Isomerization of Allylrhodium Intermediates During Allylations of Imines

Significance: The authors present a 1,4-rhodium(I) migration of allylrhodium intermediates which then react with cyclic imines to yield the alkylation product with three stereochemical elements with high selectivity. Using a chiral diene–rhodium catalyst the reaction can be performed enantioselectively. The significance of this work is the generation of stereochemically more complex products from simple starting material through rhodium(I)-catalyzed isomerization processes.

Comment: The reaction is favored in combination of two factors: 1) the steric hindrance of the initially formed allylrhodium species, and 2) the reactivity of the imine such that normal alkylation is disfavored. Through the deuterium-labeling experiments it is proposed that the 1,4-rhodium(I) migration (3a → 3b) occurs by a C–H oxidative addition–reductive elimination sequence via intermediate I.