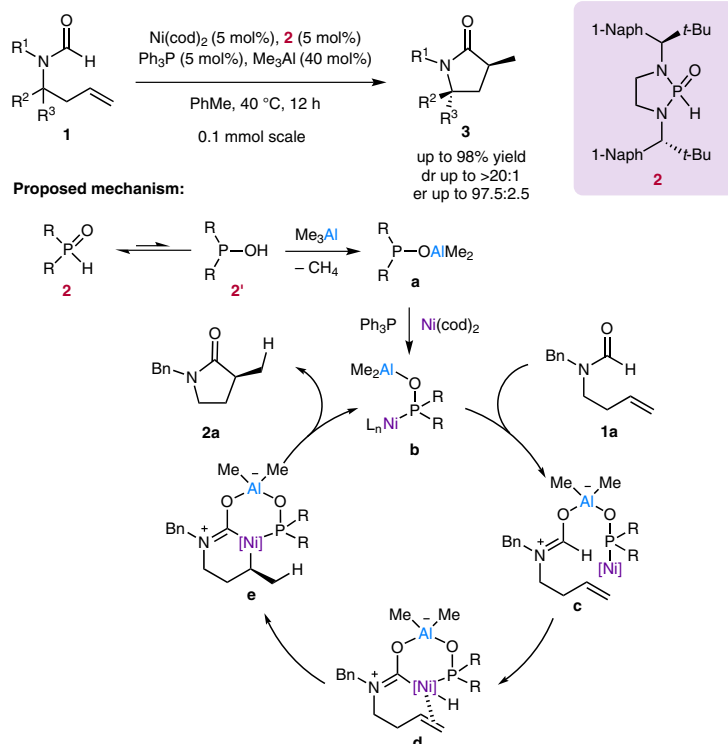


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Diaminophosphine Oxide Ligand Enabled Asymmetric Nickel-Catalyzed Hydrocarbamylation of Alkenes
J. Am. Chem. Soc. **2013**, *135*, 11772–11775.

Asymmetric Ni-Catalyzed Hydrocarbamylation of Alkenes



Significance: Secondary phosphine oxides (SPOs) have demonstrated to be versatile and robust pre-ligands 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 hydrocarbamylation of alkenes. This method provides access to enantioenriched pyrrolidones.

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

Comment: The reaction is believed to initiate via tautomerization of pentavalent phosphine oxide **2** to its trivalent phosphinuous 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 regenerates the catalyst and furnishes pyrrolidone **2a**.

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Category

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Reactions

Key words

hydrocarba-
moylation

secondary
phosphine oxide
ligand

bimetallic catalysis

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of the month

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