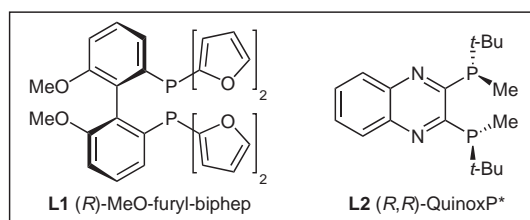
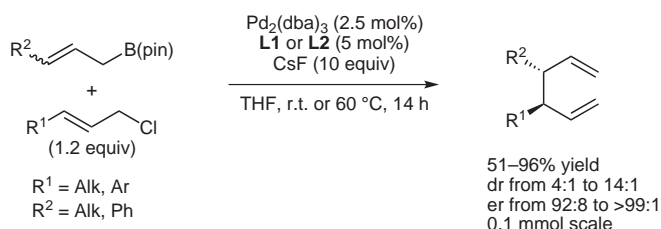
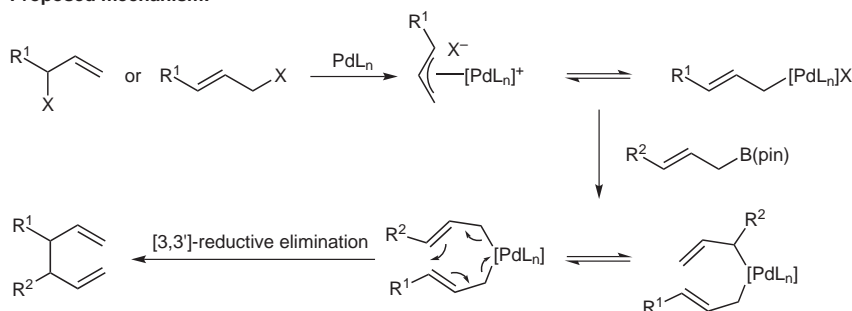


Palladium-Catalyzed Asymmetric Allyl–Allyl Cross-Coupling



Proposed mechanism:



Significance: The asymmetric allyl–allyl cross-coupling gives rise to products of the Cope rearrangement, for which no precedents of the catalytic enantioselective variant existed. Practical features are the facile formation of allyl chlorides from the corresponding alcohol without purification, and that the alkene geometry of the crotyl boronate does not need to be defined to afford the same stereochemical outcome. It is noteworthy that excellent catalyst control is required to favor the desired [3,3]-reductive elimination pathway versus the alternative [1,1'] pathway. High enantioselectivity and diastereoselectivity are additional features.

Comment: While **L1** can provide excellent reactivity with cinnamyl chlorides ($R^1 = \text{Ar}$), **L2** is found to be more suitable for non-aromatic allyl chlorides ($R^1 = \text{Alk}$). Secondary allyl chlorides are also competent in the reaction, though they generally give lower yields. The highly versatile reactivity with regards to crotyl boronate alkene geometry and secondary versus primary allyl chlorides is rationalized in the proposed mechanism. A series of isomerizations occur for the allyl fragments on the palladium complex to minimize steric effects prior to the enantio-discriminating [3,3]-reductive elimination step.