Cobalt-Catalyzed Enantioselective Hydrogenation of Enamides

**Significance:** On the basis of a discovery from high-throughput reaction studies, the authors have developed a low-catalyst-loading enantioselective hydrogenation of functionalized alkenes through activation by zinc instead of the more-usual alkyl reagents. The optimized catalytic system CoCl₂·6H₂O/(R,R)-Ph-BPE or CoCl₂·6H₂O/(R,R)-i-Pr-DuPhos realized a high reactivity and enantioselective hydrogenation in MeOH.

**Comment:** A series of mechanistic studies revealed that Co(II) metal dissociates from the Co(II)/phosphine complex in MeOH, and that Zn reduces Co(II) to Co(I) through one-electron reduction to form a more stable Co–phosphine bond, which is key to the efficient enantioselective reduction of alkenes. The hydrogenation can be applied to a large-scale reaction requiring only 0.08 mol% of the cobalt catalyst.