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Palladium-Catalyzed Carboalkoxylation of Aryl, Benzyl, and Vinylic Halides
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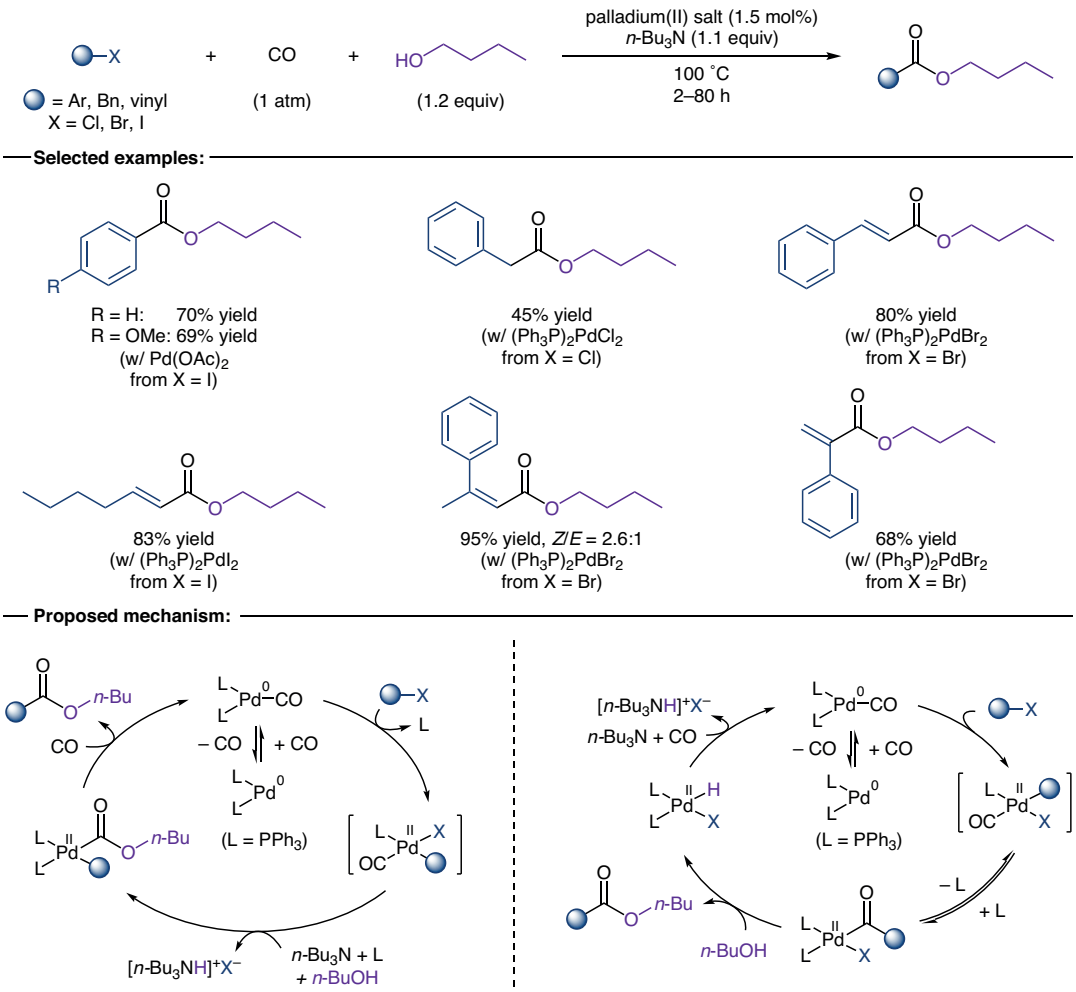
The Heck Carbonylation: Palladium-Catalyzed Alkoxycarbonylation of Organic Halides



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 alkoxycarbonylation 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 alkoxycarbonylation (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.

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