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Diaminophosphine Oxide Ligand Enabled Asymmetric Nickel-Catalyzed Hydrocarbamoylations of Alkenes *J. Am. Chem. Soc.* **2013**, *135*, 11772–11775.

Asymmetric Nickel-Catalyzed Hydrocarbamoylation of Alkenes

Significance: Secondary phosphine oxides (SPO's) have demonstrated to be versatile and robust preligands in a variety of transition-metal-catalyzed transformations due to their stability to air and moisture (see Review below). The authors report the development of a heterobimetallic catalyst system consisting of aluminum and nickel scaffolded on a chiral SPO tether, which enables the enantioselective intramolecular hydrocarbamoylation of alkenes. This method provides access to enantioenriched pyrrolidones.

Review: N. V. Dubrovina, A. Börner *Angew. Chem. Int. Ed.* **2004**, *43*, 5883–5886.

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Comment: The reaction is believed to initiate via tautomerization of pentavalent phosphine oxide 2 to its trivalent phosphinous acid form, 2', which can react with Me₃Al and form complex A. Coordination to nickel(0) generates the active heterobimetallic catalyst B, which complexes to substrate 1a via the Lewis acidic aluminum center, activating the formyl group towards insertion. Following oxidative addition of nickel into the C–H bond, migratory insertion of the pendent olefin and reductive elimination regenerate the catalyst and furnish pyrrolidone 3a.

Category

Metal-Catalyzed Asymmetric Synthesis and Stereoselective Reactions

Key words

hydrocarbamoylation

phosphine oxide ligands

bimetallic catalysis