

The Versatility of Nickel Cycloaddition Catalysts

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Transition metal catalysts possess the profound ability to mediate transformations that are otherwise energetically prohibited. They can accelerate chemical reactions, exert remarkable kinetic control over product distribution, and provide an environmentally friendly method for preparing products with normous synthetic utility. Towards this end, our group has recently discovered and developed a highly active Ni(0) catalyst that effectively mediates a variety of cycloaddition and isomerization reactions. For example, when ligated with electron rich, sterically-hindered *N*-heterocyclic carbenes, Ni⁰ facilitates the cycloaddition between unsaturated hydrocarbons (e.g. diynes, enynes) and heterocumulenes (such as CO₂ and isocyanates) as well as other derivatives (such as aldehydes, ketones, and nitriles) to afford a variety of substituted heterocycles (such as pyrones, pyridones, pyrans, and pyridines, respectively). In addition, the same catalyst system can be applied for the isomerization of vinyl cyclopropanes and the rearrangement of cyclopropylen-yne. Importantly, all reactions proceed under extremely mild conditions (room temperature, atmospheric pressures, and short reaction times), require only catalytic amounts of Ni/NHC and readily available starting materials, and afford annulated products in excellent yields (eqs. 1-6). The mechanistic details of these processes, and their potential utility in allowing access to useful molecules direct from easily prepared components, will be discussed.

