Heterogeneous Catalytic Systems for Organic Chemical Transformations in Water

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Various organic molecular transformations catalyzed by transition metals were achieved under heterogeneous aqueous conditions by use of amphiphilic resin-supported metal complexes or convoluted polymeric metal catalysts which were designed and prepared by this research group. In particular, asymmetric Suzuki-Miyaura coupling and oxidative cyclization of alkenols and alkenoic acids, both of which were performed in water under heterogeneous conditions with high recyclability of the polymeric catalysts, are highlights among the achievements of the 2008–2009 period to approach what may be considered ideal chemical processes of next generation. Representative results are summarized hereunder.

1. Synthesis of [2,6-Bis(2-oxazolinyl)phenyl]palladium Complexes via the Ligand Introduction Route1)

A series of [2,6-bis(2-oxazolinyl)phenyl]palladium (Phebox-Pd) complexes were synthesized via the ligand introduction route. *trans*-Bromo(2,6-dicarboxyphenyl)bis(triphenyl phosphine)palladium was prepared by the reaction of 2-bromoisophthalic acid with $Pd(PPh_3)_4$ in 93% yield, and the carboxy groups of the palladium complex were converted into the oxazolinyl groups to give the Phebox-Pd complexes in 44–57% yield (Scheme 1).

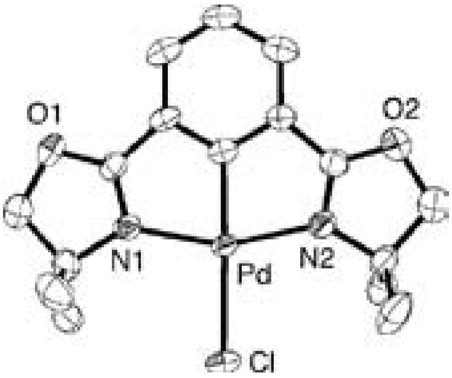
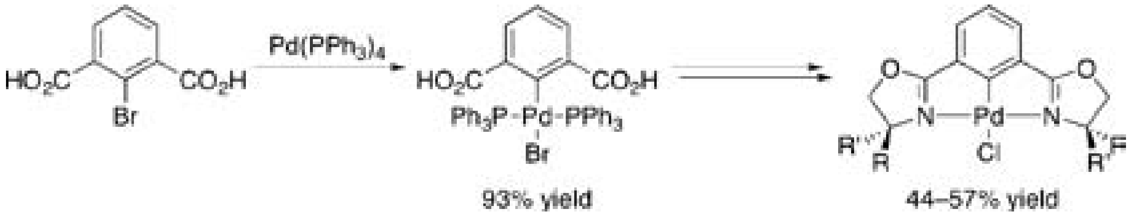


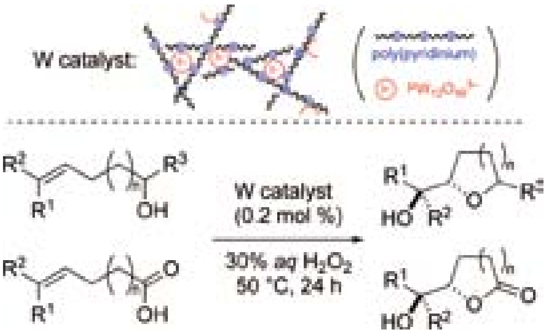
Figure 1. ORTEP drawing of Phebox-Pd complex.



Scheme 1. Ligand Introduction Route for the Synthesis of [2,6-Bis(2-oxazolinyl)phenyl]palladium Complexes.

2. Development of Tightly Convoluted Polymeric Phosphotungstate Catalysts and Their Application to an Oxidative Cyclization of Alkenols and Alkenoic Acids[2]

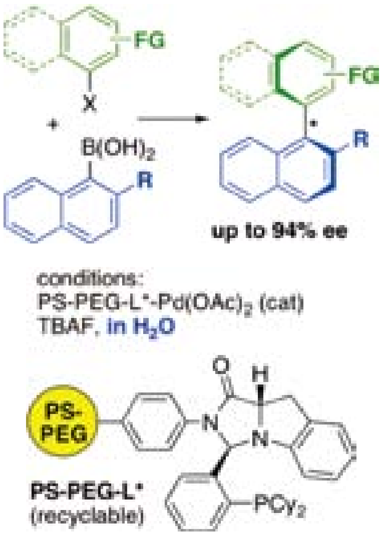
Tightly convoluted polymeric phosphotungstate catalysts were prepared via ionic-assembly of $H_3PW_{12}O_{40}$ and poly (alkylpyridinium)s. An oxidative cyclization of various alkenols and alkenoic acids was efficiently promoted by the polymeric phosphotungstate catalyst in *aq*. H_2O_2 in the absence of organic solvents to afford the corresponding cyclic ethers and lactones in high yield. The catalyst was reused four times without loss of catalytic activity. The polymeric phosphotungstate was unambiguously characterized by spectro- and microscopic studies (MAS $^{31}P\{^1H\}$ NMR, IR spectroscopy, elemental analysis, TEM, SEM, and EDS).



Scheme 2. Oxidative Cyclization of Alkenyl Alcohols and Alkenoic Acids with a Convoluted Polymeric Phosphotungstate.

3. Asymmetric Suzuki-Miyaura Coupling in Water with an Amphiphilic Resin-Supported Chiral Palladium Catalyst[3]

Asymmetric Suzuki-Miyaura coupling of aryl halides (Cl, Br, I) and aryl boronic acids was achieved in water with wide functional group tolerance by use of a readily-recyclable amphiphilic polymer (PS-PEG) resin-supported chiral imidazoindolephosphine-palladium complex to give a variety of biaryls with up to 94 % ee.



Scheme 3. Asymmetric Suzuki-Miyaura Coupling in Water with an Amphiphilic Resin-Supported Chiral Palladium Complex.

References

1) T. Kimura and Y. Uozumi, *Organometallics* **27**, 5159–5162 (2008).
2) Y. M. A. Yamada, H. Guo and Y. Uozumi, *Heterocycles* **76**, 645–655 (2008).
3) Y. Uozumi, Y. Matuura, T. Arakawa and Y. M. A. Yamada, *Angew. Chem., Int. Ed.* **48**, 2708–2710 (2009).