

The Heck Carbonylation: Palladium-Catalyzed Alkoxy carbonylation of Organic Halides

Category

Metals in Synthesis

Key words

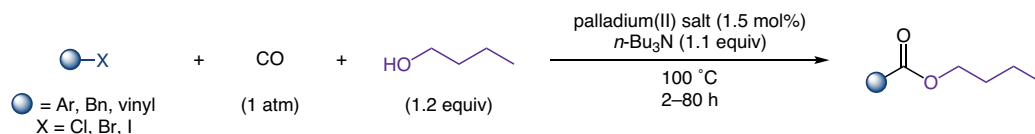
carboalkoxylation

carbon monoxide

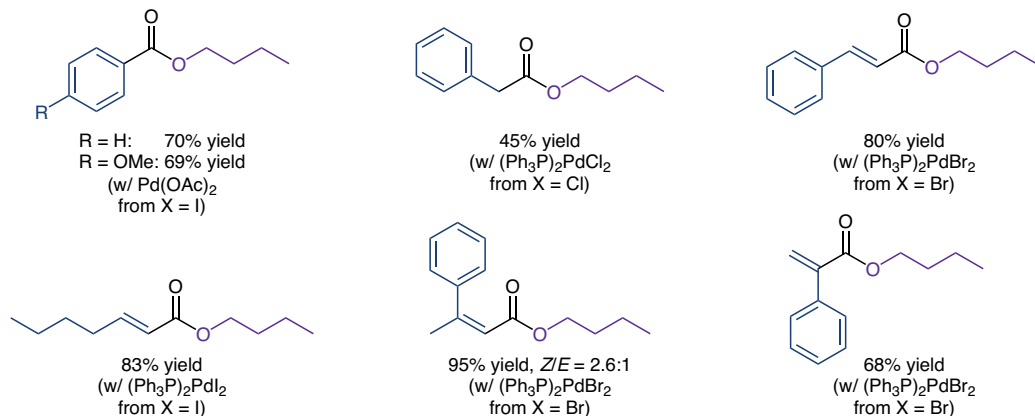
Heck carbonylation

palladium catalysis

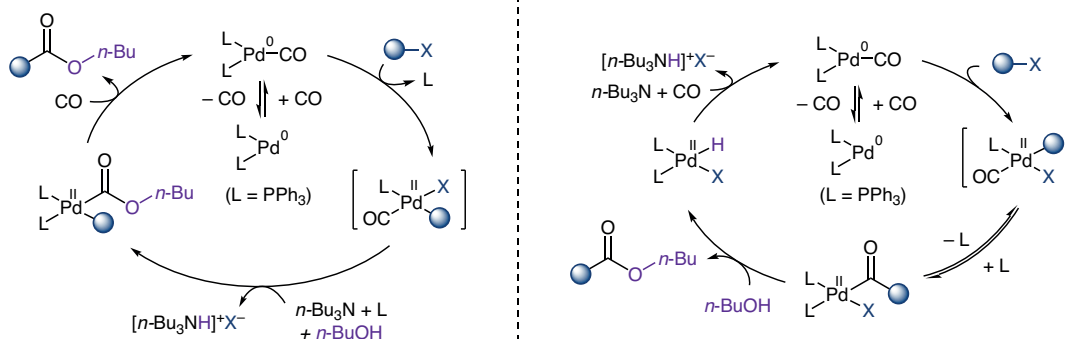
Synfact
Classic



Selected examples:



Proposed mechanism:



Significance: Two years after the invention of the famous Heck reaction (*J. Org. Chem.* **1972**, 37, 2320), Heck and co-workers reported the palladium-catalyzed alkoxy carbonylation of aryl, benzyl, and vinyl halides with an alcohol under a carbon monoxide atmosphere. This carbonylative coupling is broadly applicable and represents a pivotal transformation for the synthesis of esters.

Comment: Heck and co-workers proposed two possible mechanisms for the palladium-catalyzed alkoxy carbonylation (see scheme). The mixtures of alkene geometries observed in certain cases are likely due to a π -allylic palladium intermediate, which can lead to both *Z* and *E* products.