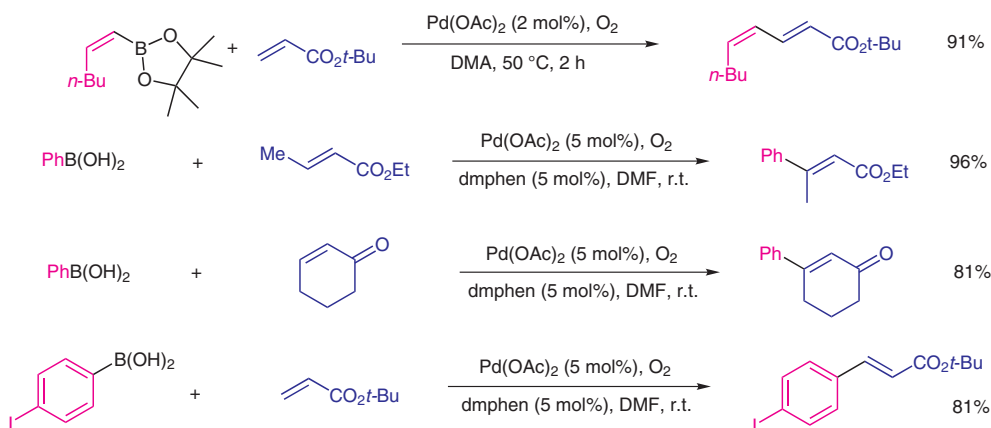
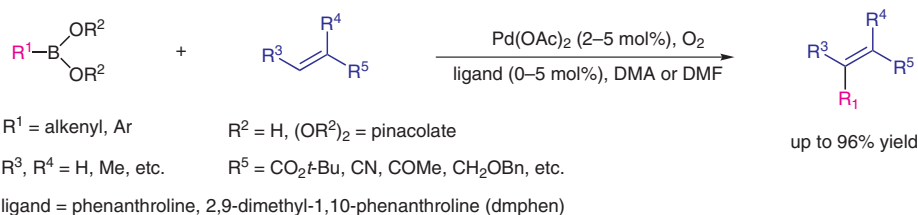


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Oxidative Palladium(II) Catalysis: A Highly Efficient and Chemoselective Cross-Coupling Method for Carbon–Carbon Bond Formation under Base-Free and Nitrogenous-Ligand Conditions

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Highly Efficient Pd-Catalyzed Oxidative sp^2 – sp^2 C–C Bond Formation



Significance: Herein, the authors report a novel approach to the formation of sp^2 – sp^2 C–C bonds, based on the oxidative Pd(II) catalysis. This method represents an alternative to the common Heck or Suzuki reactions, especially in the cases of polysubstituted olefins, for which these methods are less suitable. It represents an example of an oxidative addition of a carbon nucleophile to an alkene. Alkenyl- and arylboronic acids can be coupled in the presence of O_2 and a Pd catalyst with various alkenes, giving dienes or substituted styrenes in excellent yields. Inexpensive phenanthrolines are used as ligands for palladium. In many cases, this method outperforms the known ones for a new C–C bond formation.

Comment: Mechanistically, this reaction differs from the conventional Heck process. The formation of an alkenyl- or arylpalladium intermediate occurs from a peroxopalladium species [from Pd(0) and O_2] and an alkenyl- or arylboron compound without the formation of an ate complex. This explains the mild conditions required for the process. The following steps are a usual carbopalladation and β -hydride elimination. The configuration of the alkene double bond, therefore, is not conserved during the process. Interestingly, aza ligands were found superior to usual phosphines for this reaction.

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Category

Metal-Mediated
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