

IX-D Nano- and Complex-Catalysis

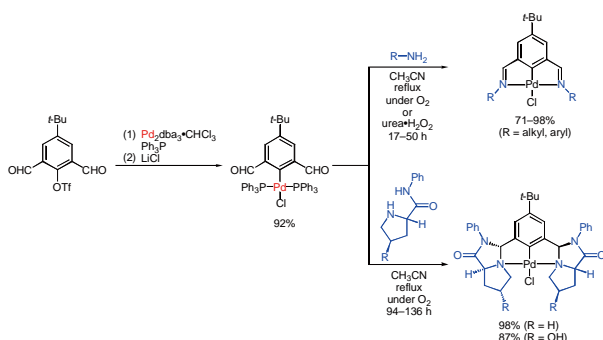
Objectives of this research group is development of nano- and complex-catalysts which exhibit novel catalytic functions, in particular, to promote efficient organic molecular transformations. Three major subjects are (1) preparation and properties of novel pincer complexes, (2) development of polymeric complex-catalysis in water, and (3) development of polymer-supported nano-metal catalysts. Representative results are shown below.

IX-D-1 NCN Pincer Palladium Complexes: Their Preparation via a Ligand Introduction Route and Their Catalytic Properties

UOZUMI, Yasuhiro; TAKENAKA, Kazuhiro; MINAKAWA, Maki

[*J. Am. Chem. Soc.* **127**, 12273–12281 (2005)]

A wide range of NCN pincer palladium complexes, [4-*tert*-2,6-bis(*N*-alkylimino)phenyl]chloropalladium (alkyl = *n*-butyl, benzyl, cyclohexyl, *t*-butyl, adamantyl, phenyl, 4-methoxyphenyl), were readily prepared from *trans*-(4-*tert*-butyl-2,6-diformyl-phenyl)chlorobis(triphenylphosphine)palladium via dehydrative introduction of the corresponding alkylimino ligand groups (ligand introduction route) in excellent yields (71–98%). NMR studies on this route for forming pincer complexes revealed the intermediacy of [4-*tert*-2,6-bis(*N*-alkylimino)phenyl]chlorobis(triphenylphosphine)palladium which is in equilibrium with the corresponding NCN pincer complexes via coordination/dissociation of the intramolecular imino groups and triphenylphosphine ligands. A series of chiral NCN pincer complexes bearing pyrroloimidazolone units as the trans-chelating donor groups, [4-*tert*-butyl-2,6-bis{(3*R*,7*aS*)-2-phenylhexahydro-1*H*-pyrrolo[1,2-*c*]imidazol-1-on-3-yl}phenyl]chloropalladium, were also prepared from the same precursor via condensation with proline anilides in high yields. The catalytic properties of the NCN imino and the NCN pyrroloimidazolone pincer palladium complexes were examined in the Heck reaction and the asymmetric Michael reaction to demonstrate their high catalytic activity and high enantioselectivity.

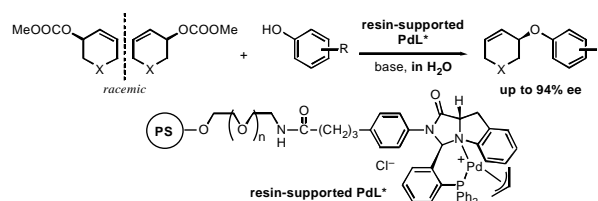


IX-D-2 Asymmetric P-Allylic Etherification of Cycloalkenyl Esters with Phenols in Water Using a Resin-Supported Chiral Palladium Complex

UOZUMI, Yasuhiro; KIMURA, Masahiro

[*Tetrahedron:Asymmetry* **17**, 161–166 (2006)]

Catalytic asymmetric allylic amination of cycloalkenyl carbonates (methyl cyclohexen-2-yl carbonate, methyl cyclohepten-2-yl carbonate, methyl 5-methoxycarbonylcyclohexen-2-yl carbonate, methyl cyclohexenyl carbonate, *t*-butyl 5-methoxycarbonyloxy-1,2,5,6-tetrahydropyridinedicarboxylate) with phenolic nucleophiles was achieved in water under heterogeneous conditions by use of a palladium complex of (3*R*,9*aS*)-3-[2-(diphenylphosphino)phenyl]-2-phenyltetrahydro-1*H*-imidazo[1,5-*a*]indole-1-one anchored on polystyrene-poly(ethylene glycol) copolymer resin (2 mol % Pd) to give the corresponding cycloalkenylamines with high enantiomeric selectivity (up to 94% *ee*).



IX-D-3 A Solid-Phase Self-Organized Catalyst of Nanopalladium with Main-Chain Viologen Polymers: α -Alkylation of Ketones with Primary Alcohols

YAMADA, Yoichi; UOZUMI, Yasuhiro

[*Org. Lett.* **8**, 1375–1378 (2006)]

A novel solid-phase self-organized catalyst of palladium nanoparticles was prepared from PdCl₂ with main-chain viologen polymers via complexation and reduction. This insoluble nanocatalyst nano-Pd-V efficiently promoted α -alkylation of ketones with primary alcohols in the presence of Ba(OH)₂·H₂O under atmospheric conditions without organic solvents. The nano-Pd-V catalyst was reused without loss of catalytic activity.

