

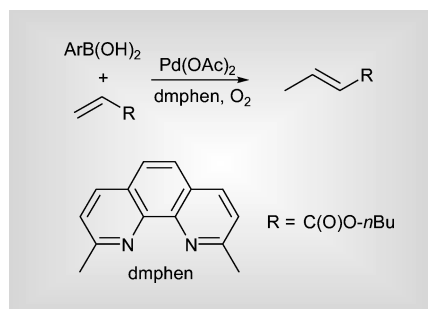


## Highlights

Markus Hölscher reviews some of the recent literature in green chemistry

### Ligand modulated Heck vinylation with molecular oxygen as oxidant

Palladium(II)-mediated vinylic substitutions of organoboronic acids are known as oxidative Heck reactions and up to now there has been no ligand-supported oxidative Heck protocol, which would help in the development of new selective and efficient reactions. Larhed *et al.* from the University of Uppsala have developed a novel protocol in which aryl boronic acids are coupled to a variety of olefins, employing a phenanthroline type ligand and molecular oxygen as reoxidant (*Chem. Commun.* 2004, 218–219).

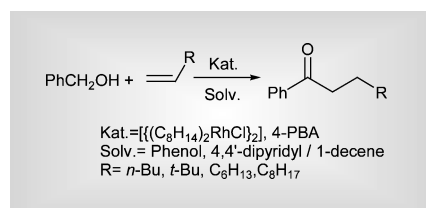


In a comparison of this setup with other N- and P-based ligands the oxidatively stable 2,9-dimethyl-1,10-phenanthroline (dmphen) proved to be an oxidatively stable ligand resulting in product yields of up to 97%, whereas the other ligands yielded lower yields and were oxidized. Upon testing different aryl boronic acids under optimized conditions this protocol gave moderate to high yields with low catalyst loadings, a cheap ligand and molecular oxygen as a "green reoxidant" of the catalyst.

### A new thermoregulated solvent system for recycling of catalysts

The hydroacylation of olefins with primary alcohols to yield ketones is an interesting example for C–H activation with organometallic catalysts. Jun *et al.* from Yonsei University, Korea have developed a novel two phase solvent system for this reaction (*J. Am. Chem. Soc.* 2004, **126**,

424–425), which is based on the temperature dependent stability of hydrogen bonds. Phenol and 4,4'-dipyridyl form a hydrogen bonded polar phase immiscible with 1-decene at room temperature. Upon heating to 150 °C the two phases mix, due to the instability of a H-bond network at elevated temperatures. This enables the reaction between benzyl alcohol and 1-hexene in the presence of a rhodium catalyst precursor and a phosphine as the ligand to take place in a homogenous phase at elevated temperatures followed by easy catalyst separation at low temperature.



Upon cooling the H-bonded network is re-established resulting in phase separation. The polar phase contains the catalyst and the nonpolar phase the ketone. When 4-diphenylphosphino-benzoic acid (4-PBA) is used as the ligand, the isolated yields of seven runs vary between 88 and 96%. ICP-MS analyses revealed the rhodium content in the nonpolar phase to be low (0.005 and 0.01% in two following runs). The amount of ketone in the polar phase also was low. Furthermore benzyl alcohol derivatives with CF<sub>3</sub> and OMe groups in *para* position performed as well as different olefins (1-octene, 1-decene, 2,2-dimethyl-1-butene) with isolated product yields in the 90% range.

### Spectroscopic determination of Lewis and Brønsted acidity in ionic liquids

Much work in the field of ionic liquids has focused on commercial applications, while the establishment of a procedure for the determination of the acidity of ILs still is missing. Recently two groups have contributed fundamental research to solve this problem. The group of Kou *et al.* from

Peking University, China has focused on Lewis acidity while Gilbert *et al.* from the University of Liège, Belgium, concentrated on Brønsted acidity. The work of Kou *et al.* describes by means of IR spectroscopic investigations the interaction between different IL/metal halide mixtures and probe molecules as pyridine and ethanenitrile (*Chem. Commun.* 2004, 236–237). The authors show that IR bands of the probe molecules associated with certain vibrations shift reliably and reproducibly when Lewis acidic centres are present. Depending on the mole fraction of the metal halide different aluminate ions are present in solution, which can also be distinguished by this method. In contrast, the work of Gilbert *et al.* uses UV/Vis spectroscopy as the analytical tool, which is used to describe Brønsted acidity in non-chloroaluminate ILs (*J. Am. Chem. Soc.* 2003, **125**, 5264–5265). In a typical experiment the acid strength of HNTf<sub>2</sub> (NTf<sub>2</sub> = N(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>) dissolved in [bmim][NTf<sub>2</sub>] could be described by the systematic decrease of a characteristic band of the unprotonated form of the probe molecule 2,4-dinitroaniline with regard to the concentration of HNTf<sub>2</sub>. Also BF<sub>4</sub> containing ILs were studied as well as the influence of water in these systems. The authors come to the conclusion that in ILs based on the BF<sub>4</sub> and NTf<sub>2</sub> anions acidity levels between –3.35 and –7.00 (in terms of the Hammett function) can be reached. These media appear to be less solvating than water.

### Silica-immobilized catalysts for asymmetric transfer hydrogenation of ketones

Optically active secondary alcohols are interesting intermediates for the synthesis of biologically active compounds. Asymmetric transfer hydrogenation of prochiral ketones consequently is an attractive method for the synthesis of these alcohols. Ruthenium catalysts containing N-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine (TsDPEN) type ligands are very selective and efficient catalysts for hydrogenations of ketones, which makes them attractive candidates for immobilization experiments. Tu *et al.* from Lanzhou University, China, have

