

IX-H Heterogeneous Aquacatalysis

Catalytic organic transformations under mild, safe, and green conditions is an important goal in synthetic organic chemistry. We recently reported that several palladium- and rhodium-catalyzed reactions, including π -allylic substitution, carbonylation, the Heck reaction, Suzuki-Miyaura cross-coupling, hydroformylation, cyclotrimerization of alkynes, and Michael-type addition of arylboronic acids, *etc.*, took place in water by use of metal-phosphine complexes anchored on to an amphiphilic polystyrene-poly(ethylene glycol) graft copolymer (PS-PEG) resin where the advantages of both aqueous- and heterogeneous-switching of a given catalytic transformation were combined in one system. Here we wish to report our progress in this subject.

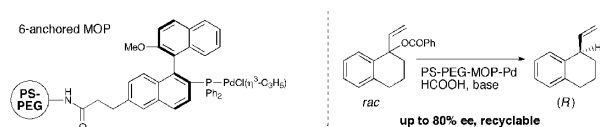
IX-H-1 PS-PEG Resin-Supported Palladium-MOP Complexes. Application in Asymmetric π -Allylic Reduction

[*Org. Lett.* 7, 291–293 (2005)]

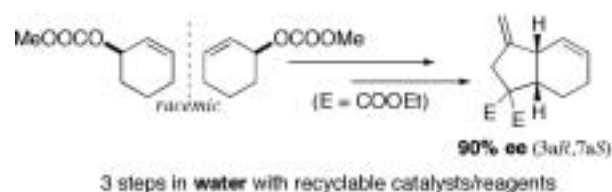
UOZUMI, Yasuhiro; HOCKE, Heiko

[*Tetrahedron* 60, 9297–9306 (2004)]

Homochiral palladium complexes of polymeric 2', 6-, and 6'-anchored 2-diphenylphosphino-1,1'-binaphthyl (MOP) ligands were prepared on polystyrene-poly(ethylene glycol) (PS-PEG) resin. The PS-PEG resin-supported palladium-MOP complexes exhibited high catalytic activity, stereoselectivity (up to 80% *ee*), and recyclability (6 times) in the asymmetric allylic reduction of 1-vinyl-1,2,3,4-tetrahydronaphth-1-yl benzoate to give 1-vinyl-1,2,3,4-tetrahydronaphthalene.



Cycloisomerization of 1,6-enynes proceeded smoothly in water under heterogeneous conditions in the presence of a palladium complex supported on polystyrene-poly(ethylene glycol) copolymer resin to give the corresponding cyclopentanes with high level of chemical greenness. Multi-step asymmetric synthesis of a hydrindane framework was achieved via palladium-catalyzed asymmetric π -allylic alkylation, propargylation, and cycloisomerization of 1,6-enynes, where all three steps were performed in water with recyclable polymeric catalysts.



IX-H-2 Hydrogenation and Dehalogenation under Aqueous Conditions with an Amphiphilic Polymer-Supported Nanopalladium Catalyst

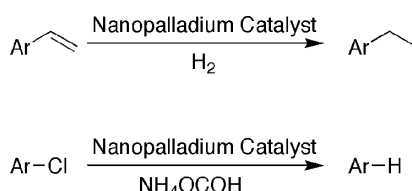
IX-H-4 Controlled Monoarylation of Dibromoarenes in Water with a Polymeric Palladium Catalyst

NAKAO, Ryu; RHEE, Hakjune; UOZUMI, Yasuhiro

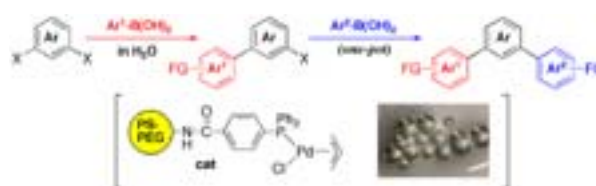
UOZUMI, Yasuhiro; KIKUCHI, Makoto

[*Org. Lett.* 7, 163–165 (2005)][*Synlett* 1775–1778 (2005)]

An amphiphilic polystyrene-poly(ethylene glycol) resin-supported nanopalladium particle catalyzed hydrogenation of olefins and hydrodechlorination of chloroarenes under aqueous conditions.



A highly selective monoarylation of dibromoarenes was performed via the Suzuki-Miyaura cross-coupling with arylboronic acids with an amphiphilic polystyrene-poly(ethylene glycol) (PS-PEG) resin-supported phosphine-palladium complex in water under heterogeneous conditions to give bromobiaryls in high yields. Introduction of two different aryl groups on a aromatic moiety was achieved in a one-pot reaction by successive addition of two kinds of arylboronic acids under similar conditions. The polymeric palladium catalyst can be readily recovered and recycled.



IX-H-3 Cycloisomerization of 1,6-Enynes: Asymmetric Multi-Step Preparation of a Hydrindane Framework in Water with Polymeric Catalysts

NAKAI, Yasushi; UOZUMI, Yasuhiro