

## Contents

### Special Issue: Reaction Control in Dynamic Complexes

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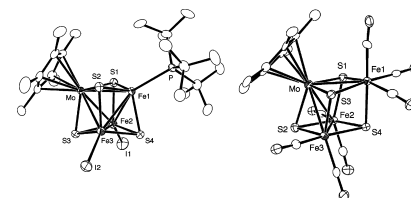
### Regular papers

**Takashi Komuro, Hiroyuki Kawaguchi,  
Jianping Lang, Takayuki Nagasawa,  
Kazuyuki Tatsumi**

*J. Organomet. Chem. 692 (2007) 1*

[MoFe<sub>3</sub>S<sub>4</sub>]<sup>3+</sup> and [MoFe<sub>3</sub>S<sub>4</sub>]<sup>2+</sup> cubane clusters containing a pentamethylcyclopentadienyl molybdenum moiety

A series of [MoFe<sub>3</sub>S<sub>4</sub>]<sup>n+</sup> (*n* = 2 and 3) clusters were synthesized, which consists of a common Cp<sup>\*</sup> (=η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>) fragment. The self-assembly reactions of Cp<sup>\*</sup>Mo(S<sup>t</sup>Bu)<sub>3</sub> (**1**) with FeCl<sub>3</sub> in the presence of Li<sup>t</sup>Bu (or LiSPh) and elemental sulfur (S<sub>8</sub>), followed by cation exchange with PPh<sub>4</sub>Br, generated (PPh<sub>4</sub>)[Cp<sup>\*</sup>MoFe<sub>3</sub>S<sub>4</sub>(S<sup>t</sup>Bu)<sub>3</sub>] (**2**) and (PPh<sub>4</sub>)[Cp<sup>\*</sup>MoFe<sub>3</sub>S<sub>4</sub>(SPh)<sub>3</sub>] (**3**). The *tert*-butyl thiolate ligands of **2** were readily replaced by benzenethiolate, chloride, and iodide to give (PPh<sub>4</sub>)[Cp<sup>\*</sup>MoFe<sub>3</sub>S<sub>4</sub>X<sub>3</sub>] (X = SPh (**3**), Cl (**4**), I (**5**)), while the reactions of **5** with P<sup>t</sup>Bu<sub>3</sub> and ArNC/cobaltocene gave rise to Cp<sup>\*</sup>MoFe<sub>3</sub>S<sub>4</sub>I<sub>2</sub>(P<sup>t</sup>Bu<sub>3</sub>) (**6**) and [Cp<sup>\*</sup>MoFe<sub>3</sub>S<sub>4</sub>(ArNC)<sub>7</sub>]I (**7**, ArNC = 2,6-diisopropylphenylisocyanide), respectively.

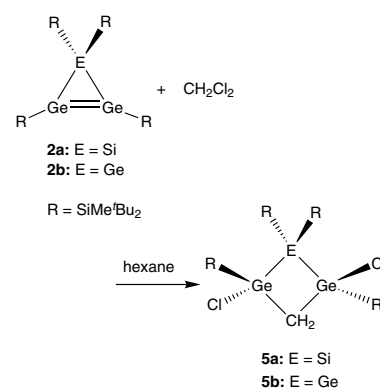


**Vladimir Ya. Lee, Hiroyuki Yasuda,  
Masaaki Ichinohe, Akira Sekiguchi**

*J. Organomet. Chem. 692 (2007) 10*

Heavy cyclopropene analogues R<sub>4</sub>SiGe<sub>2</sub> and R<sub>4</sub>Ge<sub>3</sub> (R = SiMe<sup>t</sup>Bu<sub>2</sub>) – New members of the cyclic digermenes family

1*H*-Siladigermirene R<sub>4</sub>SiGe<sub>2</sub> (**2a**) and 1*H*-trigermirene R<sub>4</sub>Ge<sub>3</sub> (**2b**) (R = SiMe<sup>t</sup>Bu<sub>2</sub>) with a Ge=Ge double bond were synthesized by the reaction of tetrachlorodigermene RGeCl<sub>2</sub>–GeCl<sub>2</sub>R with dithiosilane R<sub>2</sub>SiLi<sub>2</sub> and dilithiogermene R<sub>2</sub>GeLi<sub>2</sub>, respectively. The reactions of **2a** and **2b** with CH<sub>2</sub>Cl<sub>2</sub> resulted in the formation of unusual four-membered ring compounds **5a** and **5b** as a result of the ring expansion reaction. 1*H*-trisilirene and 3*H*-disilagermirene with an Si=Si double bond also smoothly reacted with CH<sub>2</sub>Cl<sub>2</sub> to yield the similar four-membered ring compounds.

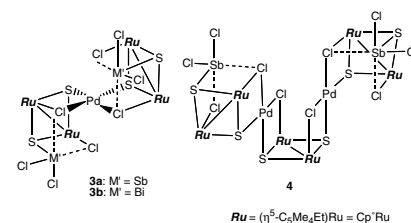


**Kazumasa Oya, Takahiko Amitsuka,  
Hidetake Seino, Yasushi Mizobe**

*J. Organomet. Chem. 692 (2007) 20*

Synthesis and X-ray structures of heptanuclear and decanuclear mixed-metal sulfido clusters containing noble metals and Group 15 metals

Reactions of incomplete cubane-type clusters [(Cp<sup>o</sup>RuCl)<sub>2</sub>(μ-SH)(μ-SM'Cl<sub>2</sub>)] (M' = Sb, Bi; Cp<sup>o</sup> = η<sup>5</sup>-C<sub>5</sub>Me<sub>4</sub>Et) with [PdCl<sub>2</sub>(cod)] (cod = 1,5-cyclooctadiene) afforded the corner-shared double cubane-type clusters [{(Cp<sup>o</sup>Ru)(Cp<sup>o</sup>RuCl)(μ-SM'Cl<sub>2</sub>)<sub>2</sub>(μ<sub>3</sub>-S)<sub>2</sub>(μ-Cl)<sub>2</sub>Pd}] (**3a**: M' = Sb, **3b**: M' = Bi) and the corner-shared triple cubane-type cluster [{(Cp<sup>o</sup>Ru)(Cp<sup>o</sup>RuCl)(μ-SSbCl<sub>2</sub>)(μ<sub>3</sub>-S)<sub>2</sub>(μ-Cl)<sub>2</sub>-Pd]<sub>2</sub>(Cp<sup>o</sup>Ru)<sub>2</sub>] (**4**).

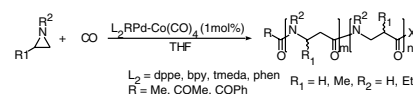


**Shin-ichi Tanaka, Hideko Hoh,  
Yoshifumi Akahane, Susumu Tsutsuminai,  
Nobuyuki Komine, Masafumi Hirano,  
Sanshiro Komiya**

*J. Organomet. Chem.* 692 (2007) 26

Synthesis and reactions of heterodinuclear organopalladium–cobalt complexes acting as copolymerization catalyst for aziridine and carbon monoxide

A series of heterodinuclear acylpalladium–cobalt complexes having a bidentate nitrogen ligand,  $L_2(RCO)Pd-Co(CO)_4$  ( $L_2 = bpy$ ,  $R = Me, Ph$ ;  $L_2 = tmeda$ ,  $R = Me, Ph$ ;  $L_2 = phen$ ,  $R = Me, Ph$ ) are prepared by metathetical reactions of  $PdRIL_2$  with  $Na^+[Co(CO)_4]^-$  followed by treatment with CO. Heterodinuclear organopalladium–cobalt complexes are shown to catalyze copolymerization of aziridines and CO under mild conditions.

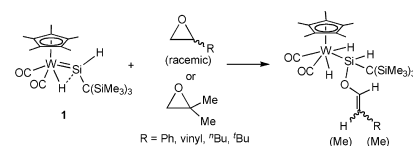


**Hisako Hashimoto, Mitsuyoshi Ochiai,  
Hiromi Tobita**

*J. Organomet. Chem.* 692 (2007) 36

Reactions of a hydrido(hydrosilylene)tungsten complex with oxiranes

Reactions of  $Cp^*(CO)_2(H)W=Si(H)[C(SiMe_3)_3]$  (**1**) with mono-substituted racemic oxiranes with a substituent R and also 2,2-dimethyloxirane produced dihydrido(vinylloxysilyl)tungsten complexes, (*E*)- and/or (*Z*)- $Cp^*(CO)_2(H)_2W\{Si(H)(OCH=CHR)[C(SiMe_3)_3]\}$  ( $R = Ph$ , vinyl, <sup>t</sup>Bu, or <sup>n</sup>Bu) and  $Cp^*(CO)_2(H)_2W\{Si(H)(OCH=CM_2)[C(SiMe_3)_3]\}$ , in high yields via regioselective ring-opening of oxiranes.

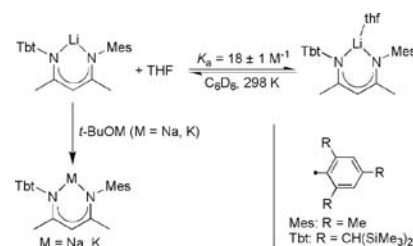


**Hirofumi Hamaki, Nobuhiro Takeda,  
Takayuki Yamasaki, Takahiro Sasamori,  
Norihito Tokitoh**

*J. Organomet. Chem.* 692 (2007) 44

Synthesis and properties of alkaline metal complexes with new overcrowded  $\beta$ -diketiminato ligands

The monomeric, solvent-free lithium  $\beta$ -diketiminato bearing a Tbt group was synthesized, and the equilibrium between the free and THF-coordinated lithium  $\beta$ -diketiminates was examined by the  $^7Li$  NMR spectra. The transformation of lithium  $\beta$ -diketiminato into the sodium and potassium analogues is also achieved.

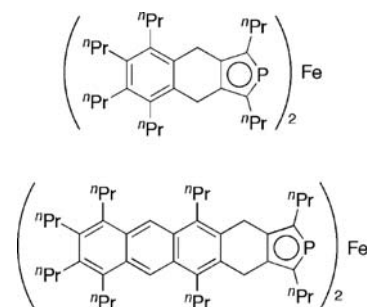


**Masamichi Ogasawara, Takeshi Sakamoto,  
Kiyohiko Nakajima, Tamotsu Takahashi**

*J. Organomet. Chem.* 692 (2007) 55

Preparation and characterization of 1,1'-diphosphaferrocenes with linearly fused six-membered carbocycles

Zirconacyclopentadiene-mediated homologation method was applied to preparation of a couple of 1,1'-diphosphaferrocene derivatives with linearly fused six-membered carbocycles. The solid-state structure of bis(hexapropyl-dihydro-*iso*-naphthophospholy)iron(II) complex was studied by X-ray single-crystal structure determination.

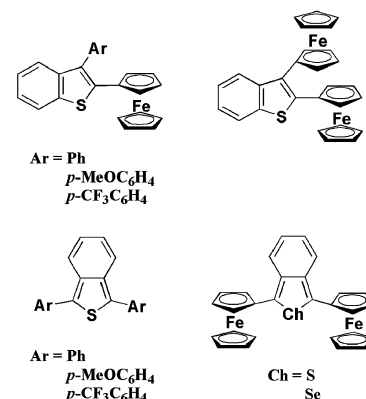


Satoshi Ogawa, Hiroki Muraoka, Kenji Kikuta, Fumihito Saito, Ryu Sato

*J. Organomet. Chem.* 692 (2007) 60

Design of reversible multi-electron redox systems using benzochalcogenophenes containing aryl and/or ferrocenyl fragments

The synthesis, structural characterization, and redox properties of benzochalcogenophenes having aryl and/or ferrocene units were described. The electrochemical properties showed reversible multi-electron transfer assigned to the chalcogenophene (organic) and ferrocene (organometallic) fragments. As a result, a new type of multi-steps reversible redox systems using neutral organic–organometallic hybrid molecules was established.

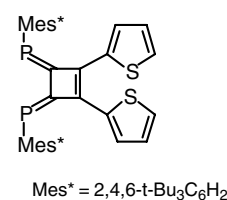


Akitake Nakamura, Subaru Kawasaki, Koza Toyota, Masaaki Yoshifuji

*J. Organomet. Chem.* 692 (2007) 70

Reactions of 1,2-di(2-thienyl)-3,4-bis[(2,4,6-tri-*t*-butylphenyl)phosphinidene]cyclobutene

A sterically protected 1,2-di(2-thienyl)-3,4-bis[(2,4,6-tri-*t*-butylphenyl)phosphinidene] cyclobutene reacted with elemental sulfur or transition metal reagents to form thiaphosphirane derivative or the corresponding transition metal complexes, respectively. Reactions of the diphosphinidene cyclobutene with butyllithium followed by treatment with electrophiles afforded functionalized diphosphinidene cyclobutene derivatives.



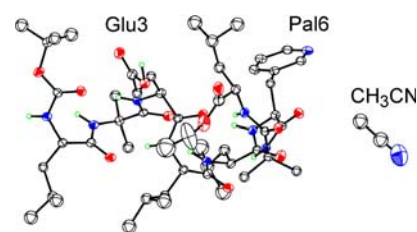
Sulfurization,  
Complex formation,  
Functional group introduction

Hiroyuki Oku, Yosuke Kimura, Mitsuo Ohama, Norikazu Ueyama, Keiichi Yamada, Ryoichi Katakai

*J. Organomet. Chem.* 692 (2007) 79

Synthesis, crystal structure, and coordination properties of a helical peptide having β-(3-pyridyl)-L-alanine and L-glutamic acid residues

A novel helical peptide, Boc-Leu-Aib-Glu-Leu-Leu-Pal-Aib-Leu-OEt (**1**) (Boc = tert-butoxycarbonyl, Aib = 2-aminoisobutylic acid, Pal = β-(3-pyridyl)-L-alanine) was synthesized and yielded fine crystals as an acetonitrile solvate. The metal ion binding properties of **1** were tested for CoCl<sub>2</sub> using UV/vis, CD, Raman, and <sup>1</sup>H NMR spectroscopies.

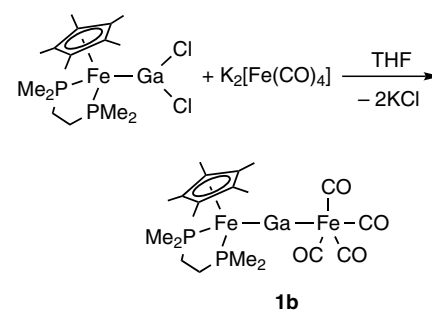


Keiji Ueno, Masakazu Hirotsu, Naoki Hatori

*J. Organomet. Chem.* 692 (2007) 88

Synthesis and structure of a dmpe-substituted dinuclear complex bridged by a substituent-free gallium atom: Electronic effect of metal fragment on the iron–gallium bonding

A dinuclear complex bridged by a substituent-free gallium atom, Cp<sup>\*</sup>(dmpe)Fe–Ga–Fe(CO)<sub>4</sub> (**1b**: Cp<sup>\*</sup> = η-C<sub>5</sub>Me<sub>5</sub>, dmpe = Me<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PMe<sub>2</sub>), was synthesized by the reaction of Cp<sup>\*</sup>Fe(dmpe)GaCl<sub>2</sub> with K<sub>2</sub>[Fe(CO)<sub>4</sub>]. Comparison of the structures of **1b** and Cp<sup>\*</sup>(dppe)Fe–Ga–Fe(CO)<sub>4</sub> (**1a**: dppe = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>) demonstrates that the Fe–Ga bonds are sensitive to the electronic character of the metal fragments.

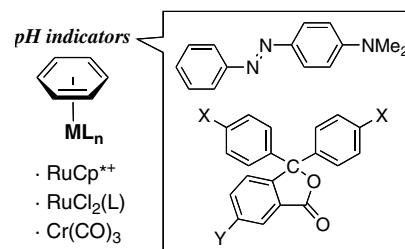


Miyuki Hirasa, Akiko Inagaki,  
Munetaka Akita

*J. Organomet. Chem.* 692 (2007) 93

Ruthenium and chromium complexes bearing pH-indicators as the  $\eta^6$ -arene ligand: Synthesis, characterization, and protonation behavior

A series of ruthenium and chromium complexes bearing pH indicators as the  $\eta^6$ -arene ligand,  $(\eta^6\text{-X})(\text{ML}_n)_y$  (X = methyl yellow, crystal violet lactone, phenolphthalein) is prepared, and their halochromic behavior depending on pH is studied.

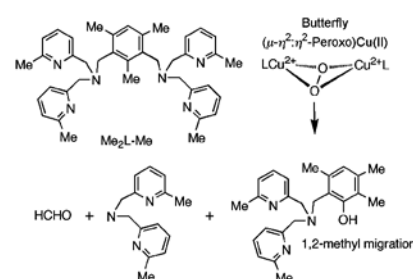


Takahiro Matsumoto, Hideki Furutachi,  
Shigenori Nagatomo, Takehiko Tosha,  
Shuhei Fujinami, Teizo Kitagawa,  
Masatatsu Suzuki

*J. Organomet. Chem.* 692 (2007) 111

Synthesis and reactivity of  $(\mu\text{-}\eta^2\text{:}\eta^2\text{-peroxo})\text{dicopper(II)}$  complexes with dinucleating ligands: Hydroxylation of xylyl linker with a NIH shift

A copper(I) complex  $[\text{Cu}_2(\text{Me}_2\text{-L-Me})]^{2+}$  reacted with  $\text{O}_2$  to produce a  $(\mu\text{-}\eta^2\text{:}\eta^2\text{-peroxo})\text{-Cu(II)}_2$  species having a butterfly structure, which is capable of performing hydroxylation of the 2-position of the xylyl linker with 1,2-methyl migration accompanied by the elimination of a bis(6-methyl-2-pyridylmethyl)-aminomethyl sidearm.

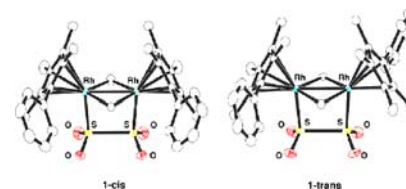


Yousuke Miyano, Hidetaka Nakai,  
Yoshihito Hayashi, Kiyoshi Isobe

*J. Organomet. Chem.* 692 (2007) 122

Synthesis and structural characterization of a photoresponsive organodirhodium complex with active S-S bonds:  $[(\text{Cp}^{\text{Ph}}\text{Rh})_2(\mu\text{-CH}_2)_2(\mu\text{-O}_2\text{SSO}_2)]$  ( $\text{Cp}^{\text{Ph}} = \eta^5\text{-C}_5\text{Me}_4\text{Ph}$ )

A photoresponsive rhodium dinuclear complex having phenyltetramethylcyclopentadienyl ( $\text{Cp}^{\text{Ph}} = \eta^5\text{-C}_5\text{Me}_4\text{Ph}$ ) and photo-sensitive dithionite ( $\mu\text{-O}_2\text{SSO}_2$ ) ligands,  $[(\text{Cp}^{\text{Ph}}\text{Rh})_2(\mu\text{-CH}_2)_2(\mu\text{-O}_2\text{SSO}_2)]$  (**1**), has been synthesized. The crystal of complex **1** consists of two independent molecules, **1-cis** and **1-trans**, with different arrangement of the  $\text{Cp}^{\text{Ph}}$  ligands.

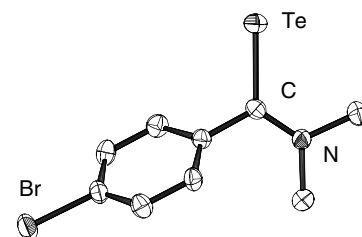
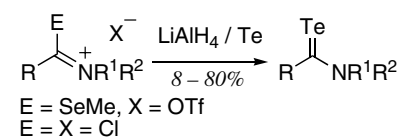


Yuichiro Mutoh, Toshiaki Murai,  
Shigeru Yamago

*J. Organomet. Chem.* 692 (2007) 129

Telluration of seleno- and chloroiminium salts leading to various telluroamides, and their structure and NMR properties

The reaction of seleno- and chloroiminium salts with a tellurating agent derived from  $\text{LiAlH}_4$  and elemental tellurium gave telluroamides. The molecular structure of an aromatic telluroamide was successfully revealed for the first time. The properties of the NMR spectra of a series of chalcogenoamides are also discussed.

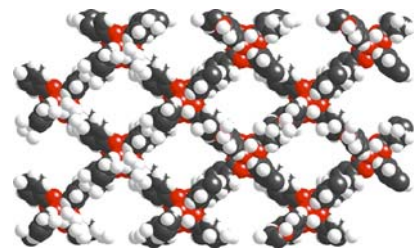


Mitsuru Kondo, Yasuhiko Irie,  
Makoto Miyazawa, Hiroyuki Kawaguchi,  
Sachie Yasue, Kenji Maeda, Fumio Uchida

*J. Organomet. Chem.* 692 (2007) 136

Synthesis and structural determination of new multidimensional coordination polymers with 4,4'-oxybis(benzoate) building ligands: Construction of coordination polymers with heteroorganic bridges

We report on the synthesis and crystal structures of two new zinc coordination polymers:  $[\text{Zn}_2(\text{oba})_2(\text{azpy})(\text{dmf})_2] \cdot 6\text{DMF}$  (azpy = 4,4'-azopyridine) (**3**) and  $[\text{Zn}_2(\text{oba})_2(\text{bpe})] \cdot 2\text{DMF} \cdot 4\text{H}_2\text{O}$  (bpe = *trans*-1,2-bis(4-pyridyl)-ethylene) (**4**). Compound **3** exhibits one-dimensional structure, and Compound **4** exhibits a three-dimensional structure that is interwoven by heteroorganic oba and bpe bridges. This structure, which is constructed by connected two-dimensional frameworks of  $[\text{Zn}_2(\text{oba})_2]$  with bpe bridges, has a high porosity with a density of only  $0.53 \text{ g cm}^{-3}$ .

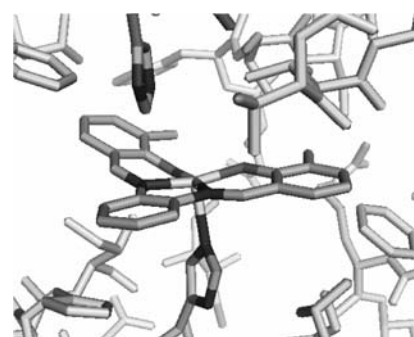


Takafumi Ueno, Tomomi Koshiyama,  
Satoshi Abe, Norihiko Yokoi,  
Masataka Ohashi, Hiroshi Nakajima,  
Yoshihito Watanabe

*J. Organomet. Chem.* 692 (2007) 142

Design of artificial metalloenzymes using non-covalent insertion of a metal complex into a protein scaffold

Artificial metalloenzymes were constructed by non-covalent insertion of a Schiff base complex into an apo-myoglobin cavity. The catalytic reactivity can be improved by molecular design of the composites based on their crystal structures.

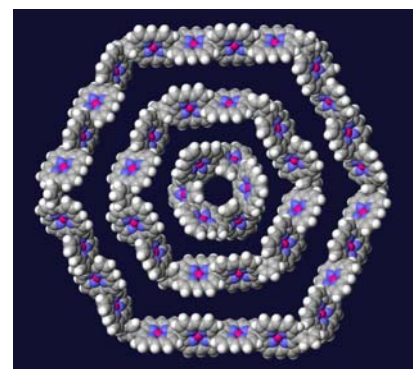


Takaaki Hori, Yasuyuki Nakamura,  
Naoki Aratani, Atsuhiko Osuka

*J. Organomet. Chem.* 692 (2007) 148

Exploration of electronically interactive cyclic porphyrin arrays

On the basis of Ag(I)-promoted coupling reaction, we have prepared cyclic porphyrin arrays including directly *meso-meso* linked porphyrin rings **CZ4-CZ8**, large porphyrin wheels **C12ZA** and **C24ZB**, and three-dimensional porphyrin boxes **D1-D3**.

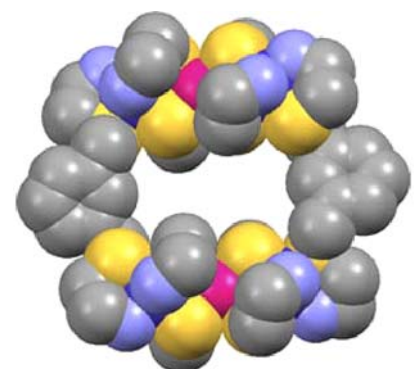


Yu Chikamoto, Nobuto Yoshinari,  
Tatsuya Kawamoto, Takumi Konno

*J. Organomet. Chem.* 692 (2007) 156

Rational synthesis of hexanuclear metallacycles by alkylation reactions of an S-bridged  $\text{Co}^{\text{III}}\text{Pd}^{\text{II}}\text{Co}^{\text{III}}$  trinuclear complex containing non-binding thiolato groups

An S-bridged  $\text{Co}^{\text{III}}\text{Pd}^{\text{II}}\text{Co}^{\text{III}}$  trinuclear complex,  $[\text{Pd}\{\text{Co}(\text{aet})_3\}_2]^{2+}$  (aet = 2-aminoethanethiolate), reacted with dibromoxylene ( $\text{xylBr}^{2+}$ ) in water, giving  $\text{Co}^{\text{III}}_4\text{Pd}^{\text{II}}_2$  hexanuclear metallacycles consisting of two  $\text{Co}^{\text{III}}\text{Pd}^{\text{II}}\text{Co}^{\text{III}}$  units and two  $\text{xyl}^{2+}$  moieties, the ring sizes and stereoisomers of which are controlled by the change of geometrical isomers of  $\text{xyl}^{2+}$  linkers (*ortho* vs. *meta*).



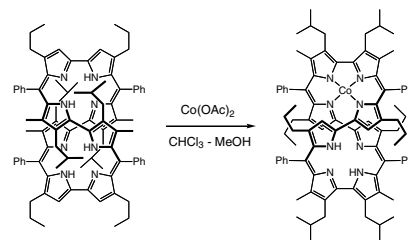


**Jun-ichiro Setsune, Megumi Mori,  
Toshifumi Okawa, Satoshi Maeda,  
Juha M. Lintuluoto**

*J. Organomet. Chem.* 692 (2007) 166

Synthesis and structures of cobalt(II) complexes of *meso*-tetraphenyltetrakis(1,0.1.0.1.0.1.0)s

*meso*-Tetraphenyltetrakis(1.0.1.0.1.0.1.0) with mixed 2,2'-bipyrrole units of different substitution pattern was metallated with Co(II). The X-ray crystallography and <sup>1</sup>H NMR spectroscopy indicated that metallation induced transposition of the 2,2'-bipyrrole units having 3,3'-di-*iso*-butyl substituents from the crossing point of the figure eight loop to the periphery.

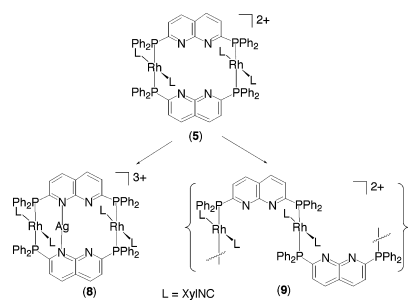


**Tomoaki Tanase, Hiroe Takenaka, Eri Goto**

*J. Organomet. Chem.* 692 (2007) 175

Dinuclear Rh(I) complex with 2,7-bis(diphenylphosphino)-1,8-naphthyridine: Synthesis, structure, and dynamic property

Dinuclear complex of [Rh<sub>2</sub>(μ-dpnpy)<sub>2</sub>(XylNC)<sub>4</sub>](PF<sub>6</sub>)<sub>2</sub> (**5**), possessing {M(μ-dpnpy)<sub>2</sub>M} metallomacrocyclic structure, was readily incorporated a silver(I) ion into the macrocycle to afford [Rh<sub>2</sub>Ag(μ-dpnpy)<sub>2</sub>(XylNC)<sub>2</sub>](PF<sub>6</sub>)<sub>3</sub> (**8**), and could also be transformed into the C<sub>6</sub> helical coordination polymer, {[Rh(μ-dpnpy)(XylNC)<sub>2</sub>](PF<sub>6</sub>)<sub>n</sub>} (**9**), where dpnpy is 2,7-bis(diphenylphosphino)-1,8-naphthyridine.

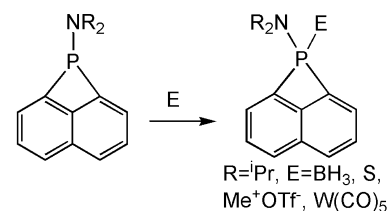


**Tsutomu Mizuta, Yukiko Iwakuni,  
Tooru Nakazono, Kazuyuki Kubo,  
Katsuhiko Miyoshi**

*J. Organomet. Chem.* 692 (2007) 184

Preparation and reaction of phosphorus peri-bridged naphthalenes and their adducts with Lewis acids

The reaction of dilithionaphthalene with R<sub>2</sub>NPCl<sub>2</sub> (R = *i*Pr and Et) gave dialkylaminonaphtho[1,8-*bc*]phosphete (phosphorus versions of single-atom peri-bridged naphthalene), the strained four-membered ring of which was retained upon formation of Lewis acid adducts with BH<sub>3</sub>, S, Me<sup>+</sup>, and W(CO)<sub>5</sub>.

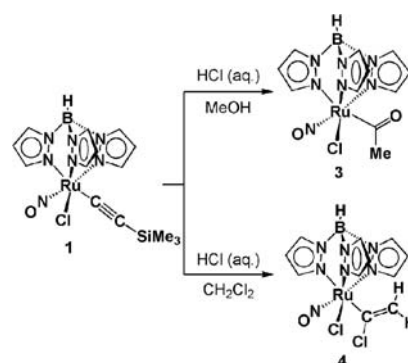


**Yasuhiro Arikawa, Taiki Asayama,  
Masayoshi Onishi**

*J. Organomet. Chem.* 692 (2007) 194

Proton-assisted addition reactions on trimethylsilylalkynyl nitrosylrutheniums of hydrotris(pyrazolyl)borate

Mono(ethynyl) TpRuCl(C≡CH)(NO) (**2**) and mono(acyl) TpRuCl{C(O)CH<sub>3</sub>}(NO) (**3**) complexes were obtained by treatment of TpRuCl(C≡CSiMe<sub>3</sub>)(NO) (**1**) with HCl (aq.) in MeOH. On the other hand, reaction between **1** and HCl (aq.) in CH<sub>2</sub>Cl<sub>2</sub> afforded η<sup>1</sup>-α-chlorovinyl TpRuCl{C(Cl)=CH<sub>2</sub>}(NO) (**4**). Similar reactivities were shown in TpRu(C≡CSiMe<sub>3</sub>)<sub>2</sub>(NO) (**5**) system also.

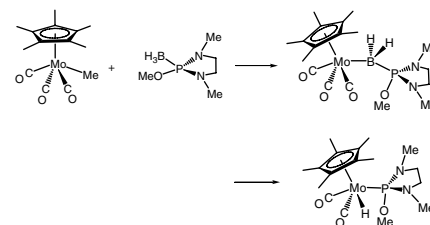


**Hiroshi Nakazawa, Masumi Itazaki,  
Masaharu Ohba**

*J. Organomet. Chem.* 692 (2007) 201

Molybdenum complexes bearing a diaminosubstituted-phosphiteboryl ligand: Syntheses, structures, and reactivity involving the Mo–B, B–P, and B–H activation

Diaminosubstituted-phosphiteboryl complexes  $\text{Cp}^*\text{Mo}(\text{CO})_3\text{BH}_2\{\text{P}(\text{NMeCH}_2)_2(\text{OMe})\}$  (**2**) were synthesized and characterized by the spectroscopic data and the X-ray crystallography. In the reaction of **2** with MeI and  $\text{PMe}_3$ , the Mo–B and the B–P bond activation takes place, respectively. Complex **2** was gradually converted in solution into  $\text{Cp}^*\text{Mo}(\text{CO})_2\text{H}\{\text{P}(\text{NMeCH}_2)_2(\text{OMe})\}$  via the B–H activation.

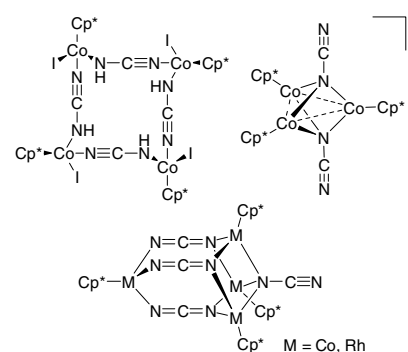


**Keiichi Takahata, Noriyuki Iwadate,  
Hidenobu Kajitani, Yoshiaki Tanabe,  
Youichi Ishii**

*J. Organomet. Chem.* 692 (2007) 208

Syntheses and properties of NCN-bridged tri- and tetranuclear complexes of cobalt and rhodium

The 16-membered macrocyclic NCNH-bridged tetracobalt(III) complex  $[\text{Cp}^*\text{CoI}(\mu_2\text{-NCNH-}N,N')_4]$ , the  $C_3$ -elongated cubane-like NCN-bridged tetracobalt(III) and tetra-rhodium(III) complexes  $[\text{Cp}^*\text{M}(\mu_3\text{-NCN-}N,N,N')_3(\mu_3\text{-NCN-}N,N,N)]$  ( $\text{M} = \text{Co}, \text{Rh}$ ), and the anionic bis(NCN)-capped tricobalt(II) complex  $\text{Na}[(\text{Cp}^*\text{Co})_3(\mu_3\text{-NCN-}N,N,N)_2]$  have been newly synthesized, the last of which is shown to undergo one quasi-reversible reduction and two quasi-reversible oxidations.

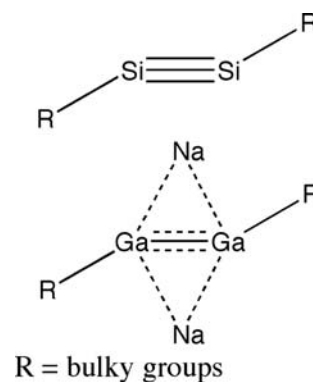


**Nozomi Takagi, Shigeru Nagase**

*J. Organomet. Chem.* 692 (2007) 217

Effects of bulky substituent groups on the Si–Si triple bonding in  $\text{RSi}\equiv\text{SiR}$  and the short Ga–Ga distance in  $\text{Na}_2[\text{RGaGaR}]$ : A theoretical study

The steric and electronic effects of bulky aryl and silyl groups ( $\text{C}_6\text{H}_2\text{-2,4,6-}\{\text{CH}(\text{SiMe}_3)_2\}_3$ ,  $\text{C}_6\text{H}_3\text{-2,6-}\{\text{C}_6\text{H}_3\text{-2,6-}i\text{Pr}_2\}_2$ ,  $\text{C}_6\text{H}_3\text{-2,6-}\{\text{C}_6\text{H}_2\text{-2,4,6-}i\text{Pr}_3\}_2$ ,  $\text{SiMe}(\text{Si}t\text{Bu}_3)_2$ , and  $\text{Si}i\text{PrDis}_2$ ) on the Si–Si triple bonding in  $\text{RSi}\equiv\text{SiR}$  and the short Ga–Ga distance in  $\text{Na}_2[\text{RGaGaR}]$  are investigated by density functional calculations with large basis sets.

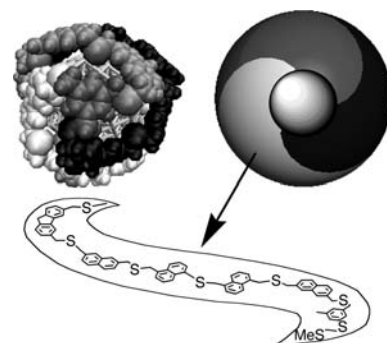


**Toshi Nagata**

*J. Organomet. Chem.* 692 (2007) 225

Automated design of protecting molecules for metal nanoparticles by combinatorial molecular simulations

New tripod oligo(dibenzyl sulfide) molecules were designed by computer modeling calculations so that they would form 1:1 complexes with an  $\text{Au}_{147}$  nanoparticle. Combinations of the aromatic fragments were examined by molecular dynamics simulations through either full search or genetic algorithm.

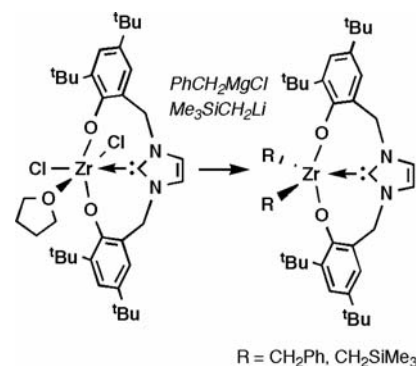


**Dao Zhang, Hidenori Aihara,  
Takahito Watanabe, Tsukasa Matsuo,  
Hiroyuki Kawaguchi**

*J. Organomet. Chem.* 692 (2007) 234

Zirconium complexes of the tridentate bis(aryloxide)-*N*-heterocyclic-carbene ligand: Chloride and alkyl functionalized derivatives

Zirconium complexes having the bis(aryloxide)-functionalized *N*-heterocyclic-carbene ligand [L]<sup>2-</sup> have been prepared by the reaction of ZrCl<sub>4</sub>(thf)<sub>2</sub> with Na<sub>2</sub>[L]. The chloride derivative [L]ZrCl<sub>2</sub>(thf) was treated with PhCH<sub>2</sub>MgCl and Me<sub>3</sub>SiCH<sub>2</sub>Li to generate the corresponding alkyl complexes, [R]ZrR<sub>2</sub> (R = CH<sub>2</sub>Ph, CH<sub>2</sub>SiMe<sub>3</sub>).

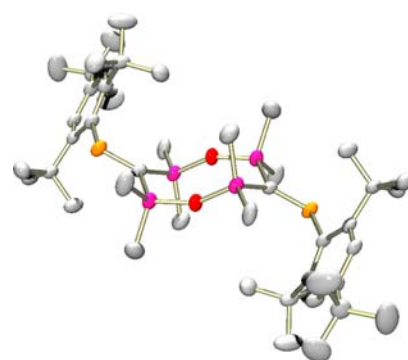


**Shigekazu Ito, Hiromichi Jin,  
Masaaki Yoshifuji**

*J. Organomet. Chem.* 692 (2007) 243

Preparation and X-ray analyses of siloxane-bridged acyclic and 8-membered cyclic phosphoethenes

Two Mes<sup>\*</sup>P=C (Mes<sup>\*</sup> = 2,4,6-tri-*t*-butylphenyl) parts were successfully combined with one or two disiloxane chain(s) by the reaction of 2-silyl-1-phosphaethenyllithium with dichlorotetramethyldisiloxane, and the structures of bis(1-bromo-2-phosphaethenyl)disiloxane and 3,7-diphosphinidene-2,2,4,4,6,6,8,8-octamethyl-1,5-dioxo-2,4,6,8-tetrasilacyclooctane were characterized by spectroscopic analyses and X-ray crystallography.

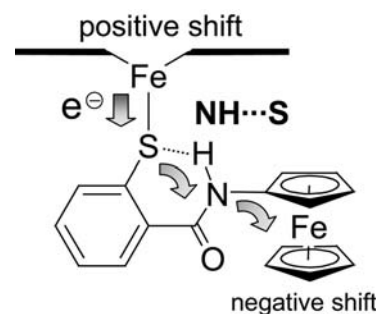


**Taka-aki Okamura, Taku Iwamura,  
Hitoshi Yamamoto, Norikazu Ueyama**

*J. Organomet. Chem.* 692 (2007) 248

Synthesis and molecular structures of S-2-FcNHCOC<sub>6</sub>H<sub>4</sub>SH and [M<sup>III</sup>(OEP)(S-2-FcNHCOC<sub>6</sub>H<sub>4</sub>)] (Fc = ferrocenyl, M = Fe, Ga): Electrochemical contributions of intramolecular SH···O=C and NH···S hydrogen bonds

A novel redox-active thiolate ligand having a ferrocene moiety, S-2-FcNHCOC<sub>6</sub>H<sub>4</sub>SH, and its porphyrin-thiolate compounds, [M<sup>III</sup>(OEP)(S-2-FcNHCOC<sub>6</sub>H<sub>4</sub>)] (M = Fe, Ga) were synthesized and characterized by X-ray analysis, spectroscopic and electrochemical measurements. The intramolecular SH···O=C and NH···S hydrogen bonds contribute to the redox potentials of Fc and iron-porphyrin moieties.

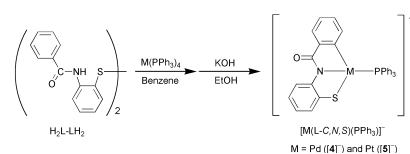


**Tatsuya Kawamoto, Satoko Suzuki,  
Takumi Konno**

*J. Organomet. Chem.* 692 (2007) 257

Synthesis and characterization of cyclometallated palladium(II) and platinum(II) complexes with amide-thiolate ligands

Cyclometallated complexes ([4]<sup>-</sup> and [5]<sup>-</sup>) with an amide-thiolate ligand were synthesized through the deprotonation of amide protons in mononuclear and dinuclear palladium(II) (1 and 2) and mononuclear platinum(II) (3) complexes, which are formed from amide disulfide (H<sub>2</sub>L-LH<sub>2</sub>) and [Pd(PPh<sub>3</sub>)<sub>4</sub>] or [Pt(PPh<sub>3</sub>)<sub>4</sub>]. The structures of 2, 3 and [4]<sup>-</sup> were determined by X-ray diffraction.

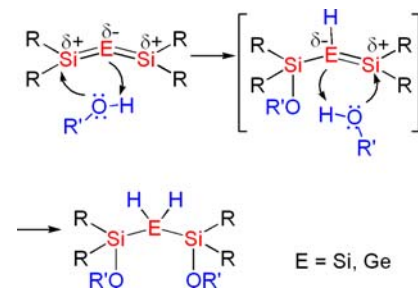




**Takeaki Iwamoto, Takashi Abe,  
Shintaro Ishida, Chizuko Kabuto, Mitsuo Kira**  
*J. Organomet. Chem.* 692 (2007) 263

Reactions of trisilaallene and 2-germadi-  
silaallene with various reagents

Heavier group-14 element congeners of allene, a trisilaallene and a 2-germadi-silaallene, react with water and alcohols to afford the corresponding 1:2 addition products in high yields in a regioselective manner. The regioselectivity is rationalized by the unique electronic characteristics of heavier group-14 allenes revealed by theoretical calculations.

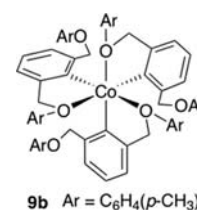


**Hirotsuna Yamada, Shiro Matsukawa,  
Yohsuke Yamamoto**

*J. Organomet. Chem.* 692 (2007) 271

Synthesis and characterization of hexa-  
coordinate cobalt(III) complexes bearing  
three *C,O*-bidentate ligands

Novel Co(III) complex (**9b**) was prepared in 58% yield utilizing the *C,O,O*-pincer type ligand. X-ray crystallography clarified that the complex **9b** has a hexacoordinated geometry with three *C,O*-bidentate ligands. In solution, a dynamic ligand exchange process was observed based on variable temperature NMR study.

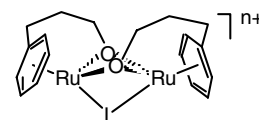


**Emi Nakatani, Yasutomo Takai,  
Hideo Kurosawa**

*J. Organomet. Chem.* 692 (2007) 278

Coordination behavior of some bridge ligands  
having S–O bond bound to four-membered  
ring unit (Ru<sub>2</sub>O<sub>2</sub>) of dinuclear areneruthenium  
complexes

The coordinatively unsaturated dinuclear are-  
neruthenium dication having the tethered alkoxy donor binds the neutral, monoanionic and dianionic ligands with S–O bond which bridge over two ruthenium atoms. Some unique solution behavior of the bridge ligands has been discussed.



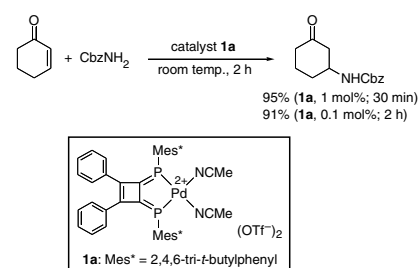
L = Me<sub>2</sub>SO (n = 2), MeSO<sub>3</sub> (n = 1), SO<sub>4</sub> (n = 0)

**Rader S. Jensen, Kazutoshi Umeda,  
Masaaki Okazaki, Fumiyuki Ozawa,  
Masaaki Yoshifuji**

*J. Organomet. Chem.* 692 (2007) 286

Synthesis and catalytic properties of cationic  
palladium(II) and rhodium(I) complexes  
bearing diphosphinidene-cyclobutene ligands

Complex **1a** bearing 1,2-diphenyl-3,4-bis(2,4,6-*tri-t*-butylphenyl)phosphinidene)cyclobutene (DPCB) efficiently catalyzes conjugate addition of benzyl carbamate (CbzNH<sub>2</sub>) to 2-cyclohexenone. The synthesis and X-structures of **1a** and related palladium(II) and rhodium(I) complexes are reported.

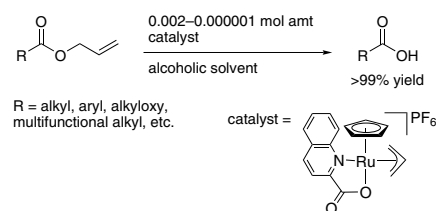


**Shinji Tanaka, Hajime Saburi,  
Takanori Murase, Yoshitaka Ishibashi,  
Masato Kitamura**

*J. Organomet. Chem.* 692 (2007) 295

Highly reactive and chemoselective cleavage of allyl esters using an air- and moisture-stable [CpRu(IV)( $\pi$ -C<sub>3</sub>H<sub>3</sub>)(2-quinolinecarboxylato)]-PF<sub>6</sub> catalyst

A new catalytic process for allyl ester cleavage has been developed by using a robust cationic CpRu(IV)  $\pi$ -allyl complex of 2-quinolinecarboxylic acid. The deprotection of various alcohols and acids can be attained simply with high reactivity and chemoselectivity under mild conditions. Furthermore, a turnover number of 1 000 000 can be achieved.

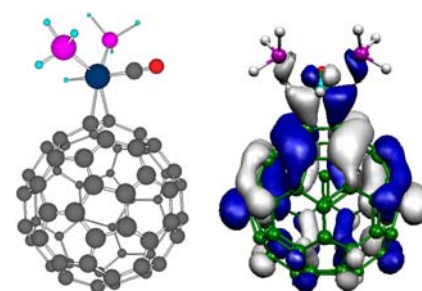


**Atsushi Ikeda, Yuu Kamenno, Yoshihide Nakao,  
Hirofumi Sato, Shigeyoshi Sakaki**

*J. Organomet. Chem.* 692 (2007) 299

Binding energies and bonding nature of MX(CO)(PH<sub>3</sub>)<sub>2</sub>(C<sub>60</sub>) (M = Rh or Ir; X = H or Cl): Theoretical study

IrH(CO)(PH<sub>3</sub>)<sub>2</sub>(C<sub>60</sub>), IrCl(CO)(PH<sub>3</sub>)<sub>2</sub>(C<sub>60</sub>), and RhH(CO)(PH<sub>3</sub>)<sub>2</sub>(C<sub>60</sub>) were theoretically investigated with DFT and MP2 to MP4(SDQ) methods. The coordinate bond of C<sub>60</sub> becomes strong in the order IrCl(CO)(PH<sub>3</sub>)<sub>2</sub>(C<sub>60</sub>) < RhH(CO)(PH<sub>3</sub>)<sub>2</sub>(C<sub>60</sub>) < IrH(CO)(PH<sub>3</sub>)<sub>2</sub>(C<sub>60</sub>), which is reasonably interpreted in terms of d orbital energy, d orbital expansion, and distortion energy of the metal moiety.

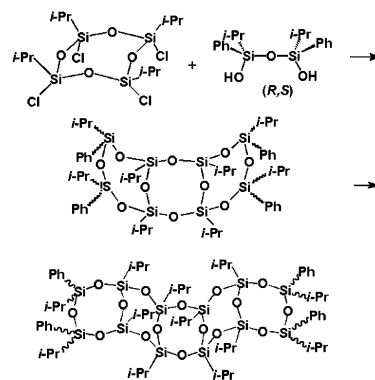


**Masafumi Unno, Tomoe Matsumoto,  
Hideyuki Matsumoto**

*J. Organomet. Chem.* 692 (2007) 307

Synthesis of laddersiloxanes by novel stereocontrolled approach

Three new pentacyclic laddersiloxanes were prepared by a new method utilizing single stereoisomer of disiloxanediol as a growing unit. Thus, (*RS*)-[*i*-PrPhSi(OH)]<sub>2</sub>O was isolated and treated with tetrachlorocyclo-tetrasiloxane, resulting in the formation of tricyclic laddersiloxanes with *cis*-Ph groups at terminals. All of the obtained isomers could be transformed into pentacyclic laddersiloxanes.

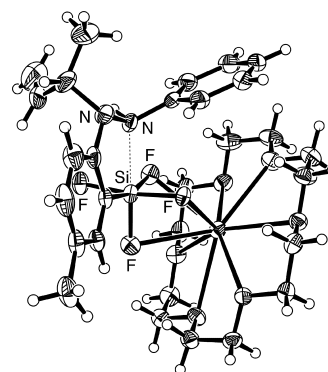


**Masaki Yamamura, Naokazu Kano,  
Takayuki Kawashima**

*J. Organomet. Chem.* 692 (2007) 313

Intramolecular allylation of the azo group of 2-(allylsilyl)azobenzenes and its photocontrol

Pentacoordinate allylsilanes bearing an azobenzene moiety were synthesized and their structures were elucidated. The reaction of the (*E*)-isomer with a fluoride ion gave a tetrafluorosilicate via intramolecular allyl-migration, whereas the (*Z*)-isomer formed by photoirradiation of the (*E*)-isomer did not react with a fluoride ion at all.

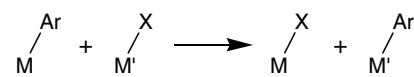


**Yuji Suzuki, Takeyoshi Yagyu,  
Kohtaro Osakada**

*J. Organomet. Chem.* 692 (2007) 326

Transmetalation of arylpalladium and platinum complexes. Mechanism and factors to control the reaction

Recent studies on aryl ligand transfer of Pd and Pt complexes revealed mechanistic details and factors that control the reactions.



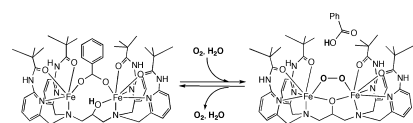
(M, M' = Pd, Pt; X = Cl, I, OH, CH<sub>2</sub>COMe)

**Hidekazu Arai, Yasuhiro Funahashi,  
Tomohiro Ozawa, Koichiro Jitsukawa,  
Hideki Masuda**

*J. Organomet. Chem.* 692 (2007) 343

Diiron(II) complexes showing a reversible oxygenation induced by a proton transfer mediated with a water molecule. Biological implication of a water molecule in hemerythrin function

The diiron complex with the hydroxide group bound dioxygen reversibly accompanying proton transfer mediated by water, which indicates that proton transfer of  $\mu$ -hydroxo to peroxy is an essential factor in the oxygenation of hemerythrin to play a role of dioxygen carrier.

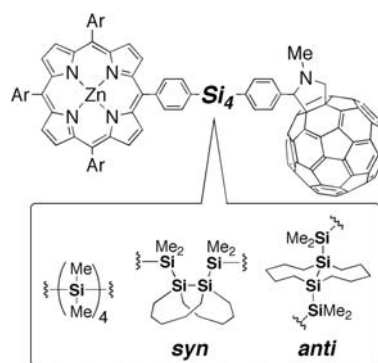


**Yuki Shibano, Mikio Sasaki, Hayato Tsuji,  
Yasuyuki Araki, Osamu Ito, Kohei Tamao**

*J. Organomet. Chem.* 692 (2007) 356

Conformation effect of oligosilane linker on photoinduced electron transfer of tetrasilane-linked zinc porphyrin-[60]fullerene dyads

Zinc porphyrin-[60]fullerene dyads linked by conformation-constrained tetrasilane were synthesized to evaluate the conformation effect of the linkers on the photoinduced electron transfer. The excited-state dynamics studies demonstrate that the lifetimes of the fluorescence and the charge-separated state show little conformation dependence, which is a characteristic of the Si-linkages.

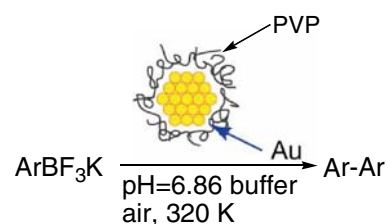


**Hidehiro Sakurai, Hironori Tsunoyama,  
Tatsuya Tsukuda**

*J. Organomet. Chem.* 692 (2007) 368

Oxidative homo-coupling of potassium aryltrifluoroborates catalyzed by gold nanocluster under aerobic conditions

Gold(0) nanoclusters, stabilized by poly(*N*-vinyl-2-pyrrolidone) (Au:PVP-*n*), work as a selective, quantitative, and reusable catalyst for the homo-coupling reaction of potassium aryltrifluoroborates in neutral aqueous media under ambient condition.

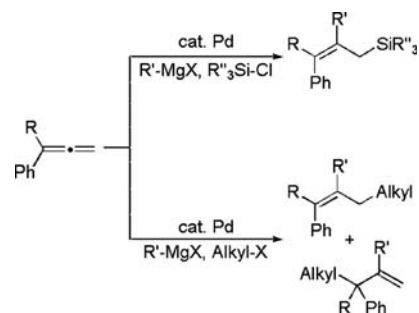


**Yuuki Fujii, Jun Terao, Hitoshi Kuniyasu, Nobuaki Kambe**

*J. Organomet. Chem.* 692 (2007) 375

Silylation and alkylation of allenes using chlorosilanes and alkyl halides in the presence of palladium catalyst and Grignard reagents

Allenes react with Grignard reagents and chlorosilanes in the presence of a palladium catalyst giving rise to carbosilylated products bearing carbon groups from Grignard reagents at the central carbon and silyl groups at the terminal carbon. When alkyl halides were used instead of chlorosilanes, the corresponding alkylated products were obtained.

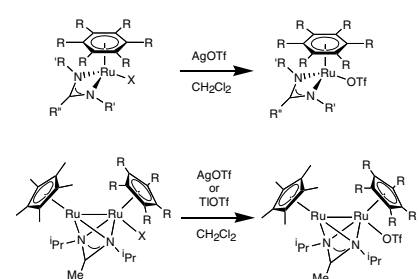


**Taizo Hayashida, Hideo Kondo, Jun-ichi Terasawa, Karl Kirchner, Yusuke Sunada, Hideo Nagashima**

*J. Organomet. Chem.* 692 (2007) 382

Trifluoromethanesulfonate (triflate) as a moderately coordinating anion: Studies from chemistry of the cationic coordinatively unsaturated mono- and diruthenium amidinates

Triflate complexes of mono- and diruthenium amidinates were synthesized, and coordination behavior of the triflate anion to the coordinatively unsaturated ruthenium species is investigated by crystallography and variable temperature  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectroscopy. Differences in reactivity between triflate complexes and its TFPB homologues were also examined.

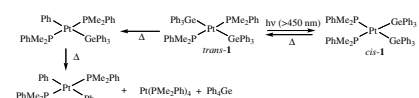


**Kunio Mochida, Takashi Fukushima, Michiko Suzuki, Wakako Hatanaka, Mariko Takayama, Yoko Usui, Masato Nanjo, Kuniyoshi Akasaka, Takako Kudo, Sanshiro Komiya**

*J. Organomet. Chem.* 692 (2007) 395

Thermal reactivity of *cis*- and *trans*-bis(triphenylgermyl)bis(tertiary phosphine)platinum(II)

The complex *cis*-Pt(Ph<sub>3</sub>Ge)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> underwent smooth isomerization to give the *trans*-isomer at room temperature via an associative five-coordinated intermediate. Thermodynamic parameters and activation energy for the *cis* to *trans* isomerization were obtained. Heating of *trans*-Pt(Ph<sub>3</sub>Ge)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> at 50 °C produced *trans*-PtPh(Ph<sub>3</sub>Ge)(PMe<sub>2</sub>Ph)<sub>2</sub> followed by the formation of *trans*-PtPh<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>, Pt(PMe<sub>2</sub>Ph)<sub>4</sub>, and Ph<sub>4</sub>Ge finally.

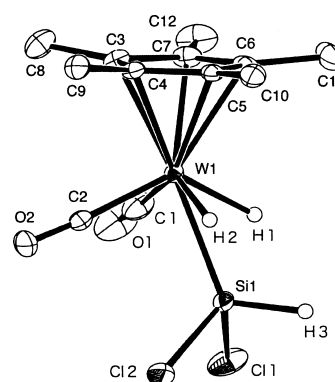


**Hiroyuki Sakaba, Takeshi Hirata, Chizuko Kabuto, Kuninobu Kabuto**

*J. Organomet. Chem.* 692 (2007) 402

Synthesis and structure of a tungsten dichlorosilyl dihydride complex

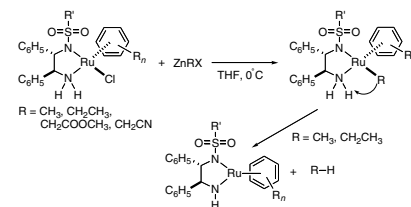
The tungsten dichlorosilyl dihydride Complex Cp<sup>\*</sup>(CO)<sub>2</sub>W(H)<sub>2</sub>(SiHCl<sub>2</sub>) was synthesized and characterized by X-ray crystallography.



**Takashi Koike, Takao Ikariya***J. Organomet. Chem.* 692 (2007) 408

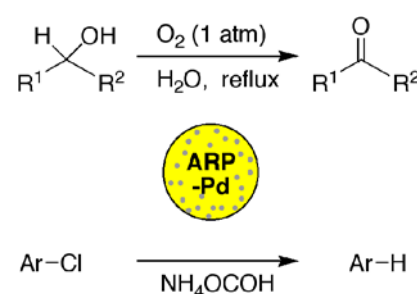
Synthesis and properties of alkylruthenium complexes bearing primary and secondary amine ligands

A series of 18-electron alkylruthenium complexes,  $\text{Ru}(\text{R})[\kappa^2(\text{N},\text{N}')-(\text{S},\text{S})-\text{R}'\text{SO}_2\text{NCHPhCHPhNH}_2]$ - $(\eta^6\text{-arene})$  ( $\text{Ph} = \text{C}_6\text{H}_5$ ,  $\text{R}' = p\text{-CH}_3\text{C}_6\text{H}_4$  and  $\text{CH}_3$ ), bearing an N-sulfonylated diamine ligand, was synthesized from the reaction of  $\text{RuCl}[\kappa^2(\text{N},\text{N}')-(\text{S},\text{S})-\text{R}'\text{SO}_2\text{NCHPhCHPhNH}_2]$ - $(\eta^6\text{-arene})$  with alkylzinc reagents. The transmetalation proceeded smoothly to give the desired alkyl complexes in good yield and selectivity. Although the isolable functionalized alkyl Ru complexes were thermally stable, the simple methyl- and ethyl-Ru complexes underwent intramolecular deprotonation of NH protons to give the amido Ru complexes and byproducts, alkanes.

**Yasuhiro Uozumi, Ryu Nakao, Hakjune Rhee***J. Organomet. Chem.* 692 (2007) 420

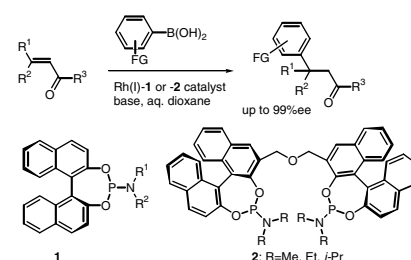
Development of an amphiphilic resin-dispersion of nanopalladium catalyst: Design, preparation, and its use in aquacatalytic hydrodechlorination and aerobic oxidation

An amphiphilic polystyrene-poly(ethylene glycol) resin-dispersion of nanopalladium particles catalyzed aerobic oxidation of alcohols and hydrodechlorination of aryl halides under heterogeneous aqueous conditions.

**Kazunori Kurihara, Noriyuki Sugishita, Kengo Oshita, Dongguo Piao, Yasunori Yamamoto, Norio Miyaura***J. Organomet. Chem.* 692 (2007) 428

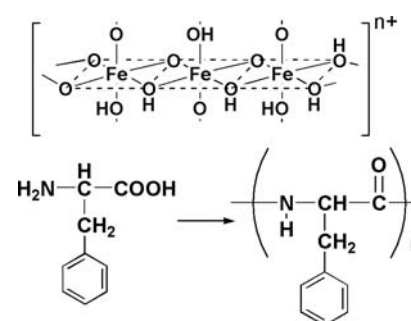
Enantioselective 1,4-addition of arylboronic acids to  $\alpha,\beta$ -unsaturated carbonyl compounds catalyzed by rhodium(I)-chiral phosphoramidite complexes

Chiral bidentate phosphoramidites (**2**) were newly synthesized for the rhodium(I)-catalyzed asymmetric 1,4-addition of arylboronic acids to  $\alpha,\beta$ -unsaturated carbonyl compounds. The complex between  $[\text{Rh}(\text{nbd})_2]\text{BF}_4$  and **2** ( $\text{R} = \text{Me}$ ) completed the addition to cyclic enones within 2 h at room temperature in the presence of  $\text{Et}_3\text{N}$  with 96–99.8% ee. The catalyst resulted in 66–94% ee for acyclic enones.

**Kensuke Naka, Yoshihiro Tampo, Yoshiki Chujo***J. Organomet. Chem.* 692 (2007) 436

Effect of iron (III) hydroxide sol as a support for oligomerization of L-phenylalanine in aqueous solution

An oligomerization of L-phenylalanine in aqueous solution was studied in the presence of iron (III) hydroxide sols. Adsorption study of L-phenylalanine indicated that assemblies of L-phenylalanine onto the iron hydroxide sols were predominant factor to improve the yield of the oligomerization product.



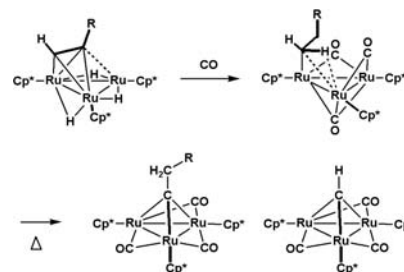


**Ryu-ichi Tenjimbayashi, Eisuke Murotani, Toshifumi Takemori, Toshiro Takao, Hiroharu Suzuki**

*J. Organomet. Chem.* 692 (2007) 442

Synthesis, structure, and property of a triruthenium cluster having a  $\mu$ -alkyl ligand: Transformation of a  $\mu_3(\perp)$ -alkyne ligand into a  $\mu$ -alkyl ligand via a  $\mu_3$ -vinylidene complex

A triruthenium  $\mu$ -alkyl complex, which contains a two-electron and three-center interaction among Ru, C, and H atoms, has been synthesized by the reaction of a perpendicularly coordinated 1-alkyne complex with carbon monoxide. The agostic C–H bond was cleaved upon pyrolysis to afford  $\mu_3$ -alkylidyne and  $\mu_3$ -methylidyne complexes.

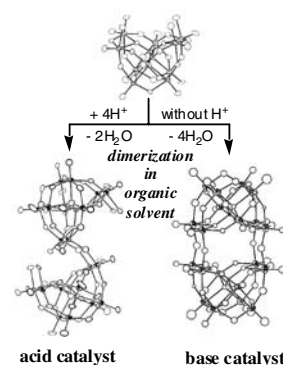


**Akihiro Yoshida, Shiro Hikichi, Noritaka Mizuno**

*J. Organomet. Chem.* 692 (2007) 455

Acid–base catalyses by dimeric disilicoicosatungstates and divacant  $\gamma$ -Keggin-type silicodecatungstate parent: Reactivity of the polyoxometalate compounds controlled by step-by-step protonation of lacunary W=O sites

The catalytic properties of disilicoicosatungstates,  $[\{\gamma\text{-SiW}_{10}\text{O}_{32}(\text{H}_2\text{O})_2\}_2(\mu\text{-O})_2]^{4-}$  (**2**) and  $[\text{H}(\gamma\text{-SiW}_{10}\text{O}_{32})_2(\mu\text{-O})_4]^{7-}$  (**3**), and their parent divacant  $\gamma$ -Keggin type silicodecatungstate,  $[\gamma\text{-SiW}_{10}\text{O}_{34}(\text{H}_2\text{O})_2]^{4-}$  (**1**), toward C–C bond formation have been investigated. The aquo ligands containing **2** exhibits the acidic nature and catalyzes the Mukaiyama-aldol condensation, while **1** and **3** are rather basic and catalyze Knoevenagel condensation.

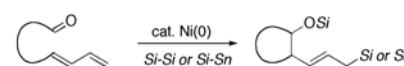


**Nozomi Saito, Miwako Mori, Yoshihiro Sato**

*J. Organomet. Chem.* 692 (2007) 460

Nickel(0)-catalyzed disilylative and silastannylative cyclizations of 1,3-diene and tethered aldehyde

Nickel(0)-catalyzed bimetallic cyclization of 1,3-diene and a tethered aldehyde in the presence of  $\text{PhF}_2\text{SiSiMe}_3$  or  $\text{Me}_3\text{SiSnBu}_3$  gave the corresponding cyclized product having an allylmetal moiety in the side chain in good yields.

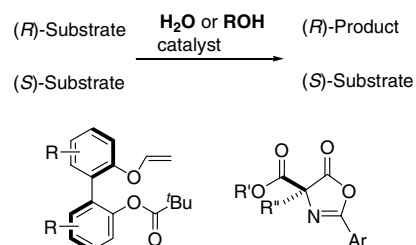


**Makoto Tokunaga, Hiroshi Aoyama, Junya Kiyosu, Yuki Shirogane, Tetsuo Iwasawa, Yasushi Obora, Yasushi Tsuji**

*J. Organomet. Chem.* 692 (2007) 472

Metal complexes-catalyzed hydrolysis and alcoholysis of organic substrates and their application to kinetic resolution

Metal complexes-catalyzed hydrolysis and alcoholysis of organic substrates such as vinyl ethers and azlactones and its application to kinetic resolution has been achieved with moderate to high selectivities. Oxidative carbon–carbon bond cleavage reactions, which were found in the course of the study of asymmetric hydrolysis were also described.

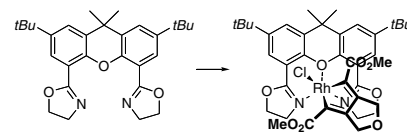


Hirofumi Uchimura, Jun-ichi Ito, Seiji Iwasa, Hisao Nishiyama

*J. Organomet. Chem.* 692 (2007) 481

Oxidative addition reactions and stereochemistry on rhodium/4,5-bis(2-oxazoliny)xanthene complexes

The reaction of 4,5-bis(2-oxazoliny)xanthene (Xabox) ligand and rhodium(I) complex with chloroacetate and diyne gave oxidative addition complexes. The diyne complex exhibited catalytic activity for cyclotrimerization reaction.

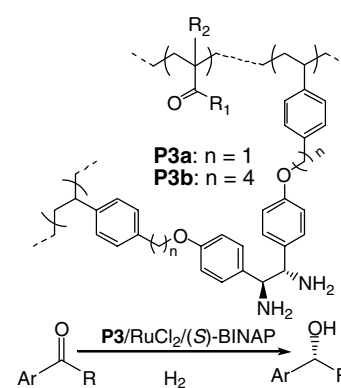


Shinichi Itsuno, Masahiro Chiba, Miyuki Takahashi, Yukihiro Arakawa, Naoki Haraguchi

*J. Organomet. Chem.* 692 (2007) 487

Asymmetric hydrogenation of aromatic ketones using polymeric catalyst prepared from polymer-supported 1,2-diamine

The polymer-supported chiral 1,2-diamines were synthesized by copolymerization of the chiral 1,2-diamine monomer and various kinds of achiral monomers. The asymmetric hydrogenation of aromatic ketones with polymer-supported catalyst prepared from the polymeric chiral 1,2-diamine ligand leads to the corresponding secondary alcohols in quantitative yield with high level of enantioselectivity.

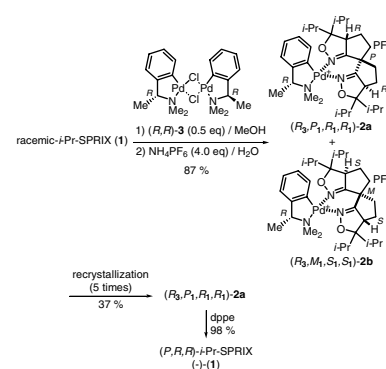


Shinobu Takizawa, Junichi Yogo, Tetsuya Tsujihara, Kiyotaka Onitsuka, Hiroaki Sasai

*J. Organomet. Chem.* 692 (2007) 495

Optical resolution of tetra isopropyl-substituted spiro bis(isoxazoline) *i*-Pr-SPRIX

The optical resolution of racemic tetra isopropyl-substituted spiro bis(isoxazoline) ligand (*i*-Pr-SPRIX) is achieved by fractional recrystallization of palladium complexes **2a** and **2b** prepared from ( $\pm$ )-SPRIX **1** and di- $\mu$ -chlorobis{(*R,R*)-2-[1-(dimethylamino)ethyl]phenyl-*C, N*}dipalladium(II) (*R,R*)-**3** followed by the decomplexation from palladium by the treatment with 1,2-bis(diphenylphosphino)ethane. The X-ray crystal structure of the complex **2a** reveals that ( $-$ )-*i*-Pr-SPRIX has (*P,R,R*)-configuration.

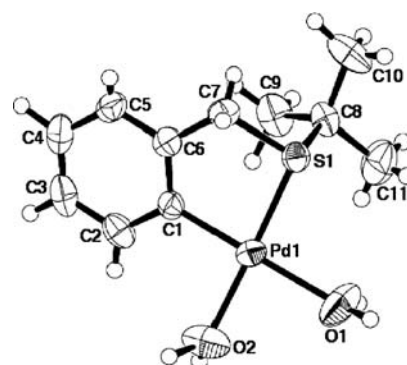


Keiji Uehara, Shunichi Fukuzumi, Seiji Ogo

*J. Organomet. Chem.* 692 (2007) 499

Synthesis and crystal structure of a new water-soluble sulfur-containing palladacyclic diaqua complex

A new water-soluble sulfur-containing palladacyclic diaqua complex [(SC)Pd<sup>II</sup>(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub>-(SO<sub>4</sub>)<sub>2</sub> {**[1]**<sub>2</sub>(SO<sub>4</sub>), SC = C<sub>6</sub>H<sub>4</sub>-2-(CH<sub>2</sub>S<sup>t</sup>Bu)} was synthesized. The structures of **[1]**(PF<sub>6</sub>)<sub>2</sub> was unequivocally determined by X-ray analysis.

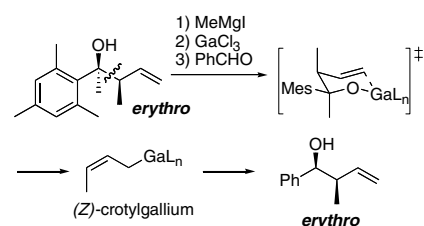


Sayuri Hayashi, Koji Hirano,  
Hideki Yorimitsu, Koichiro Oshima

*J. Organomet. Chem.* 692 (2007) 505

Gallium-mediated allyl transfer from bulky homoallyl alcohol to aldehydes or alkynes: Control of dynamic  $\sigma$ -allylgalliums based on retro-allylation reaction

A new method for the preparation and control of dynamic  $\sigma$ -allylgalliums is disclosed. Upon treatment with a Grignard reagent and gallium trichloride, bulky homoallyl alcohols undergo gallium-mediated retro-allylation reaction to provide  $\sigma$ -allylgallium reagents. (*Z*)- and (*E*)-crotylgalliums were generated stereospecifically, starting from *erythro*- and *threo*-homoallyl alcohols, respectively. The stereochemically defined crotylgallium reagents effected stereoselective allylation of aldehydes. Allylgallation reaction of alkynes with homoallyl alcohol via retro-allylation is also described.

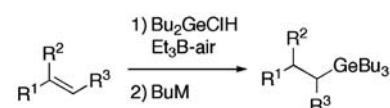


Katsukiyo Miura, Kazunori Ootsuka,  
Akira Hosomi

*J. Organomet. Chem.* 692 (2007) 514

Homolytic hydrogermylation of alkenes with dibutylchlorogermane

In the presence of  $\text{Et}_3\text{B}$ -dry air, dibutylchlorogermane ( $\text{Bu}_2\text{GeClH}$ ) reacted smoothly with alkenes at room temperature to give hydrogermylation products in high yields. This homolytic hydrogermylation was applicable to various alkenes including electron-deficient, electron-rich, and internal alkenes. Tributylgermane ( $\text{Bu}_3\text{GeH}$ ) showed much lower reactivity than  $\text{Bu}_2\text{GeClH}$ .

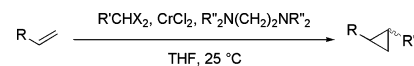


Kazuhiko Takai, Shota Toshikawa,  
Atsushi Inoue, Ryo Kokumai, Masato Hirano

*J. Organomet. Chem.* 692 (2007) 520

Heterosubstituted cyclopropanation of alkenes with organochromium reagents derived from heterosubstituted dihalomethanes,  $\text{CrCl}_2$ , and tetraalkylethylenediamine

Iodocyclopropanes of *trans* configuration are produced stereoselectively from terminal alkenes by treatment with a reagent derived from iodoform, chromium(II) chloride, and *N,N,N',N'*-tetraethylethylenediamine in THF. Similarly, cyclopropylsilanes and -boronic esters are obtained by using  $\text{R}_3\text{SiCHI}_2$ , and a combination of  $\text{Cl}_2\text{CHB(OR)}_2$  and LiI instead of iodoform, respectively.

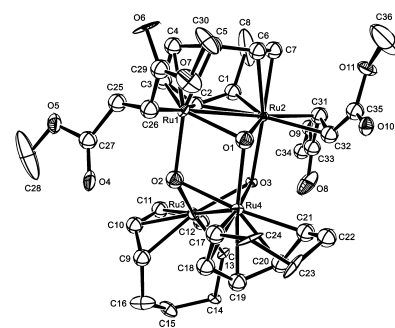


Teruyuki Kondo, Fumiaki Tsunawaki,  
Toshi-aki Suzuki, Yasuyuki Ura, Kenji Wada,  
Syuhei Yamaguchi, Hideki Masuda,  
Kenji Yoza, Motoo Shiro, Take-aki Mitsudo

*J. Organomet. Chem.* 692 (2007) 530

Synthesis and characterization of a novel ( $\mu_3$ -oxo)tetraruthenium cluster

A novel ( $\mu_3$ -oxo)tetraruthenium cluster (**2**) was synthesized in an isolated yield of 73% by the reaction of a zerovalent ruthenium complex,  $\text{Ru}(\eta^6\text{-1,3,5-cyclooctatriene})(\eta^2\text{-dimethyl fumarate})_2$  (**1**), with water under reflux in 1,4-dioxane for 6 h. The structure of **2** has been determined by X-ray crystallography.

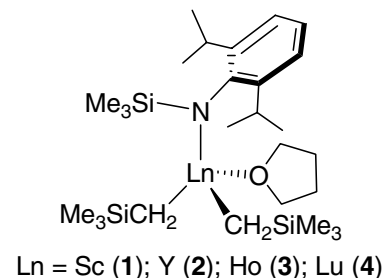


**Yunjie Luo, Masayoshi Nishiura, Zhaomin Hou**

*J. Organomet. Chem.* 692 (2007) 536

Rare earth metal bis(alkyl) complexes bearing a monodentate arylamido ancillary ligand: Synthesis, structure, and Olefin polymerization catalysis

The reaction of  $\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(\text{thf})_2$  with 1 equiv. of 2,6- $\text{Pr}_2\text{C}_6\text{H}_3\text{NH}(\text{SiMe}_3)$  gave the corresponding mono-amido-ligated rare earth metal bis(alkyl) complexes  $[\text{2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)]\text{Ln}(\text{CH}_2\text{SiMe}_3)_2(\text{thf})$  ( $\text{Ln} = \text{Sc}$  (1), Y (2), Ho (3), Lu (4)), which on treatment with 1 equiv. of  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  in toluene, became active for the polymerization of isoprene, 1-hexene and styrene.

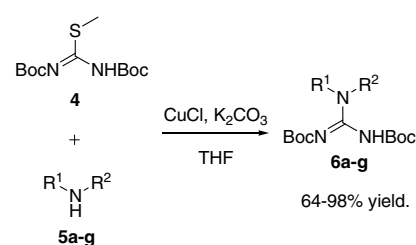


**Hitoshi Ube, Daisuke Uraguchi, Masahiro Terada**

*J. Organomet. Chem.* 692 (2007) 545

Efficient synthetic protocol for substituted guanidines via copper(I)-mediated intermolecular amination of isothiourea derivatives

An efficient synthetic protocol for substituted guanidines using copper(I)-salts-mediated intermolecular amination was developed. The synthesis of bis-Boc protected guanidines via the amination of *S*-methyl-*N,N'*-bis-Boc-isothiourea and *N,N'*-bis-Boc-thiourea with a variety of primary/secondary amines and anilines proceeded under mild reaction conditions without having to use highly toxic metal salts.

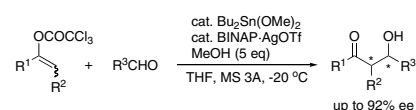


**Akira Yanagisawa, Toshikazu Ichikawa, Takayoshi Arai**

*J. Organomet. Chem.* 692 (2007) 550

Dibutyltin dimethoxide and BINAP · silver(I) complex-catalyzed asymmetric aldol reaction of alkenyl trichloroacetates with aldehydes

A catalytic asymmetric aldol reaction of alkenyl trichloroacetates with aldehydes was achieved using dibutyltin dimethoxide and BINAP · silver(I) complex as catalysts in a mixed solvent consisting of THF and MeOH. Various optically active  $\beta$ -hydroxy ketones were diastereoselectively obtained with good enantioselectivity up to 92% ee.



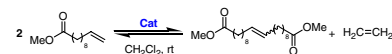
**Takashi Oikawa, Yoichi Masui, Tsunehiro Tanaka, Yoshiki Chujo, Makoto Onaka**

*J. Organomet. Chem.* 692 (2007) 554

Lewis acid-modified mesoporous alumina: A new catalyst carrier for methyltrioxorhenium in metathesis of olefins bearing functional groups

Methyltrioxorhenium doped on zinc chloride-modified mesoporous alumina (MTO/ $\text{ZnCl}_2$ //*meso*- $\text{Al}_2\text{O}_3$ ) can work as an efficient heterogeneous catalyst for metathesis reactions of functionalized olefins as well as simple olefins without double bond migration and oligomerization.

$\text{CH}_3\text{ReO}_3 / \text{ZnCl}_2$  // *mesoporous*  $\text{Al}_2\text{O}_3$  catalyzes the metathesis:

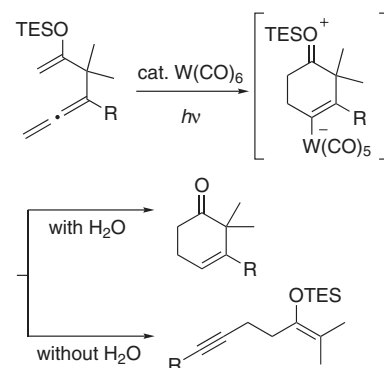


**Tomoya Miura, Koichi Kiyota,  
Hiroyuki Kusama, Nobuharu Iwasawa**

*J. Organomet. Chem.* 692 (2007) 562

W(CO)<sub>5</sub>(L)-catalyzed 6-*endo*-selective cyclization and formal Cope rearrangement of allenyl silyl enol ethers

On treatment of 5-siloxy-1,2,5-trienes with a catalytic amount of W(CO)<sub>6</sub> under photoirradiation, two types of synthetically useful compounds, that is, 6-*endo*-cyclized products or formal Cope rearrangement products, are obtained selectively via the same intermediates simply by changing reaction conditions. In these reactions, electrophilic activation of the allene moiety is effectively achieved by coordination of W(CO)<sub>5</sub>, allowing intramolecular attack by neutral carbon nucleophiles in a 6-*endo* manner.

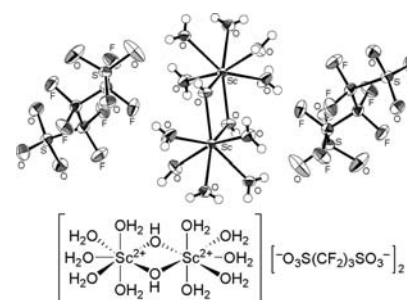


**Manabu Hatano, Eri Takagi, Manabu Arinobe,  
Kazuaki Ishihara**

*J. Organomet. Chem.* 692 (2007) 569

Dimeric scandium(III) and monomeric lanthanide(III) complexes with perfluoropropane-1,3-disulfonates as counter anions

Novel scandium(III) and lanthanide(III) complexes with perfluoropropane-1,3-disulfonate as counter anions were synthesized for the first time. By X-ray analysis, the corresponding Sc(III) complex was found to be a  $\mu$ -OH-bridged dimeric structure without bonding between the Sc(III) centers and perfluoropropane-1,3-disulfonates, namely [Sc( $\mu$ -OH)(H<sub>2</sub>O)<sub>5</sub>]<sub>2</sub>[O<sub>3</sub>S(CF<sub>2</sub>)<sub>3</sub>SO<sub>3</sub>]<sub>2</sub>. The dimeric Sc(III) complex, in strong contrast to monomeric lanthanide(III) complexes, was an efficient Lewis acid catalyst for the hydrolysis of esters.

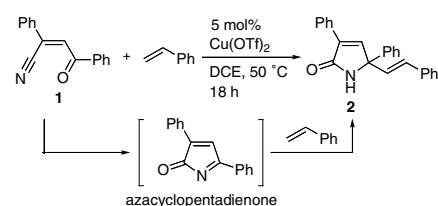


**Masahito Murai, Shigekazu Kawai, Koji Miki,  
Kouichi Ohe**

*J. Organomet. Chem.* 692 (2007) 579

Copper-catalyzed transformation of carbonyl-ene-nitrile compounds: Vinylation, imino ene reaction, and alkylation of 2-aza-2,4-cyclopentadienone intermediates generated via Ritter-type hydration and dehydrative cyclization reactions

1*H*-pyrrolin-2(5*H*)-one derivatives are easily obtained from carbonyl-ene-nitrile compounds and alkenes or alkynes by copper(II)-catalyzed tandem sequence involving vinylation or allylation as well as Ritter-type hydration and dehydrative cyclization.

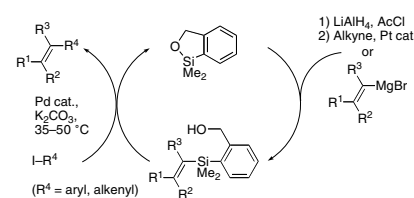


**Yoshiaki Nakao, Hidekazu Imanaka,  
Jinshui Chen, Akira Yada, Tamejiro Hiyama**

*J. Organomet. Chem.* 692 (2007) 585

Synthesis and cross-coupling reaction of alkenyl[(2-hydroxymethyl)phenyl]dimethylsilanes

Highly stable alkenyl[2-(hydroxymethyl)phenyl]dimethylsilanes, which are prepared by hydrosilylation of alkynes catalyzed or the reaction of 1,1-dimethyl-2-oxa-1-silaindan with alkenyl Grignard reagents, undergo cross-coupling reaction with various aryl and alkenyl iodides under reaction conditions employing K<sub>2</sub>CO<sub>3</sub> as a base at 35–50 °C in highly regio- and stereospecific manners.



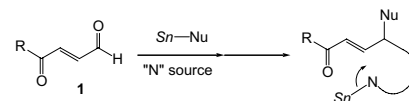


**Ikuya Shibata, Hirofumi Kato,  
Makoto Yasuda, Akio Baba**

*J. Organomet. Chem.* 692 (2007) 604

One-pot synthesis of heterocyclic compounds initiated by chemoselective addition to  $\beta$ -acyl substituted unsaturated aldehydes with nucleophilic tin complexes

Various heterocyclic compounds such as 2-monosubstituted pyrroles, oxazolidones were prepared by chemoselective addition of nucleophilic tin complexes to  $\beta$ -acyl substituted unsaturated aldehydes in an one-pot procedure.

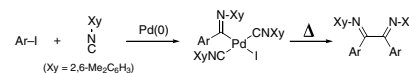


**Masashi Morishita, Hideki Amii**

*J. Organomet. Chem.* 692 (2007) 620

A study on ligand-coupling reactions of imidoyl palladium complexes

A new ligand-coupling reaction of imidoypalladium(II) complexes is described. Heating a toluene solution of imidoypalladium complexes gave rise to the  $\alpha$ -diimines (1,4-diazabutadienes).

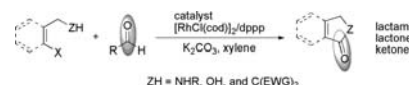


**Tsumoru Morimoto, Masahiko Fujioka,  
Koji Fuji, Ken Tsutsumi, Kiyomi Kakiuchi**

*J. Organomet. Chem.* 692 (2007) 625

Rh(I)-catalyzed CO gas-free carbonylative cyclization of organic halides with tethered nucleophiles using aldehydes as a substitute for carbon monoxide

The CO gas-free carbonylative cyclization of organic halides, with tethered nitrogen, oxygen, and carbon nucleophiles, with aldehydes as a substitute for carbon monoxide can be achieved in the presence of a catalytic amount of a rhodium complex. The reaction involves the decarbonylation of the aldehyde by the rhodium catalyst, and the successive carbonylation of an organic halide utilizing the rhodium carbonyl that is formed in situ. Aldehydes having electron-withdrawing groups showed a higher ability to donate the carbonyl moiety.

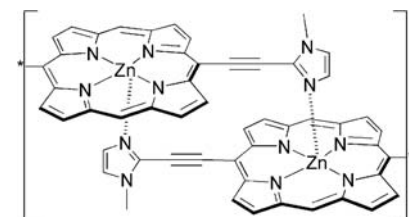


**Akiharu Satake, Osami Shoji, Yoshiaki Kobuke**

*J. Organomet. Chem.* 692 (2007) 635

Supramolecular array of imidazolethynyl-zinc-porphyrin

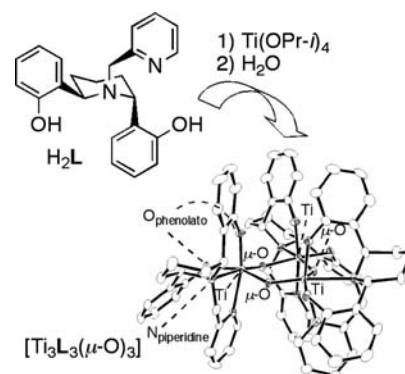
Novel imidazolethynyl-zinc-porphyrin and its *meso,meso*-linked bisporphyrin were synthesized effectively by the reaction of the corresponding bromoporphyrins and 2-imidazolethynyl in the presence of palladium-arsenic catalyst. The complementary coordination was observed by  $^1\text{H}$  NMR and UV-Vis spectroscopy.



**Tohru Okamatsu, Ryo Irie, Tsutomu Katsuki***J. Organomet. Chem.* 692 (2007) 645

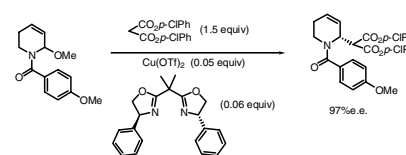
Unique tripodal chiral tertiary amine, 2,6-*trans*-1,2,6-trisubstituted piperidine with pyridine and bis(phenol) donor groups: Its stereoselective coordination to titanium(IV) ion

A new chiral tertiary amine ( $H_2L$ ) based on 2,6-*trans*-disubstituted piperidine scaffold appended with pyridine and bis(phenol) functionalities was synthesized and demonstrated to work as a tetradentate tripodal ligand, forming  $[Ti_3L_3(\mu-O)_3]$  with unified chiralities induced at the metal center by the  $N^{\wedge}O$  chelate and the chair-like  $(Ti-\mu-O)_3$  ring conformations.

**Yoshihiro Matsumura, Diashirou Minato, Osamu Onomura***J. Organomet. Chem.* 692 (2007) 654

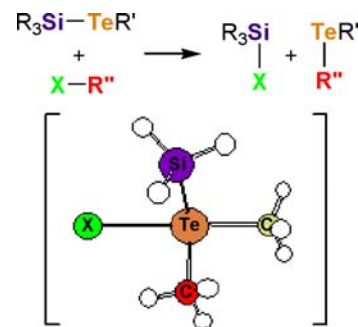
Highly enantioselective introduction of bis(alkoxycarbonyl)methyl group into the 2-position of piperidine skeleton

A  $Cu(OTf)_2$  catalyzed coupling reaction between 1-(*p*-methoxybenzoyl)-3,4-dihydro-2-methoxypiperidine, which were easily prepared by utilizing electrochemical oxidation, and di-*p*-chlorophenyl malonate to afford 2-piperidinyl malonate with up to 97% ee in the presence of chiral bisoxazoline ligand.

**Shigeru Yamago, Kazunori Iida, Jun-ichi Yoshida***J. Organomet. Chem.* 692 (2007) 664

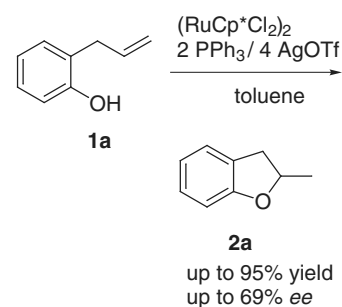
Experimental and theoretical studies on formal  $\sigma$ -bond metathesis of silyl tellurides with alkyl halides

Silyl tellurides reacted with alkyl halides to give corresponding alkyl tellurides and silyl halides in good to excellent yields. After removal of the volatile silyl halides and solvent under vacuum, the essentially pure divalent organotellurium compounds were obtained. Theoretical calculations reveal a stepwise pathway involving tetravalent organotellurium intermediate.

**Tetsuo Ohta, Yohei Kataoka, Akio Miyoshi, Yohei Oe, Isao Furukawa, Yoshihiko Ito***J. Organomet. Chem.* 692 (2007) 671

Ruthenium-catalyzed intramolecular cyclization of hetero-functionalized allylbenzenes

Intramolecular cyclization of 2-allylphenol (**1a**) to 2,3-dihydro-2-methylbenzofuran (**2a**) using ruthenium catalyst in good yield with moderate enantioselectivity.

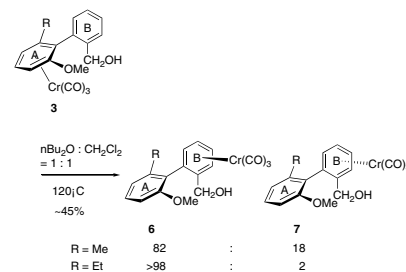


**Ken Kamikawa, Kouta Nishino,  
Tomohiro Sakamoto, Shunsuke Kinoshita,  
Hiroyuki Matsuzaka, Motokazu Uemura**

*J. Organomet. Chem.* 692 (2007) 678

Stereoselective tricarbonylchromium migration reactions in axially chiral biaryl chromium complexes

The tricarbonylchromium group in thermodynamically unstable biaryl chromium complexes with a coordinating heteroatom at the side chain stereoselectively migrated to the other arene face to release the steric repulsion.

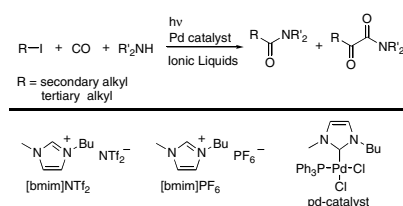


**Takahide Fukuyama, Takaya Inouye,  
Ilhyong Ryu**

*J. Organomet. Chem.* 692 (2007) 685

Atom transfer carbonylation using ionic liquids as reaction media

Photo-induced atom transfer carbonylation of a wide variety of RI proceeded well using ionic liquids in the presence of Pd-carbene complex, whereas primary RI were not suitable for the present system because of competing  $\text{S}_{\text{N}}2$  reactions.

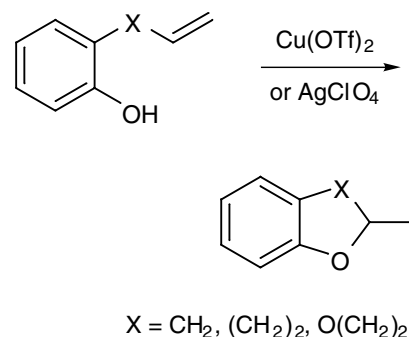


**Yoshihiko Ito, Risa Kato, Kentaro Hamashima,  
Yohei Kataoka, Yohei Oe, Tetsuo Ohta,  
Isao Furukawa**

*J. Organomet. Chem.* 692 (2007) 691

Intramolecular cyclization of phenol derivatives with C=C double bond in a side chain

Phenols with olefinic side chain were effectively cyclized to 2,3-dihydrobenzofuran, 3,4-dihydro-2H-1-benzopyrane, 3,4-dihydro-2H-1,5-benzodioxepin by copper or silver catalyst.



**Eiji Ihara, Naohiro Omura, Tomomichi Itoh,  
Kenzo Inoue**

*J. Organomet. Chem.* 692 (2007) 698

Anionic polymerization of methyl methacrylate and *tert*-butyl acrylate initiated with the YCl<sub>3</sub>/lithium amide/*n*BuLi systems

The anionic polymerization of methyl methacrylate (MMA) was initiated with a mixture of lithium amide of various secondary amines and *n*BuLi in the presence of YCl<sub>3</sub>. The resulting PMMAs had very narrow molecular weight distributions, having an amino group at their  $\alpha$ -chain ends.

