RESEARCH ACTIVITIES VII
Coordination Chemistry Laboratories

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

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

Transition metal-mediated organic transformations have emerged as a powerful tool in the domain of synthetic organic chemistry. Catalytic asymmetric reactions have attracted significant interest for their synthetic utility. One of the most exciting and challenging subjects in research on the catalytic asymmetric synthesis is development of the novel chiral ligands. Recently, we have designed and prepared a series of homochiral monophosphine ligands bearling axially chiral binaphthyl backbone, so-called MOP, which were identified as effective chiral ligands in various asymmetric catalysis, in particular hydrosilylation of olefins.

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

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

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

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

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

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

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

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

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

UOZUMI, Yasuhiro; KAWATSURA, Motoi; HAYASHI, Tamio

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

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

VII-B Green and Risk-Free Catalysis

Catalytic organic transformations under mild, safe, and green conditions is an important goal in synthetic organic chemistry. We recently reported that several palladium-catalyzed reactions, including π-allylic substitution, carbonylation, the Heck reaction, and Suzuki-Miyaura cross-coupling, took place in water by use of palladium-phosphine complexes bound to an amphiphilic polystyrene-poly(ethylene glycol) graft copolymer (PS-PEG) resin. PS-PEG resin-supported rhodium complexes was designed and prepared with a view toward using them in water. Rhodium-catalyzed hydroformylation, cyclotrimerization of alkynes, and Michael-type addition of arylboronic acids were found to proceed smoothly in water. Palladium-Catalyzed doublecarbonylation under very mild and safe conditions using Pd/PPh_3/DABCO/THF system was also investigated.

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

UOZUMI, Yasuhiro; NAKAZONO, Maki

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

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

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

UOZUMI, Yasuhiro; ARII, Taro; WATANABE, Toshihiro

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

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