

# **Denmark Group Meeting**

**28 August 2001**

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**Palladium Catalysis in Ionic Liquids**

## Germane Properties<sup>1</sup>

- Polar phases (close to CH<sub>3</sub>OH);
- Solvent properties largely determined by ability of salt to act as a hydrogen-bond donor and/or acceptor;
- Effect of delocalizing charge on cation is unknown.



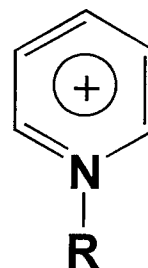
(a)



(c)



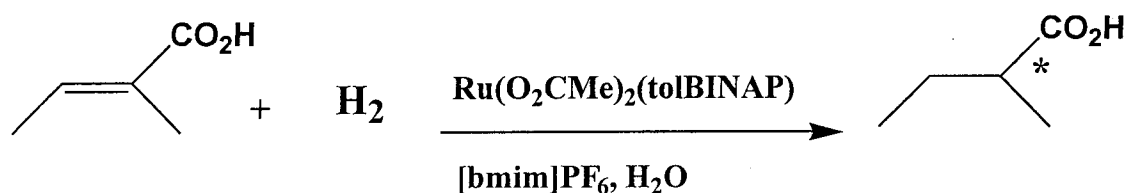
(b)



(d)



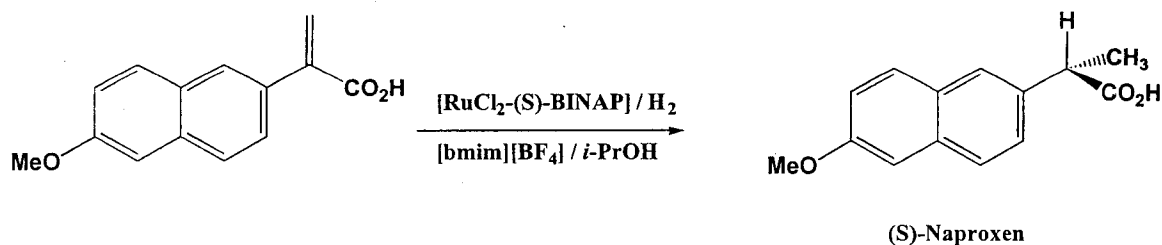
## Transition Metal Catalysis



92% ee, 100% conversion

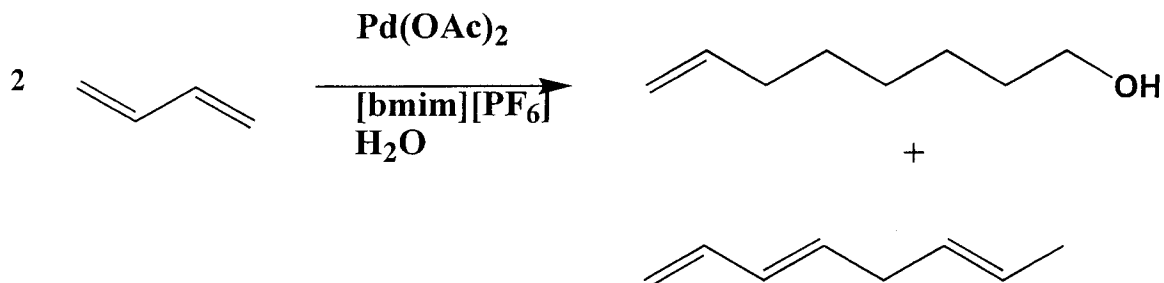
### Asymmetric Hydrogenation and Catalyst Recycling

Asymmetric hydrogenation of tiglic acid catalyzed by  $\text{Ru}(\text{O}_2\text{CMe})_2((R)\text{-tolBINAP})$  in wet ionic liquid ( $[\text{bmim}]\text{PF}_6$  with added water,  $\text{bmim} = 1\text{-}n\text{-butyl-3-methylimidazolium}$ ) gave 2-methylbutanoic acid with high enantioselectivity and conversion. The product was extracted with supercritical  $\text{CO}_2$  ( $\text{scCO}_2$ ) giving a clean separation of product and catalyst. The catalyst/ionic liquid solution was then reused repeatedly without significant loss of enantioselectivity or conversion.<sup>2</sup>

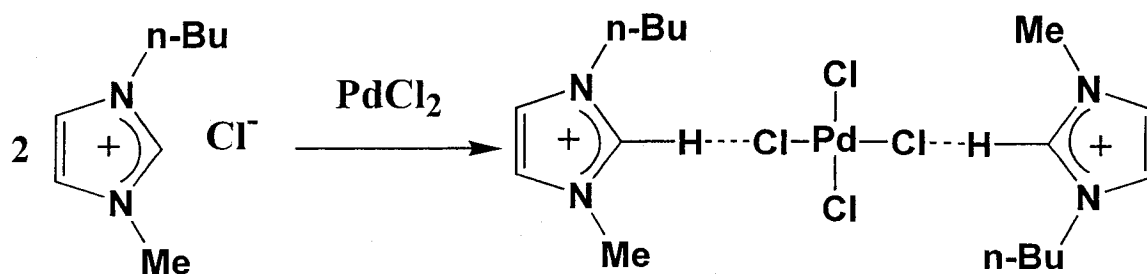


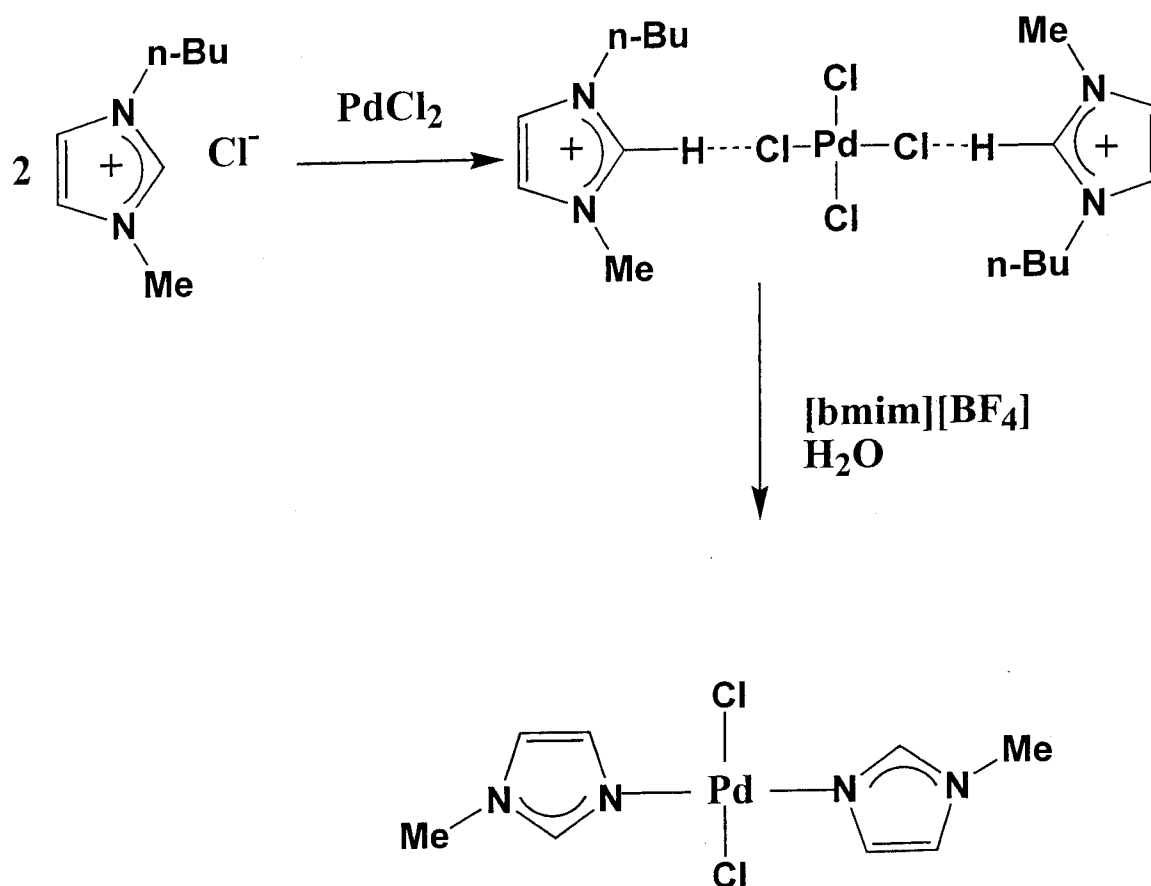
- The chiral catalyst gives asymmetrically hydrogenated 2-phenylacrylic acid and 2-(6-methoxy-2-naphthyl)acrylic acid<sup>3</sup>

## Selective Catalytic Hydrodimerization of 1,3-Butadiene



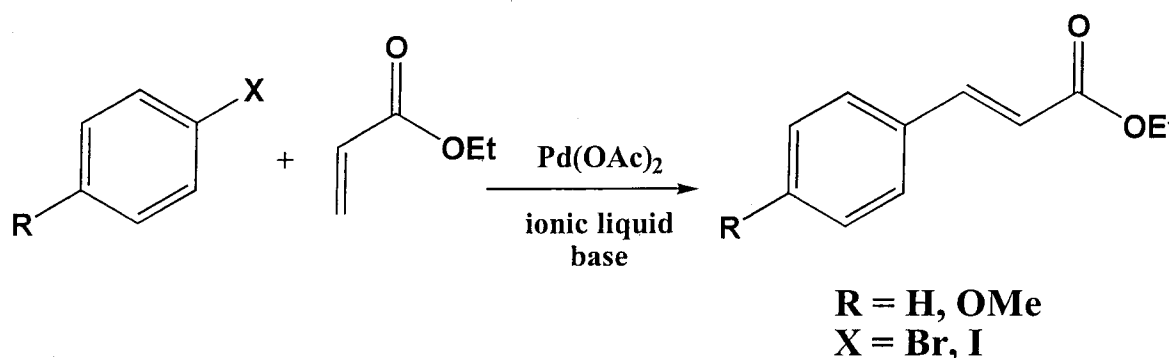
- Products' selectivity and catalytic activity depend on reaction conditions;
- 1,3-Butadiene conversion up to 28% and selectivity of 94% on telomer were achieved with  $(\text{Bmim})_2\text{PdCl}_4$  dissolved in  $[\text{Bmim}][\text{BF}_4]^4$
- Structure of catalyst precursor  $(\text{bmim})_2\text{PdCl}_4$  determined by X-ray diffraction analysis



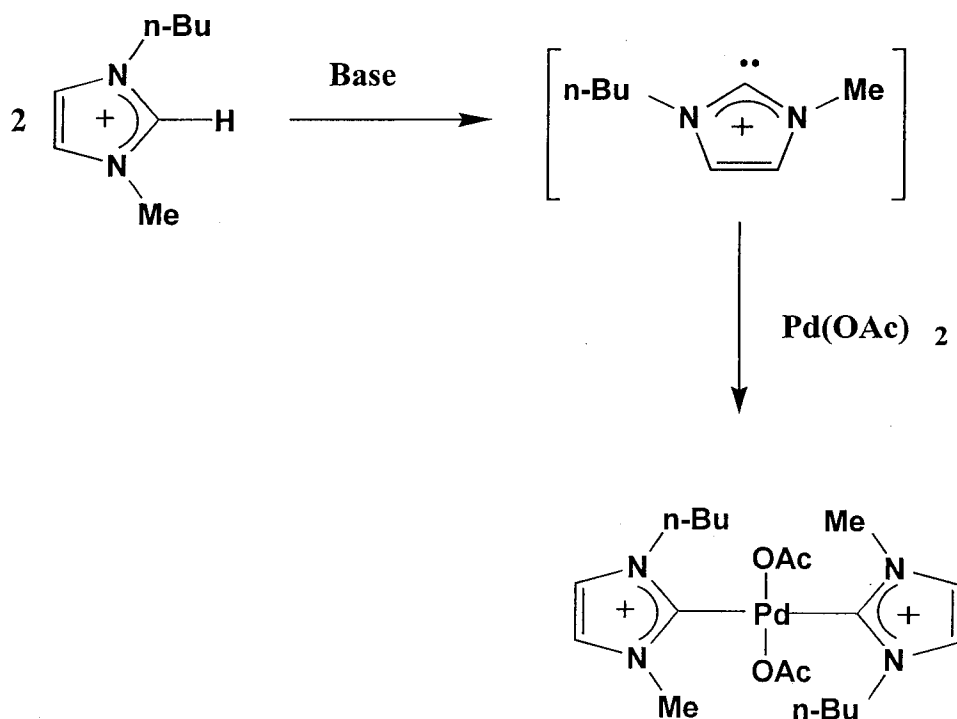


- The Pd compound was also isolated from the ionic catalyst solution after the catalytic reaction;
- Authors conclude that this is the true catalyst precursor on the hydrodimerization of 1,3-butadiene

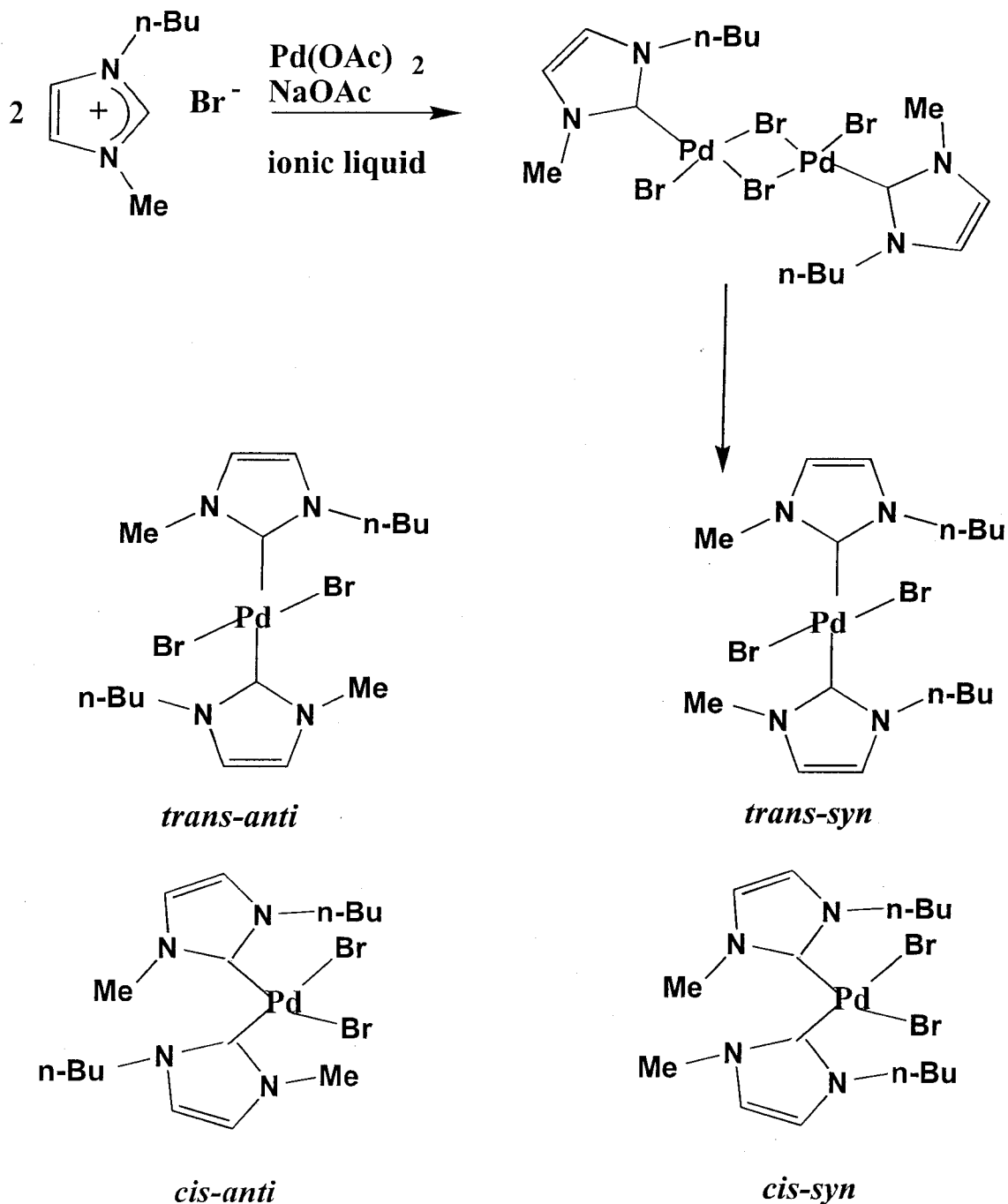
## Heck Reaction in Ionic Liquids



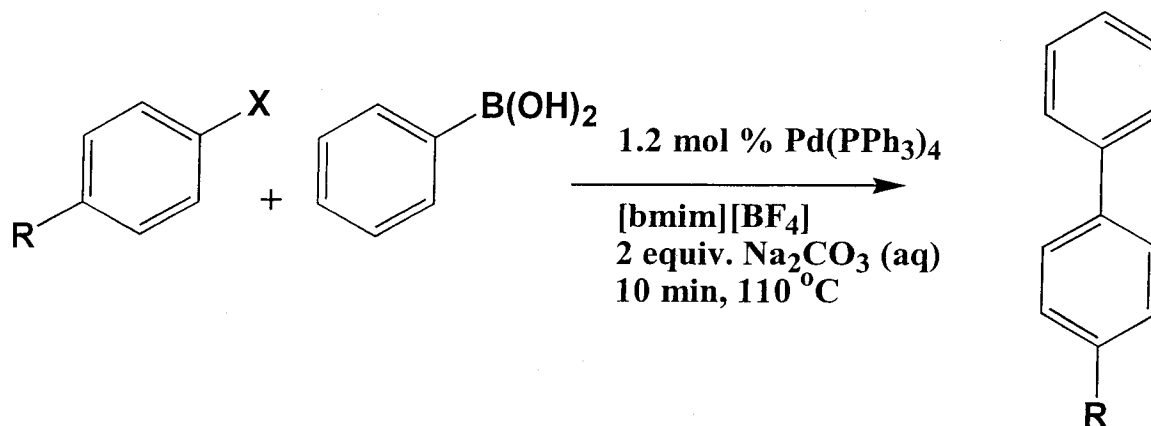
- Excellent yields in ionic liquids<sup>5</sup>
- IIs provide a medium that dissolves the Pd catalyst and allows the product and byproducts to be easily separated
- Reason for solubility of Pd catalyst is given below:



## *In Situ* Identification of N—Heterocyclic Carbene Complexes of Palladium<sup>6</sup>



## Palladium catalyzed Suzuki cross-coupling



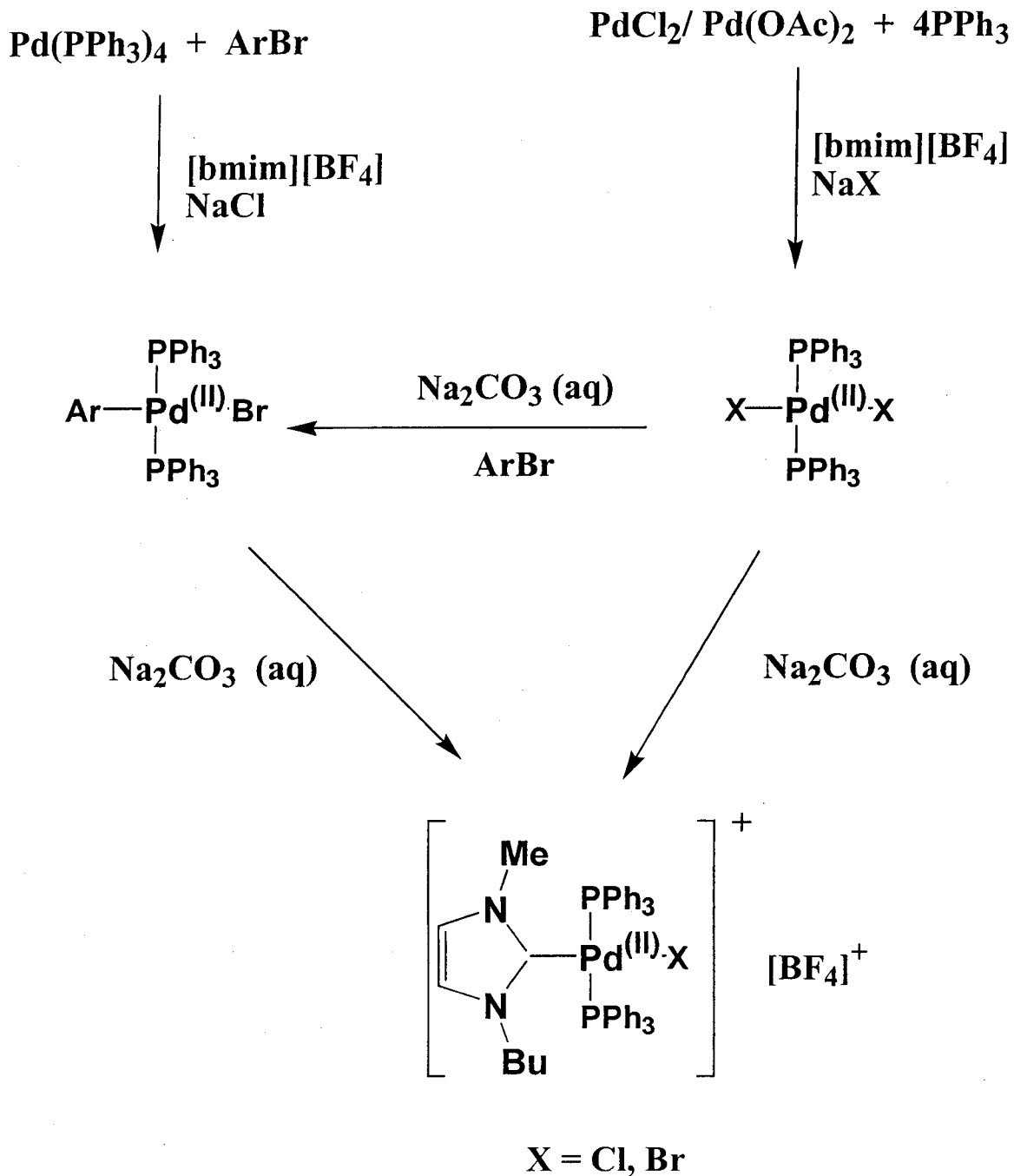
- Bromobenzene with phenylboronic acid under original Suzuki conditions affords biphenyl with 88% yield in 6 h;
- In [bmim][BF<sub>4</sub>] a 93% yield in 10 min;
- 4-methoxybiphenyl results in a 40% yield in 6 h in original conditions;
- In [bmim][BF<sub>4</sub>] an 81% yield in 10 min.<sup>7</sup>

### N.B.

- Reactions show a significant increase in reactivity at reduced catalyst concentration, esp. with respect to non-activated arylbromides;
- Homo-coupled products can be eliminated, affording isolated products in high purity;
- Reactions can be performed under air without loss of yield or catalyst decomposition;
- Procedures developed permit repetitive catalytic runs with loss of catalyst activity.



## *In Situ* formation of Mixed Phosphine-Imidazolylidene Palladium Complexes



Mathews et al.<sup>8</sup>

- (1) Welton, T. *Chemical Reviews*. 1999, *99*, 2071-2083.
- (2) Brown, R. A.; Pollet, P.; McKoon, E.; Eckert, C. A.; Liotta, C. L.; Jessop, P. G. *J. Am. Chem. Soc.* *122*(32):7638-7647, 2000 Aug 16 2001, *123*, 1254-1255.
- (3) Suarez, P. A. Z.; Dullius, J. E. L.; Einloft, S.; De Souza, R. F.; Dupont, J. *Polyhedron* 1996, *15*, 1217-1219.
- (4) Dullius, J. E. L.; Suarez, P. A. Z.; Einloft, S.; Desouza, R. F.; Dupont, J.; Fischer, J.; Decian, A. *Organometallics* 1998, *17*, 815-819.
- (5) Carmichael, A. J.; Earle, M. J.; Holbrey, J. D.; McCormac, P. B.; Seddon, K. R. *Organic Letters* 1999, *1*, 997-1000.
- (6) Xu, L. J.; Chen, W. P.; Xiao, J. L. *Organometallics* 2000, *19*, 1123-1127.
- (7) Mathews, C. J.; Smith, P. J.; Welton, T. *Chemical Communications*. 2000, *14*, 1249-1250.
- (8) Mathews, C. J.; Smith, P. J.; Welton, T.; White, A. J. P.; Williams, D. J. *Organometallics* 2001, in press.