

Rhodium-Mediated Substrate Controlled Markovnikov and Anti-Markovnikov Hydroamination

Seth C. Ensign and Kami L. Hull

The catalytic addition of an amine across an unsaturated carbon-carbon bond has been one of the most intractable challenges in organometallic chemistry for decades. Hydroamination is particularly appealing as an atom-economical solution. However, this seemingly facile reaction is complicated by high activation energies and highly negative entropy values. To promote this otherwise demanding transformation, we have shown that remote Lewis-basic directing groups can be used to bind the metal center and increase the reactivity of an otherwise electronically unactivated olefin. In addition, this group often enforces a high degree of regioselectivity as it proceeds through a favored metallacycle intermediate.

N-allyl imines undergo Rh-catalyzed hydroamination to form 1,2-diamines and the Markovnikov product while homoallyl amines form 1,4-diamines and the anti-Markovnikov product. These reactions are tolerant of a variety of secondary cyclic amines, are functional group tolerant and (in the case of N-allyl imines) show a high degree of diastereoselectivity. The formation of 1,4-diamines to generate the anti-Markovnikov product represents an unprecedented report of a rhodium-catalyzed transformation.

