Asymmetric Ni-Catalyzed Hydrocarbamoylation 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 hydrocarbamoylation of alkenes. This method provides access to enantioenriched pyrrolidones.


**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 Me$_3$Al 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.

**Proposed mechanism:**

1. Tautomerization of pentavalent phosphine oxide 2 to trivalent phosphinous acid 2′.
2. Reaction with Me$_3$Al to form complex a.
3. Coordination to nickel(0) to generate active heterobimetallic catalyst b.
4. Complexation to substrate 1a via the Lewis acidic aluminum center.
5. Oxidative addition of nickel into the C–H bond.
6. Migratory insertion of the pendent olefin.
7. Reductive elimination regenerates the catalyst and furnishes pyrrolidone 2a.