Asymmetric Coupling of 1,3-Dienes and *C*-Nucleophiles by Ni/Cu Cooperative Catalysts Bearing Planer Chiral Diphosphine Ligand

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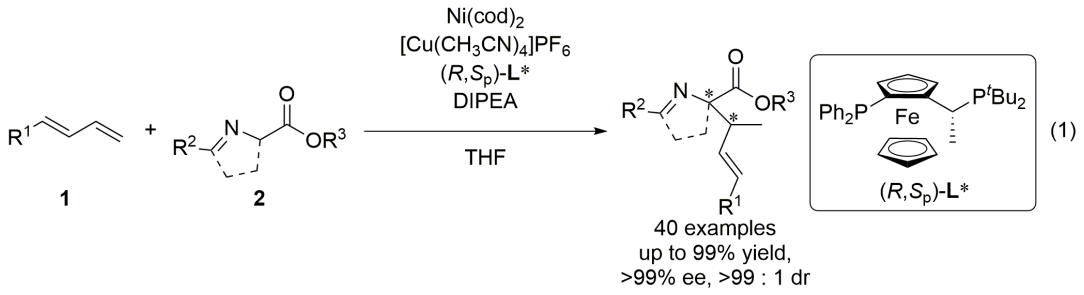
Keywords: Nickel; Copper; π-Allyl Complex; Enolate Complex; Asymmetric Allylic Alkylation

Asymmetric hydrofunctionalization of 1,3-dienes with *C*-nucleophiles is one of atom- and step-economical reactions to construct a chiral quaternal carbon center in high yield and high enantioselectivity. Such the reaction has mainly been demonstrated by using noble Pd and Rh catalysts,[1] and the catalytic system using earth abundant metals such as first-row transition metals is highly demanded.[2] Herein, we report that a combination of two metals, Ni and Cu, in the presence of chiral JOSIPHOS-type diphosphine ligand **L*** became a cooperative catalyst for asymmetric coupling of 1,3-dienes **1** and low-activated *C*-nucleophiles **2** to generate vicinal stereocenters in high yields and high stereoselectivities (eq. 1). We propose a reaction mechanism through two catalytic cycles, *i.e.*, the Ni cycle for activation of diene **1** to form allylic intermediate, and the Cu cycle for deprotonation of *C*-nucleophiles **2** based on controlled experiments and kinetics. In fact, we isolated a cationic Ni(II) π-allyl complex by treating $Ni(cod)_2$ with **L***, diene **1**, and ammonium salt, and a Cu(I) enolate complex by reacting Cu(I) precursor, **L***, and the potassium enolate of **2**. Their solid structures were characterized by spectral data along with X-ray single crystal analyses. Stoichiometric reaction of these isolated Ni and Cu complexes gave the desired coupling product under room temperature, indicating that the both two complexes were key reaction intermediates. In addition, we conducted kinetic studies and control experiments using a deuterated *C*-nucleophile.



1) For reviews, see, Adamson, N. J.; Malcolmson, S. J. *ACS Catal.* **2020**, *10*, 1060. 2) For examples of Ni catalyzed reactions, see, (a) Cheng, L.; Li, M.-M.; Xiao, L.-J.; Xie, J.-H.; Zhou, Q.-L. *J. Am. Chem. Soc.* **2018**, *140*, 11627; (b) Shao, W.; Besnard, C.; Guénée, L.; Mazet, C. *J. Am. Chem. Soc.* **2020**, *142*, 16486.