

Ionic Liquid-Promoted Regioselective Catalysis by Palladium

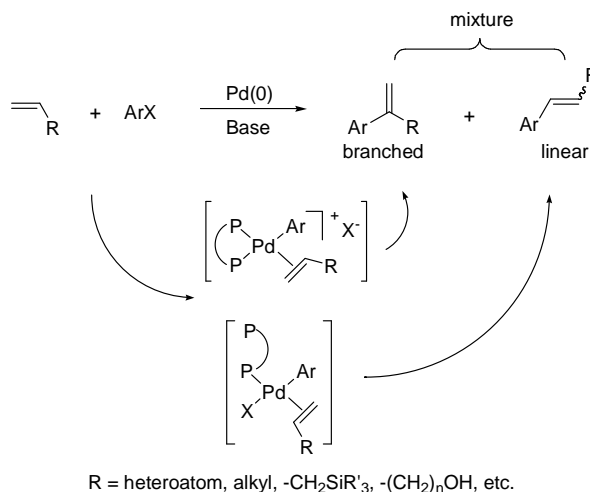
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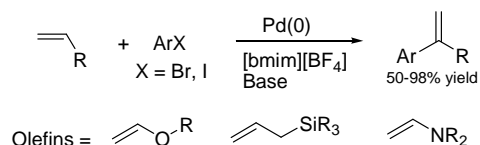
Palladium catalysed arylation and vinylation of olefins by aryl or vinyl halides, that is, the Heck reaction, is now one of the most important tools in synthetic chemistry. However, the reaction works well generally only with olefins bearing electron-withdrawing substituents such as CO_2R , CN, and Ph. With electron-rich olefins such as acyclic enol ethers, silanes, and enol amides, a mixture of linear and branched regioisomers usually results, thus limiting the wider applicability of the reaction in synthetic chemistry (Scheme 1). This is so, because it is believed that the reaction proceeds *via* two pathways, one ionic leading to the branched product and the other neutral giving rise to the linear variant. Scheme 1 shows the key intermediates involved in the two pathways proposed in the literature. The problem can be addressed by using aryl triflates or stoichiometric halide scavengers [Ag(OTf) and Tl(OAc) being most often used].¹ However, triflates are thermally labile and in general not commercially available and the inorganic additives create new problems, i.e. waste salts, toxicity and added cost.

In the course of our investigation into metal-catalysed reactions in imidazolium ionic liquids,² we have discovered that the ionic pathway, hence the production of branched olefins, can be promoted by the ionic liquid solvents.³ Thus, the palladium catalysed Heck arylation of a range of electron-rich olefins has been accomplished in the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF₄], using as the arylating agents aryl bromides and iodides instead of the commonly used, but commercially unavailable and expensive aryl triflates (Scheme 2). The reaction proceeded with high efficiency and remarkable regioselectivity without the need for costly or toxic halide scavengers, leading exclusively to the branched products. Several lines of evidence point to the unique regiocontrol stemming from the ionic environment provided by the ionic liquid, which alters the reaction pathway in such a way that the ionic mechanism is made favorable. The method is simple, highly effective and environmentally appealing and contributes to the extension of Heck reaction to a wider range of substrates. This presentation will address the full details of the reaction and our preliminary mechanistic studies.

Scheme 1



Scheme 2



References

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3. Xu, L.; Chen, W.; Ross, J.; Xiao, J. *Org. Lett.* **2001**, *3*, 295