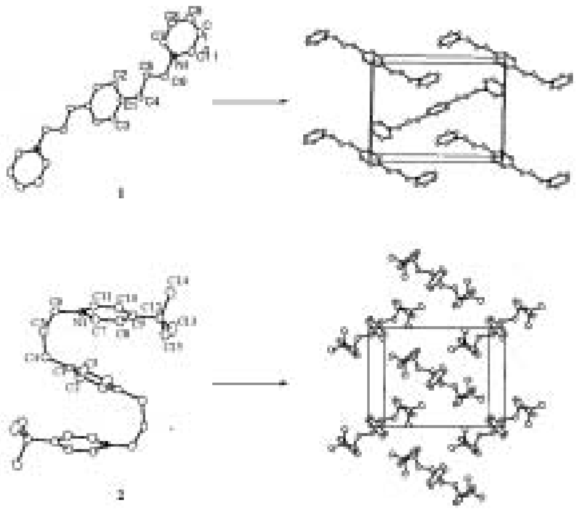
Monocarbonyl Ru(II) Complexes with semiquinone, $([Ru(CO)(sq)(L)]^n$ (sq = 3,5-di-*tert*-butyl-1,2-benzosemiquinone, L = terpyridine($[\mathbf{1}]^+$), 2,6-bis(N,N-dimethylaminomethyl)-pyridine($[\mathbf{2}]^+$), 2,6-dipyrid-2-ylphenyl($[\mathbf{3}]^0$), 2-(2,2’-bipyrid-6-yl)phenolato($[\mathbf{4}]^0$), n = 1+ or 0), and dicarbonyl Ru(II) complexes with two semiquinones, $[Ru(CO_2)_2(sq)_2]$ ($[\mathbf{5}]^0$) and $[Ru(CO)_2(phsq)_2]$ (phsq = 9,10-phenanthrasemiquinone, $[\mathbf{6}]^0$), were synthesized. Red shift of ν(CO) bands caused by one-electron reduction of semiquinone is in a range of –41 to –56 cm^{-1}. Unusual large red shift of ν(CO) bands compared with analogous Ru(II)–polypyridyl results from the strong interaction between carbonyl and dioxolene across Ru(II).



VII-D-11 Regulation of Inter- and Intra-Molecular A–D–A π-π Stacking. Solid State Structures of Bis(pyridinium) Compounds

KOIZUMI, Take-aki; TSUTSUI, Kanako; WADA, Tohru; TANAKA, Koji

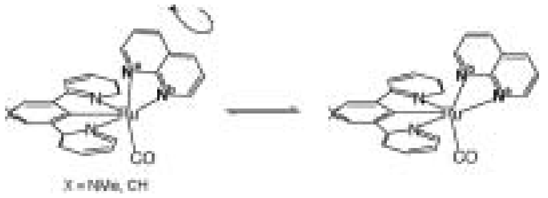
The synthesis and molecular structures of bis(pyridinium) compounds, [1,4-(4-R-$C_5H_4N^+CH_2$-$CH_2CH_2)_2C_6H_4][X^-]_2$ (**1**, R = H, X = I; **2**, R = t-Bu, X = Br) are investigated. The compound **1** is a linear structure in the solid state and the crystal packing geometry of **1** is defined as isolated triplets formed by the phenylene ring of a molecule and two pyridinium rings of two neighboring molecules. On the other hand, compound **2** has an S-shaped arrangement, and an intramolecular acceptor-donor-acceptor triplet is formed among the central phenylene ring and two terminal pyridinum rings in the same molecule. Such a distinct difference in the crystal structures of **1** and **2** is ascribed to the substituent in the pryridinium unit. The steric repulsion of the bulky tert-butyl group hinders intermolecular A–D–A π-π stacking.



VII-D-12 Synthesis, Structures and Fluxional Behavior of Ruthenium(II) Complexes Bearing a Bidentate 1,8-Naphthyridine Ligand

KOIZUMI, Take-aki[1]; TOMON, Takashi[1]; TANAKA, Koji
([1]IMS, CREST/JST)

The ruthenium complexes bearing 1,8- naphthyridine (napy) and terpyridine analogous (N,C,N)-tridentate ligands were synthesized and characterized. Reaction of $RuCl_2(\eta^2\text{-napy})(DMSO)_2$ with 2 equiv of $AgPF_6$ and subsequent addition of LH and CO gave $[RuL(\eta^2\text{-napy})(CO)][PF_6]_n$ (**6a**: L = N-methyl-3,5-di(2-pyridyl)-4-pyridyl, *n* = 2; **6b**: L = 2,6-di(2-pyridyl)-phenyl, *n* = 1) *via* the formation of $[RuL(\eta^2\text{-napy})(DMSO)][PF_6]_n$ (**5a**: L = N-methyl-3,5-di(2-pyridyl)-4-pyridyl, *n* = 2; **5b**: L = 2,6-di(2-pyridyl)phenyl, *n* = 1). The crystal structures of **5a** and **6a** show that these complexes have distorted octahedral coordination with the tridentate (N,C,N)-ligand as mer-fashion, two nitrogen of bidentate napy and sulfur of DMSO (**5a**) or carbon of the CO (**6a**) ligand. Detailed irradiation and variable-temperature ^1H-NMR studies reveal fluxional process of the chelated napy ligand in solution.



VII-D-13 Acid-Base Equilibrium of 6-Hydroxy-2,2’-Bipyridine Ligated on Ruthenium-Carbonyl Complexes and Cyclometalation Driven by Ligand Based Redox Reaction

TOMON, Takashi[1]; KOIZUMI, Take-aki[1]; TANAKA, Koji
([1]IMS, CREST/JST)

Two isomers of $[Ru(trpy)(bpy\text{-}O)(CO)](PF_6)$ ($[\mathbf{1}]^+$ and $[\mathbf{2}]^+$) (trpy = terpyridine, bpy-O = 2-(2’-pyridyl)-6-pyridonato) were prepared; pyridonato in bpy-O of $[\mathbf{1}]^+$ and $[\mathbf{2}]^+$ is located in a position *trans* and *cis* to CO. Treatments of $[\mathbf{1}]^+$ and $[\mathbf{2}]^+$ with HPF_6 produced $[\mathbf{1}H]^{2+}$ and $[\mathbf{2}H]^{2+}$ with bpy-OH (bpy-OH = 6-hydroxy-2, 2’-bipyridine), and the reactions of $[\mathbf{1}H]^{2+}$ and $[\mathbf{2}H]^{2+}$ with Et_3N regenerated $[\mathbf{1}]^+$ and $[\mathbf{2}]^+$. The molecular structures of $[\mathbf{1}](PF_6)$, $[\mathbf{2}](PF_6)\cdot H_2O$ and $[\mathbf{2}H](PF_6)_2\cdot 2H_2O$ were determined by X-ray analysis. The cyclic voltammograms of $[\mathbf{1}]^+$ and $[\mathbf{2}]^+$ displayed one nearly reversible redox couple at $E_{1/2}$ = –1.65 V and –1.51 V, and one irreversible cathodic wave at $E_{p,c}$ = –1.97 and $E_{p,c}$ = –2.15 V, respectively. The complex of $[\mathbf{1}]^+$ showed the υ(C≡O) band at 1979 cm^{-1}, which shifted to 1932 and 1853 cm^{-1} upon one- and two-electron reduction of $[\mathbf{1}]^+$, respectively, and the intensity of the 1853 cm^{-1} band became weak compared with those of the 1979 and 1932 cm^{-1} bands due to loss of CO from $[\mathbf{1}]^-$. $[\mathbf{2}]^+$ and $[\mathbf{2}]^0$ also displayed the υ(C≡O) band at 1997 and 1953 cm^{-1}, the latter of which moved to 1587 cm^{-1} upon one electron reduction of $[\mathbf{2}]^0$. Reoxidation of $[\mathbf{2}]^-$ at 0 V almost fully regenerated the IR spectra of $[\mathbf{2}]^+$. Unusual large red shift of the υ(C≡O) band between $[\mathbf{2}]^0$ and $[\mathbf{2}]^-$ (Δυ = 345 cm^{-1}) is ascribed to a cyclometalation resulting from an attack of pyridonato oxygen to carbonyl carbon of $[\mathbf{2}]^-$.

VII-E Silanechalcogenolato Complexes

The development of synthetic routes to mixed-metal chalcogenido clusters is a critical prerequisite for study of these important materials. It is well known that $(Me_3Si)_2E$ (E = S, Se, Te) is a good chalcogen transfer reagent, which can replace a halide, alkoxide, acetate, and oxide with a chalcogen ligand by taking advantage of formation of Si–Cl and Si–O bonds. Therefore the corresponding $M–ESiMe_3$ species hold great promise for synthetic precursors of chalcogenido clusters. However, because of the high lability of Si–E bond, there is a strong tendency to restrict the use of these complexes. Thus, their stabilization is required to develop cluster synthesis based on silanechalcogenolato complexes.

In this work, we have chosen to stabilize silanethiolato complexes by the chelating effect of the ligands. The chelating effect in coordination chemistry has most pronounced kinetic and thermodynamic consequences. This strategy could suppress the undesired degradation process of silanethiolato complexes *via* aggregation and/or ligand redistribution.

VII-E-1 Coordination Chemistry of Silanedithiolato Ligands Derived from Cyclotrisilathiane: Synthesis and Structures of Complexes of Iron(II), Cobalt(II), Palladium(II), Copper(I), and Silver(I)

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

[*Inrog. Chem.* **42**, 5340 (2003)]

The coordination chemistry of chelating silanedithiolato ligands has been investigated on Fe(II), Co(II), Pd(II), Cu(I), and Ag(I). Treatment of $M(OAc)_2$ (M = Fe, Co, Pd) with cyclotrisilathiane $(SSiMe_2)_3$ in the presence of Lewis bases resulted in formation of $Fe(S_2SiMe_2)(pmdeta)$ (**1**), $Fe(S_2SiMe_2)(Me_3tacn)$ (**2**), $Co(S_2SiMe_2)(pmdeta)$ (**3**), and $Pd(S_2SiMe_2)(PEt_3)_2$ (**4**). The analogous reactions of M(OAc) (M = Cu, Ag) in the presence of PEt_3 gave rise to the dinuclear complexes $M\{(SSiMe_2)_2S\}(PEt_3)_3$ [M = Cu (**5**), Ag (**6**)]. Complexes were characterized in solution by ^1H, $^{31}P\{^1H\}$, and $^{29}Si\{^1H\}$ NMR and in the solid state by single-crystal X-ray diffraction. Mononuclear complexes **1**, **2**, and **3** have a four-membered MS_2SiMe_2 ring, and these five-coordinate complexes adopt trigonal-bipyramidal (for the pmdeta adducts) or square-pyramidal (for the Me_3tacn adduct) geometries. In dimer **6**, the $(SSiMe_2)_2S^{2-}$ silanedithiolato ligand bridges two metal centers, one of which is three-coordinate and the other four-coordinate. The chelating effect of silanedithiolato ligands leads to an increase in the stability of silylated thiolato complexes.

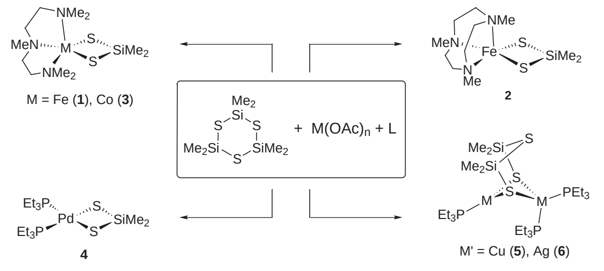


Figure 1.

VII-E-2 Copper and Silver Complexes Containing the $S(SiMe_2S)_2{}^{2-}$ Ligand: Efficient Entries into Heterometallic Sulfido Clusters

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

[*Angew. Chem., Int. Ed.* **42**, 465 (2003)]

Reactions of copper and silver acetates with cyclotrisilathane in the presence of PEt_3 afforded the silanedithiolate-bridged dinuclear complexes $[M_2\{(SSiMe_2)_2S\}(PEt_3)_3]$ (M = Cu (**1a**), Ag (**1b**)) in high yields. Although these complexes are thermally stable in solution, they are found to react smoothly under mild conditions with metal halides, giving mixed-sulfido clusters. Treatment of **1a** with $[CpTiCl_3]$ and $[TiCl_4(thf)_2]$ produced copper-titanium sulfido clusters $[Cp_2Ti_2Cu_6S_6(PEt_3)_6]$ (**2**) and $[ClTiCu_3S_3(PEt_3)_4]$ (**3**), respectively. Addition of [CpLi] to **3** resulted in the formation of **2**. Structures of **1a**, **2**, and **3** have been determined by X-ray analysis.

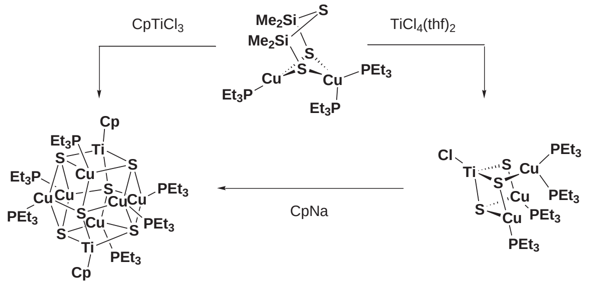


Figure 1.

VII-F Coordination Chemistry of Sterically Hindered Ligands and Multidentate Ligands and Activation of Small Molecules

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

VII-F-1 Titanium N-Hetrocyclic Carbene Complexes Incorporating an Imidazolium-Linked Bis(phenol)

AIHARA, Hidenori; MATSUO, Tsukasa; KAWAGUCHI, Hiroyuki

[*Chem. Commun.* 2204 (2003)]

We synthesized and fully characterized titanium(II) complexes supported by a bis(aryloxido) ligand with an N-heterocyclic carbene (NHC) function. The use of NHC as ligands has attracted considerable attention, because their complexes are highly active and very stable catalysts for various organic reactions. However, the vast majority of NHC systems contain late transition metals. This is due to the lack of NHC derivatives suitable for studies of early transition metal chemistry. Thus we designed the aryloxido-functionalized NHC hybrid ligand, in which the carbene unit is flanked by two aryloxide groups. The aryloxido group acts as an anchor and reduces the tendency for NHC dissociation. This enables us to explore the effect of NHC on the properties of early transition metal complexes. In this context, we use this ligand (**L**) to prepare titanium complexes, which were fully characterized. Furthermore, another interesting aspect of this system is that these aryloxido-carbene complexes of titanium showed a high activity for ethylene polymerization. This is a first example of ethylene polymerization promoted by NHC complexes.

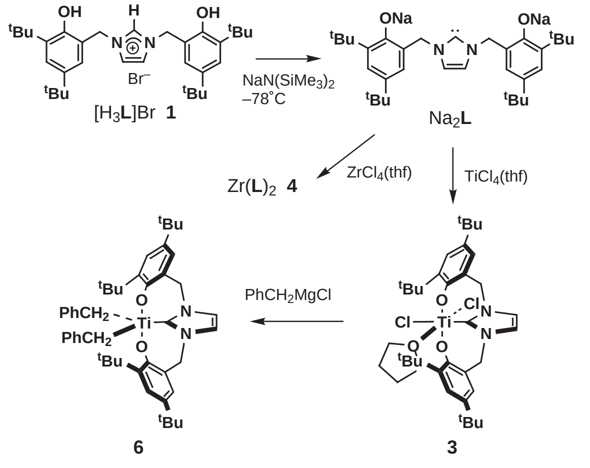


Figure 1.

VII-F-2 Unusual Coordination Modes of Arylthiolates in Mo{η^5-SC_6H_3-2,6-$(SiMe_3)_2$}{η^7-SC_6H_3-2,6-$(SiMe_3)_2$}

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

[*J. Am. Chem. Soc.* **125**, 2070 (2003)]

Although arylthiolate ligands are ubiquitous in transition metal coordination chemistry, they are invariably S-bonded for either terminal or bridging coordination. This is probably because the affinity of transition metal elements to thiolate sulfurs is strong relative to the metal-aryl π interactions. In contrast, analogous aryloxide complexes have occasionally been found to assume π coordination geometries at the aryl substituents, in an η^5-pentadienyl or an η^3-allyl bonding manner, leaving the C=O portion intact. As a part of our ongoing study on activation of small molecules by means of coordinatively unsaturated transition metal complexes, we were interested in preparation of molybdenum complexes of the 2,6-disubstituted arylthiolates, SC_6H_3-2-Ph-6-$SiMe_3$ and SC_6H_3-2,6-$(SiMe_3)_2$. This work describes the reactions of $MoCl_3(thf)_3$ with the lithium salts of these arylthiolates, which resulted in isolation of the unexpected π-sandwiched bis-arylthiolato complex, Mo{η^5-SC_6H_3-2,6-$(SiMe_3)_2$}{η^7-SC_6H_3-2,6-$(SiMe_3)_2$} (**1**). We also report here that the π-bonding in **1** is labile and the treatment with acetonitrile gave rise to the S-bonded bis-arylthiolato complex carrying three acetonitrile molecules, one of which is coordinated in an η^2-mode, Mo{SC_6H_3-2,6-$(SiMe_3)_2$}$_2$(η^1-CH_3CN)$_2$(η^2-CH_3CN) (**2**).

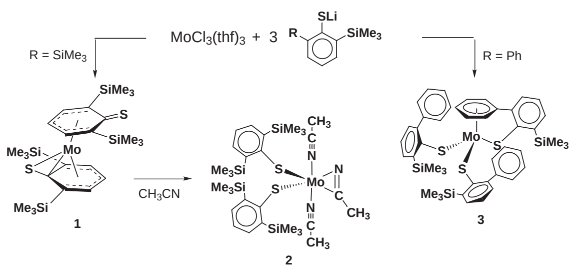
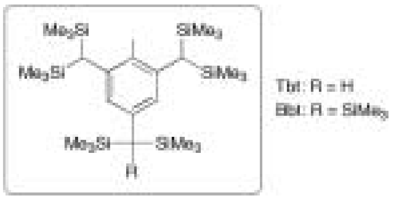


Figure 1.

VII-G 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)methyl]phenyl (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 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* **21**, 4024–4026 (2002)]

Since aromatic compounds play very important roles in organic chemistry, much attention has been also paid to the chemistry of silaaromatic compounds. However, there are few reports on the synthesis and isolation of silaaromatic compounds stable at room temperature because of their high reactivity. Very recently, we have successfully synthesized 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**) readily dimerizes in solution even at room temperature to give the corresponding [2+4] dimmer **2**.

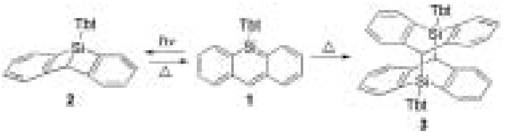
VII-G-2 Photochemical and Thermal Reactions of a Kinetically Stabilized 9-Silaanthracene: The First Spectroscopic Observation of a 9,10-Dewar-9-Silaanthracene Isomer

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

[*J. Am. Chem. Soc.* **125**, 10804–10805 (2003)]

In recent decades, much attention has been paid to the chemistry of silaaromatic compounds. Recently we have succeeded in the synthesis of novel silaaromatic species such as silabenzene, 1-silanaphthalene, 2-silanaphthalene, and 9-silaanthracene by taking advantage of an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) group. In this paper we present the photochemical and thermal reaction of the stable 9-silaanthracene **1**.

Irradiation of **1** with the light of λ = 300–500 nm afforded the corresponding 9,10-Dewar-9-silaanthracene **2**, the formation of which was experimentally demonstrated by the ^{1}H, ^{13}C, and ^{29}Si NMR spectra. It should be noted that **2** is the first example of spectroscopically identified 9,10-Dewar-9-silaanthracene. Dewar isomer **2** was found to be a marginally stable species in solution and to undergo gradual thermal tautomerization into **1** even at –80 °C in hexane. On the other hand, thermal reactions of 9-silaanthracene **1** afforded the head-to-tail [4+4] dimer **3** either in solution or in the solid state. The dimer **3** was thermally very stable and its molecular structure was definitively determined by X-ray crystallographic analysis. The isolation and characterization of **3** are of particular note as the first unambiguous experimental evidence for the [4+4] dimer of 9-silaanthracene derivatives.



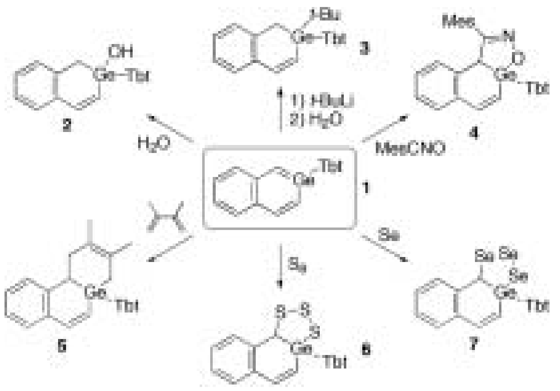
VII-G-3 Synthesis and Properties of the First Stable Neutral Germaaromatic Compound, 2-{2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}-2-Germanaphthalene

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

[*Organometallics* **22**, 481–489 (2003)]

While there have been relatively many informations on silaaromatic compounds, the studies on germaaromatic compounds are very few. In this paper, we present the synthesis and properties of the first stable 2-germanaphthalene.

The first stable neutral germaaromatic compound, 2-germanaphthalene **1** was synthesized by taking advantage of an extremely bulky and efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt). 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, which indicate the delocalization of π-electrons in the 2-germanaphthalene ring of **1**. 2-Germanaphthalene **1** reacted with water, *t*-BuLi, mesitonitrile oxide, 2,3-dimethyl-1,3-butadiene, elemental sulfur, and elemental selenium to give the corresponding adducts **2**–**7** across the Ge–C double bond.



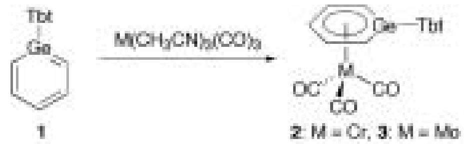
VII-G-4 η^6-Germabenzene Complexes of Chromium and Molybdenum

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

[*Angew. Chem., Int. Ed.* **42**, 115–117 (2003)]

Germabenzenes are the most fundamental germaaromatic compounds having a simple 6π-electron ring system. However, very little has been known about the synthesis and characterization of germaaromatic compounds due to their extremely high reactivity. Very recently, we have succeeded in the synthesis and properties of the first stable germabenzene **1** bearing an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt). Meanwhile, in recent decades there has been considerable interest in the transition metal complexes containing sila- and germaaromatic compounds as ligands from the viewpoints of their coordination fashion and unique structure. However, the molecular structure and reactivity of η^6-sila- and germabenzene complexes have never been known.

The first η^6-germabenzene complexes, [M(η^6-C_5H_5GeTbt)(CO)$_3$] [M = Cr (**2**), Mo (**3**)], were synthesized by the ligand exchange reaction of the corresponding acetonitrile complexes, [M(CH_3CN)$_3$(CO)$_3$] (M = Cr, Mo) with **1**. These reactions are interesting also as the first examples showing the aromatic character of the germabenzene **1** from the standpoint of its reactivity. The low-temperature X-ray crystallographic analysis of Cr complex **2** revealed that the germabenzene ring was almost planar and η^6-coordinated to the Cr(CO)$_3$ group.



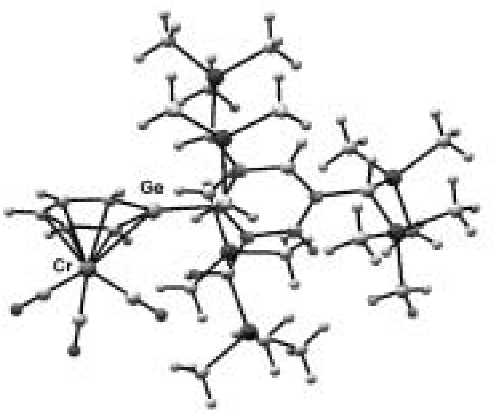


Figure 1. Molecular Structure of Germabenzene Complex of Chromium **1**.

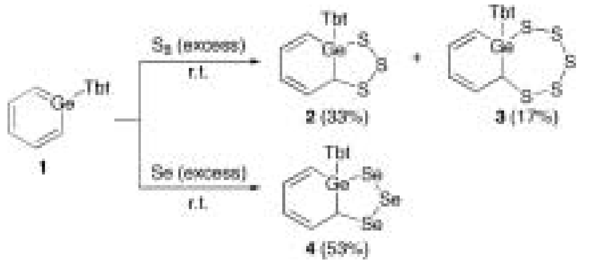
VII-G-5 Reaction of Stable Germabenzene with Chalcogens: Synthesis and Structure of a Novel Germanium Analog of Pentathiepane, 1,2,3,4,5,6-Pentathiagermepane

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

[*J. Organomet. Chem.* **672**, 66–71 (2003)]

Much attention has been paid to the chemistry of cyclic polychalcogenides from the standpoints of chemical and physical properties as well as from that of biological activities. In contrast to the widely explored chemistry of transition metal polychalcogenido complexes, very little has been known for cyclic polychalcogenides containing a heavier group 14 element. We examined the synthesis of cyclic polychalcogenides containing germanium by the reactions of a stable germabenzene **1** bearing a 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) group with elemental sulfur and selenium.

Treatment of a germabenzene **1** with elemental sulfur gave a 1,2,3,4-trithiagermolane **2** together with a novel 1,2,3,4,5,6-pentathiagermepane **3**, which is the germanium analog of pentathiepane. On the other hand, the reaction of **1** with elemental selenium gave only 1,2,3,4-triselenagermolane **4**. All the newly obtained polychalcogenides containing a germanium atom were characterized by NMR spectroscopy and elemental analysis. The molecular structures of **2** and **3** were determined by X-ray crystallographic analysis. In addition, the thermal interconversion between pentasulfide **3** and trisulfide **2** plus 1/4 S_8 was confirmed.



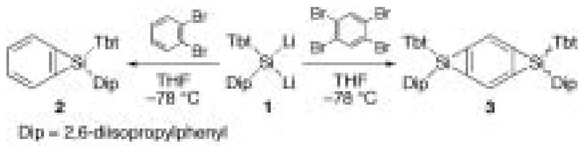
VII-G-6 Syntheses and Structures of Silicon Analogues of Cyclopropabenzenes

TAJIMA, Tomoyuki[1]**; HATANO, Ken**[2]**; SASAKI, Takayo**[1]**; SASAMORI, Takahiro**[1]**; TAKEDA, Nobuhiro**[1]**; TOKITOH, Norihiro**[3]**; TAKAGI, Nozomi; NAGASE, Shigeru**
([1]Kyoto Univ.; [2]Kyushu Univ.; [3]IMS and Kyoto Univ.)

[*Chem. Lett.* **32**, 220–221 (2003); *J. Organomet. Chem.* **686**, 118–126 (2003)]

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. However, there is no example for the synthesis of its heteroatom analogs, heteracyclopropabenzenes, as stable compounds until our project started. In this paper, we present the synthesis of the first stable silacyclopropazenzene and bis(silacyclopropa)benzenes, which are the first stable heteracyclopropabenzenes, by taking advantage of 2,4,6-tris[bis(trimethylsilyl)-methyl]phenyl (Tbt) group.

The reactions of an very crowded diaryldilithiosilane **1** with *o*-dibromobenzene and 1,2,4,5-tetrabromobenzene resulted in the formation of the first stable silacyclopropabenzene **2** and bis(silacyclopropa)benzenes **3**, respectively. The crystallographic analyses and theoretical calculations revealed that the deformation in benzene rings of **2** ans **3** is less than that of cyclopropabenzenes, which show severe deformation of the benzene rings caused by the fused cyclopropane rings. The successful isolation of **2** is noteworthy because no carbon analogues, bis(cyclopropa)benzenes, have been synthesized yet.



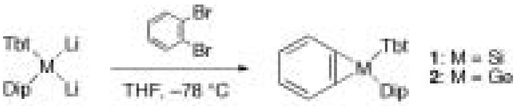
VII-G-7 Synthesis and Isolation of the First Germacyclopropabenzene: A Study to Elucidate the Intrinsic Factor for the Ring Deformation of Cyclopropabenzene Skeletons

TOKITOH, Norihiro[1]**; HATANO, Ken**[2]**; SASAKI, Takayo**[3]**; SASAMORI, Takahiro**[3]**; TAKEDA, Nobuhiro**[3]**; TAKAGI, Nozomi; NAGASE, Shigeru**
([1]IMS and Kyoto Uniiv.; [2]Kyushu Univ.; [3]Kyoto Univ.)

[*Organometallics* **21**, 4309–4311 (2002)]

Cyclopropabenzenes have attracted much attention because it is expected that the fused cyclopropane rings result in the severe deformation of the benzene rings. Recently, we have synthesized silacyclopropabenzene **1** as the first example of a stable heteracyclopropabenzene by the reaction of a sterically hindered dilithiosilane, Tbt(Dip)$SiLi_2$ (Tbt = 2,4,6-tris[bis(trimethylsilyl)-methyl]phenyl, Dip = 2,6-diisopropylphenyl), with 1,2-dibromobenzene. This successful synthesis 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 formation 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.



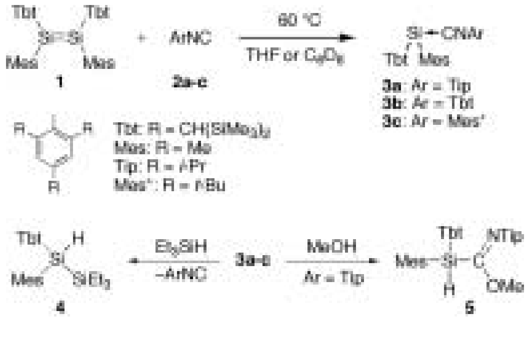
VII-G-8 Synthesis and Properties of the First Stable Silylene-Isocyanide Complexes

TAKEDA, Nobuhiro[1]**; KAJIWARA, Takashi**[1]**; SUZUKI, Hiroyuki**[2]**; OKAZAKI, Renji**[2]**; TOKITOH, Norihiro**[3]
([1]Kyoto Univ.; [2]Univ. Tokyo; [3]IMS and Kyoto Univ.)

[*Chem. Eur. J.* **9**, 3530–3543 (2003)]

Recently, various types of compounds containing a stable double bond to silicon have been synthesized by taking advantage of steric protection due to bulky substituents. On the other hand, the chemistry of compounds containing silicon as part of a cumulated double-bond system has been less explored. As for heavier analogues of ketenimines (>C=C=N–), it has been reported that a stannaketenimine (>SnCN–) is rather stannylene-isocyanide complex (>Sn←CN–) than cumulative compound (>Sn=C=N–), while 1-phospha-3-silaallene (>SiCP–) and 1-phospha-3-germaallene (>GeCP–) represent allenic character (>M=C=P–). However, there is no report for stable silicon analogues (>SiCN–) and their properties have not been revealed, although their properties have attracted much interest.

We successfully synthesized Tbt(Mes)SiCNAr (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Mes = mesityl) (**3a-c**), by the reactions of a kinetically stabilized disilene **1**, with bulky isocyanides **2a-c**. The spectroscopic data of **3a-c** and theoretical calculations indicated that the **3a-c** are not classical cumulative compounds but the first stable silylene-Lewis base complexes. The reaction with triethylsilane giving silylene adduct **4** indicated the dissociation of the complexes **3a-c** to the corresponding silylene [Tbt(Mes)Si:] and isocyanides **2a-c** at room temperature. In additrion, **3a** reacted with methanol to give methanol adduct **5** *via* electrophilic attack on the silicon atom, which is most likely resulted from the contribution of the zwitterionic resonance structures [Tbt(Mes)Si$^-$–C$^+$=N–Ar] and [Tbt(Mes)Si$^-$–C≡N$^+$–Ar].



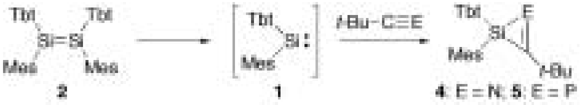
VII-G-9 Stable 2*H*-Azasilirene and 2*H*-Phosphasilirene: Addition Reaction of an Overcrowded Silylene to a Nitrile and a Phosphaalkyne

TOKITOH, Norihiro[1]; SUZUKI, Hiroyuki[2]; TAKEDA, Nobuhiro[3]; KAJIWARA, Takashi[3]; SASAMORI, Takahiro[3]; OKAZAKI, Renji[2];
([1]IMS and Kyoto Univ.; [2]Univ. Tokyo; [3]Kyoto Univ.)

[*Silicon Chem.* in press]

In recent decades, there has been much interest in the chemistry of divalent silicon species, silylenes, from the viewpoint of not only fundamental chemistry but also applied chemistry such as material science and organic syntheses. Much attention has been paid to their reactivities such as addition to olefins, alkynes, isocyanides, and so on in comparison with the reactivities of carbenes. On the other hand, we have succeeded in the formation of very crowded silylene **1** bearing a 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) group by thermolysis of the corresponding disilene **2** at 60 °C or that of silylene–isocyanide complex **3** at room temperature.

In this paper, we present the reaction of an overcrowded silylene **1** with pivalonitrile and *t*-butylphosphaalkyne to give the corresponding [1+2]cycloadducts, 2*H*-azasilirene and 2*H*-phosphasilirene derivatives, **4** and **5**, respectively. This is the first example of the isolation of a stable 2*H*-azasilirene derivative, and the X-ray crystallographic analysis of **4** unambiguously revealed its three-membered ring structure in the solid state. In addition, DFT calculations supported three-membered ring character in the structures of the 2*H*-azasilirene **4** and 2*H*-phosphasilirene **5**.



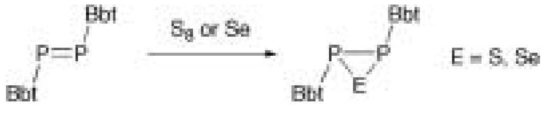
VII-G-10 Synthesis and Reactions of New Diphosphenes Bearing Extremely Bulky Substituents

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

[*J. Phys. Org. Chem.* **16**, 450–462 (2003)]

Multiple-bond compounds between heavier group 15 elements have fascinated chemists for a long time. Since the first isolation of the diphosphene Mes*P=PMes* (Mes* = 2,4,6-tri-*t*-butylphenyl), intensive studies have been performed using several steric protection groups on the chemistry of a variety of diphosphenes.

In this paper, we present the synthesis of new diphosphenes, Tbt–P=P–Tbt (**1**) and Bbt–P=P–Bbt (**2**), having extremely bulky substituents, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) and 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl groups (Bbt), which are effective to the stabilization of distibenes (Ar–Sb=Sb–Ar) and dibismuthenes (Ar–Bi=Bi–Ar). The X-ray crystallographic analysis revealed their unique structures in the solid state. Furthermore, the conformations of these extremely overcrowded diphosphenes, **1** and **2**, are twisted in different ways in spite of the close structural similarity between Tbt and Bbt groups. DFT calculations were performed to estimate the energy difference between the two conformations of diphosphenes. In addition, their structures and physical properties were compared with those of their heavier congeners, distibenes (Ar–Sb=Sb–Ar, Ar = Tbt and Bbt) and dibismuthenes (Ar–Bi=Bi–Ar, Ar = Tbt and Bbt) having the same substituents. Although the reactivities of the extremely hindered diphosphenes might be considerably suppressed owing to the severe steric congestion, it was found that they can react with elemental sulfur and selenium to give the corresponding thia- and selenadiphosphirane derivatives, respectively.



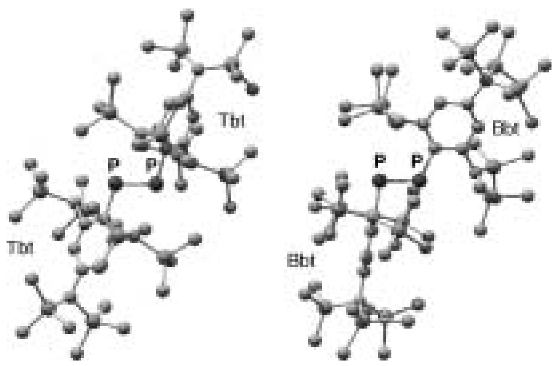


Figure 1. Molecular Structures of **1** (left) and **2** (right).

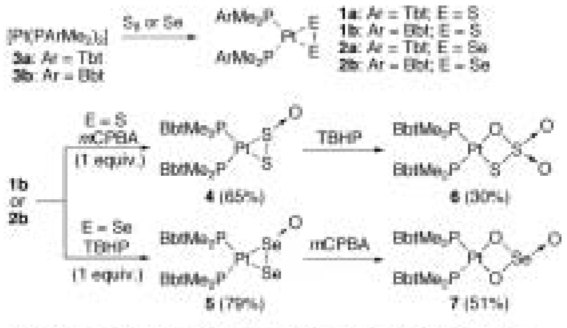
VII-G-11 Synthesis, Structure, and Properties of the First Disulfur and Diselenium Complexes of Platinum

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

[*Chem. Lett.* **32**, 170–171 (2003), *Bull. Chem. Soc. Jpn.* **76**, 1577–1587 (2003)]

Much attention has been focused on the chemistry of transition metal complexes having O_2, S_2, and Se_2 ligands from the viewpoints of not only fundamental chemistry but also catalysis and biochemistry. However, the disulfur and diselenium complexes of platinum remain unknown probably due to the strong propensity of sulfur and selenium ligands for bridging metal atoms.

We succeeded in the synthesis of the first disulfur and diselenium complexes of platinum, **1** and **2**, by taking advantage of bulky phosphine ligands bearing a 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) or 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)-methyl]phenyl (Bbt) group, which sterically protect the mononuclear complexes from the oligomerization. Complexes **1** and **2** were synthesized by the reaction of zerovalent platinum complexes **3** with elemental sulfur and selenium, respectively. Crystallographic analysis of **1b** and **2b** showed that their central Pt atoms have tetracoordinated, planar geometries, and their PtE_2 (E = S, Se) parts have three-membered-ring structures. The oxidation of **1b** and **2b** with an equimolar amount of *m*-chloroperbenzoic acid or *t*-butyl hydroperoxide in dichloromethane afforded the corresponding disulfur and diselenium monoxide complexes, **4** and **5**, respectively. An interesting difference in reactivity between **4** and **5** was shown in the further reactions with an excess of oxidants, which produced the corresponding *O,S*-coordinated thiosulfate complex **6** and the *O,O*-coordinated selenite complex **7**, respectively. The dynamic behavior in solution was revealed by the variable-temperature NMR spectroscopy for **1b**, **2b**, **6**, and **7**, which indicates the existence of the intramolecular CH···E (E = O, S, Se) interactions between the methine hydrogens of the *o*-bis(trimethylsilyl)-methyl groups and the Pt-bonded heteroatoms.



mCPBA = m-chloroperbenzoic acid; TBHP = tert-butyl hydroperoxide

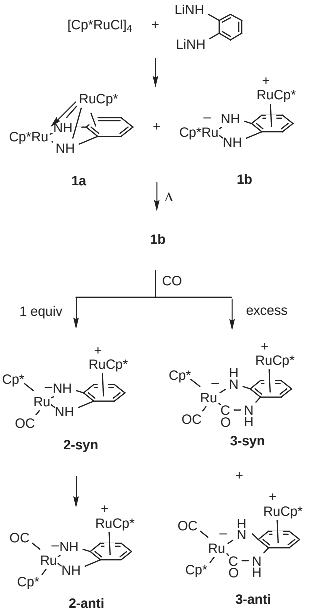
VII-H Preparation and Properties of the Homo- and Heterometallic Clusters

This project focuses on the development of a systematic synthetic route to a series of the homo- and heterometallic clusters as templates or catalysts for new types of activation and transformation of organic, inorganic, and organometallic molecules at the well-defined multimetallic reaction sites.

VII-H-1 Synthesis and Reactivities of Amido-Bridged Dinuclear Ruthenium Complexes

TAKEMOTO, Shin[1]; OSHIO, Shinya[1]; OGURA, Shin-ichiro[1]; MATSUZAKA, Hiroyuki[2]
([1]Osaka Prefecture Univ.; [2]IMS and Osaka Prefecture Univ.)

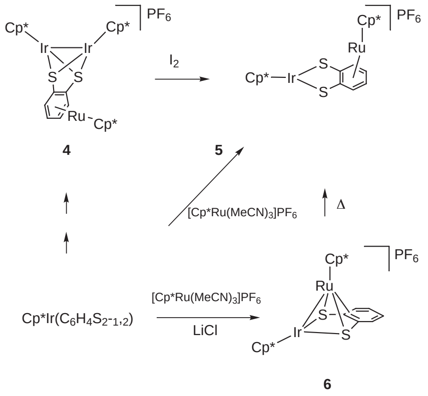
Novel dinuclear ruthenium 1,2-phenylenediamido complexes (**1a**) and (**1b**) were prepared and their reactivities have been examined in detail. Complex **1a** is cleanly converted to **1b** in refluxing acetonitrile. Treatment of 1b with 1 equiv of CO yields the carbonyl adduct (**2**), which further reacts with excess CO to form the amido/carbamoyl/carbonyl complex (**3**).



VII-H-2 Preparation, Structure, and Reactivity of the Benzenedithiolato-Bridged Ir/Ru Mixed-Metal Clusters

TAKEMOTO, Shin[1]; SHIMADZU, Daisuke[1]; OGURA, Shin-ichiro[1]; MATSUZAKA, Hiroyuki[2]
([1]Osaka Prefecture Univ.; [2]IMS and Osaka Prefecture Univ.)

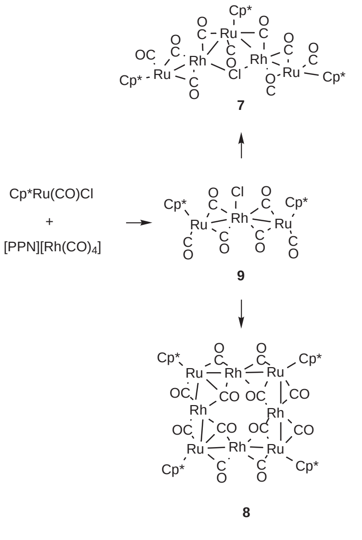
A series of the iridium/ruthenium mixed-metal clusters containing a bridging benzenedithiolato ligand were selectively synthesized in good yields and their chemical reactivities have been examined in detail. Oxidation of the Ir(II) centers in the novel Ir_2R mixed-metal cluster **4** with I_2 readily proceeded to give the IrRu cluster **5** together with $[Cp^*IrI(\mu_2\text{-}I)]_2$. Direct treatment of $Cp^*Ir(\text{-}C_6H_4S_2\text{-}1,2)$ with $[Cp^*Ru(MeCN)_3]PF_6$ alternatively afforded **5**, whereas similar reaction in the presence of LiCl selectively produced **6**, the isomeric form of **5**, which was quantitatively converted to **5** in refluxing acetonitrile.



VII-H-3 Selective Transformation of the Oligomeric Ru_2Rh Cluster to the Ru_3Rh_2 and the Ru_4Rh_4 Framework

TAKEMOTO, Shin[1]; HAYASHI, Hirokazu[1]; KASHIWAKURA, Miki[1]; MATSUZAKA, Hiroyuki[2]
([1]Osaka Prefecture Univ.; [2]IMS and Osaka Prefecture Univ.)

Selective heteronuclear metal-metal bond formation reaction readily proceeded to give the Ru_3Rh and Ru_4Rh_4 mixed-metal clusters (**7** and **8**) from mononuclear precursors *via* oligomeric Ru_2Rh complex (**9**).



VII-I Precise Synthesis of Functional Macromolecules Using Organometallic Complexes

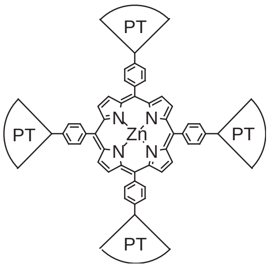
Macromolecules, in which not only molecular weight and chemical sequence but also secondary structures are well controlled, attract much attention due to their novel properties and functionalities. Precise synthesis of such macromolecules is one of the goals for the development of new functional materials. This project focuses on precise synthesis of helical or dendritic macromolecules using organometallic complexes, which act as living polymerization catalysts or building blocks. We also examined the physical and chemical properties of the resulting polymers.

VII-I-1 Platinum-Acetylide Dendrimers Possessing a Porphyrin Core

ONITSUKA, Kiyotaka[1]; KITAJIMA, Hotaka[2]; FUJIMOTO, Masanori[2]; IUCHI, Asako[2]; TAKEI, Fumie[2]; TAKAHASHI, Shigetoshi[2]
([1]IMS and Osaka Univ.; [2]Osaka Univ.)

[*Chem. Commun.* 2576 (2002)]

Intramolecular energy transfer from platinum-acetylide moieties to the porphyrin core was observed in novel organometallic dendrimers that were prepared from a tetra(4-ethynylphenyl)porphyrin-bridged tetranuclear platinum-acetylide core and platinum-acetylide dendrons by a convergent method.

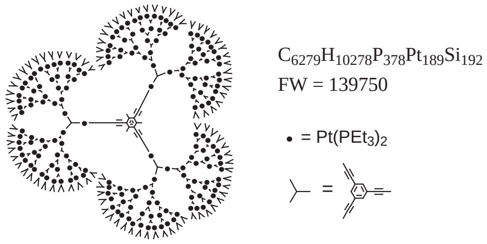


VII-I-2 A Divergent Approach to the Precise Synthesis of Giant Organometallic Dendrimers Using Platinum-Acetylides as Building Blocks

ONITSUKA, Kiyotaka[1]; SHIMIZU, Atsushi[2]; TAKAHASHI, Shigetoshi[2]
([1]IMS and Osaka Univ.; [2]Osaka Univ.)

[*Chem. Commun.* 280 (2003)]

Giant platinum-acetylides dendrimers were precisely synthesized by a divergent method; the sixth generation dendrimer, the diameter of which is larger than 10 nm, has 189 Pt atoms per molecule, and its molecular weight is as high as 139,750.



VII-I-3 Preparation and Photochemical Properties of Polyisocyanides with Regularly Arranged Porphyrin Pendants

TAKEI, Fumie[2]; NAKAMURA, Sugiko[2]; ONITSUKA, Kiyotaka[1]; ISHIDA, Akito[2]; TOJO, Sachiko[2]; MAJIMA, Tetsuro[2]; TAKAHASHI, Shigetoshi[2]
([1]IMS and Osaka Univ.; [2]Osaka Univ.)

[*Chem. Lett.* 506 (2003)]

A novel triblock polyisocyanide having free-base- and zincporphyrins as pendants was prepared by living polymerization with a Pt-Pd μ-ethynediyl complex as an initiator, and irradiated at 420 or 556 nm in a THF solution to cause intramolecular energy transfer from the zinc-porphyrin to the free-base-porphyrin.

VII-J Development of New Catalytic Reactions for Synthesis of N-Heterocyclic Compounds

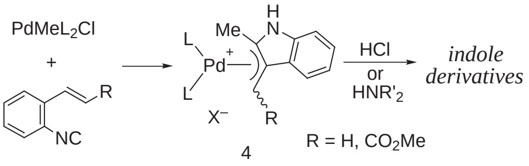
Heterocyclic compounds are found in a wide variety of biologically active natural products, and considerable attention has been directed toward the development of new synthetic methods for useful heterocycles. Our research effort has been directed toward the discovery of new catalytic reactions for the synthesis of *N*-heterocyclic frameworks using *ortho*-functionalized aryl isocyanides.

VII-J-1 Structure and Reactivity of (η^3-Indolylmethyl)palladium Complexes Generated by the Reaction of Organopalladium Complexes with *o*-Alkenylphenyl Isocyanide

ONITSUKA, Kiyotaka[1]; YAMAMOTO, Mari[2]; SUZUKI, Shinobu[2]; TAKAHASHI, Shigetoshi[2]
([1]IMS and Osaka Univ.; [2]Osaka Univ.)

[*Organometallics* **21**, 581 (2002)]

The reaction of methylpalladium complexes with *o*-alkenylphenyl isocyanides results in the successive intramolecular insertion of the alkenyl and isocyano groups followed by the 1,3-migration of hydrogen to give (η^3-indolylmethyl)palladium complexes (**4**) in good yields. Treatment of **4** with diethylamine causes nucleophilic attack at the exo methylene carbon to give 2-methyl-3-aminomethylindole, whereas the reactions with HCl produce 2,3-dimethylindole derivatives.

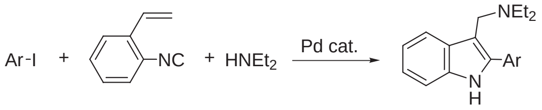


VII-J-2 A Novel Route to 2,3-Disubstituted Indoles *via* Palladium-Catalyzed Three-Component Coupling of Aryl Iodide, *o*-Alkenylphenyl Isocyanide and Amine

ONITSUKA, Kiyotaka[1]; SUZUKI, Shinobu[2]; TAKAHASHI, Shigetoshi[2]
([1]IMS and Osaka Univ.; [2]Osaka Univ.)

[*Tetrahedron Lett.* **43**, 6197 (2002)]

Three-component coupling reactions of aryl iodide, *o*-alkenylphenyl isocyanide and amine in the presence of palladium catalysts produced 2,3-substituted indoles in moderate yields.



VII-K Synthesis of Transition Metal Complexes Containing a Novel Metal-Silicon and Metal-Gallium Bonding

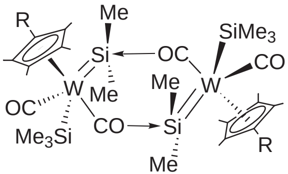
Synthesis of transition metal complexes with unprecedented bonds between a metal and a heavy main group element is one of current topics on inorganic chemistry. In this project, we have investigated the synthesis, structure, and reactivities of metal complexes containing a metal-silicon unsaturated bonding and a metal-hydrogen-gallium 3c2e bonding. We also developed a versatile preparative method of anionic metal complexes $CpM(CO)_2^-$ (M = Fe, Ru).

VII-K-1 Synthesis of Self-Stabilized and Donor-Free Silyl(silylene)tungsten Complexes

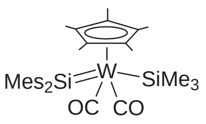
UENO, Keiji[1]; WATANABE, Nobuhiko[2]; ASAMI, Satsuki[2]; SAKAI, Mihoko[2]; OGINO, Hiroshi[3]
([1]IMS and Gunma Univ.; [2]Tohoku Univ.; [3]Univ. Air)

[*Organometallics* **21**, 1326–1328 (2002)]

Photolysis of Cp’W$(CO)_3$Me (**1a**: Cp’ = η-C_5Me_5; **1b**: Cp’ = η-C_5Me_4Et) in the presence of excess $HSiMe_2SiMe_3$ afforded a self-stabilized silyl(silylene)tungsten complex with a dimeric structure, [Cp’W$(CO)_2(=SiMe_2)(SiMe_3)]_2$ (**2a**: Cp’ = η-C_5Me_5; **2b**: Cp’ = η-C_5Me_4Et), respectively. In contrast, photolysis of **1a** in the presence of $HSiMe_2SiMeMes_2$ (Mes = 2,4,6-$Me_3C_6H_2$) resulted in the formation of the first donor-free silyl(silylene) complex with only alkyl and aryl substituents on the silicon atoms Cp’W$(CO)_2(=SiMes_2)(SiMe_3)$ (**3**).



2a: R = Me
2b: R = Et



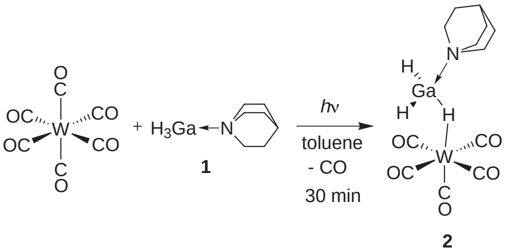
3

VII-K-2 Synthesis of the First Gallane-Coordinated Transition Metal Complex

UENO, Keiji[1]; YAMAGUCHI, Takeshi[2]; UCHIYAMA, Kei[2]; OGINO, Hiroshi[3]
([1]IMS and Gunma Univ.; [2]Tohoku Univ.; [3]Univ. Air)

[*Organometallics* **21**, 2347–2349 (2002)]

The first gallane-coordinated metal complex $(OC)_5W(\eta^1\text{-}GaH_3\cdot\text{quinuclidine})$ (**2**) was synthesized by photolysis of a *ca.* 1:1 mixture of $W(CO)_6$ and quinuclidine-coordinated gallane $H_3Ga\cdot$quinuclidine (**1**) in toluene and by the reaction of $(OC)_5W(THF)$ with 1 eq of gallane **1** in THF. X-ray crystal structure analysis of **2** revealed that gallane **1** is bound to the tungsten fragment *via* a W–H–Ga 3-center 2-electron bond.



VII-K-3 Convenient Preparation of Li[(η^5-C_5Me_5)M$(CO)_2$] (M = Ru, Fe) by the Reaction of (η^5-C_5Me_5)M$(CO)_2$H with *n*-BuLi

OKAZAKI, Masaaki[1]; SATOH, Kazuyuki[1]; AKAGI, Tadahiro[1]; IWATA, Masatoshi[1]; JUNG, Kyeong A.[1]; SHIOZAWA, Rie[1]; UENO, Keiji[2]; TOBITA, Hiromi[1]; OGINO, Hiroshi[3]
([1]Tohoku Univ.; [2]IMS and Gunma Univ.; [3]Univ. Air)

[*J. Organomet. Chem.* **645**, 201–205 (2002)]

The anionic ruthenium and iron complexes Li[(η^5-C_5Me_5)M$(CO)_2$] (M = Ru (**1-Ru**), Fe (**1-Fe**)) were generated by deprotonation of the transition metal hydride (η^5-C_5Me_5)M$(CO)_2$H with *n*-BuLi in tetrahydrofuran (THF). The reaction proceeded at –45 °C immediately. Reactions of **1** with various electrophiles (Me_3SiCl, $p\text{Tol}_2HSiCl$, Me_2SiCl_2, $MeSiCl_3$, $SiCl_4$, $Me_3SiSiMe_2Cl$, and Ph_2GeCl_2) afforded the corresponding nucleophilic substitution products (η^5-C_5Me_5)M$(CO)_2ER_3$ (E = Si, Ge) *via* salt-elimination.