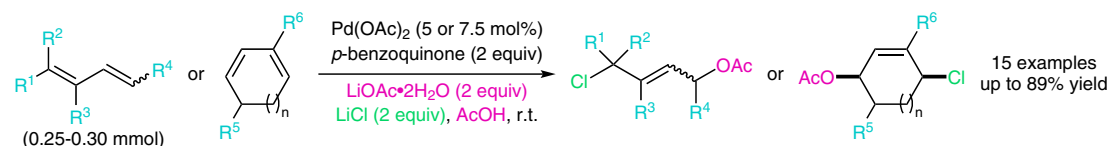


J.-E. BÄCKVALL*, J.-E. NYSTRÖM, R. E. NORDBERG (ROYAL INSTITUTE OF TECHNOLOGY, STOCKHOLM, SWEDEN)

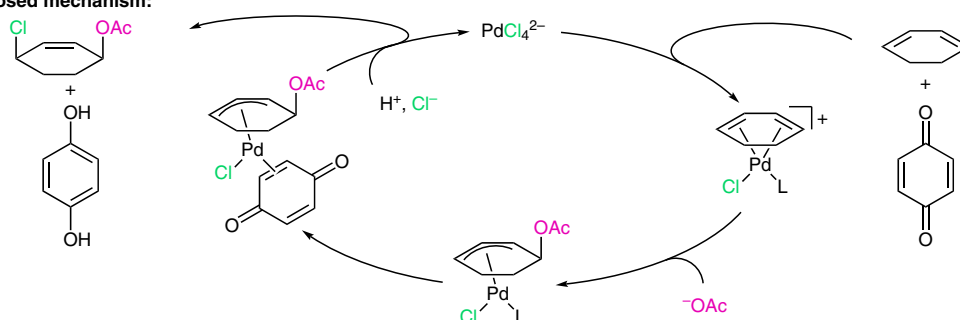
Stereo- and Regioselective Palladium-Catalyzed, 1,4-Acetoxychlorination of 1,3-Dienes. 1-Acetoxy-4-chloro-2-alkenes as Versatile Synthons in Organic Transformations

J. Am. Chem. Soc. **1985**, *107*, 3676–3686, DOI: 10.1021/ja00298a043.

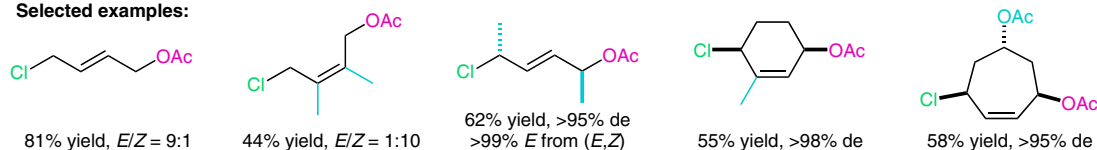
1,4-Acetoxychlorination of Dienes: The Bäckvall Reaction



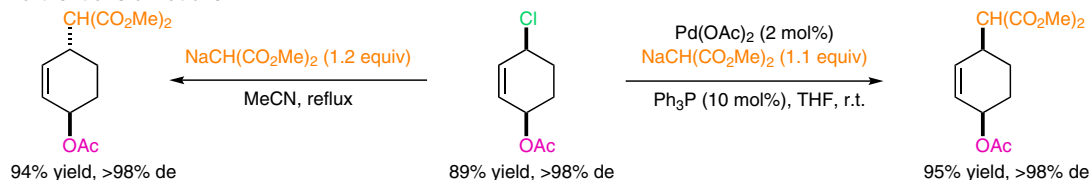
Proposed mechanism:



Selected examples:



Further transformations:



Significance: Bäckvall and co-workers reported the regioselective 1,4-acetoxychlorination of 1,3-dienes using palladium catalysis under mild oxidative conditions. While cyclic dienes reacted with a lower palladium loading and with high stereoselectivity for the *cis*-isomer, large R^2 or R^3 substituents increased the amount of (*Z*)-isomer for acyclic dienes. The stereospecific nature of the reaction was shown using two isomers of the same diene (*E,E* and *E,Z*) to give the *syn*- and *anti*-diastereomers, respectively, with high selectivity.

Comment: Synthetic utility was demonstrated by reaction of the product with nucleophiles under metal-catalyzed or S_N2 conditions, to give products with retention or inversion of stereochemistry, respectively. Through investigation of reaction rates, a first-order dependence of *p*-benzoquinone (BQ) was observed, suggesting the coordination of BQ to palladium facilitates the external *trans*-attack by chloride. The authors proposed that the regioselectivity of the reaction was governed by thermodynamic considerations.