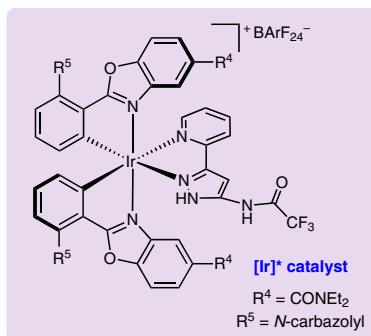
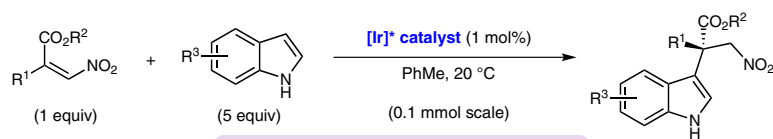


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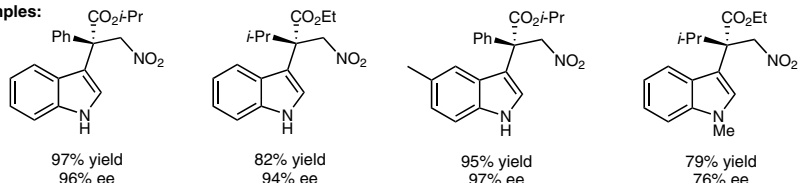
L.-A. CHEN, X. TANG, J. XI, W. XU, L. GONG,* E. MEGGERS* (XIAMEN UNIVERSITY, P. R. OF CHINA AND PHILIPPS-UNIVERSITÄT MARBURG, GERMANY)
Chiral-at-Metal Octahedral Iridium Catalyst for the Asymmetric Construction of an All-Carbon Quaternary Stereocenter
Angew. Chem. Int. Ed. **2013**, *52*, 14021–14025.

Chiral-at-Metal Iridium Catalyst for the Asymmetric Conjugate Addition



20 examples
72–97% yield
up to 98% ee

Selected examples:



Significance: In the majority of transition-metal-catalyzed asymmetric transformations, chiral information is typically stored within the ligand framework. In comparison, the use of chiral-at-metal complexes for enantioselective catalysis is a relatively unexplored area (see Review below). This particular report outlines the use of an inert chiral-at-metal iridium catalyst for the asymmetric conjugate addition of indoles to β,β' -disubstituted nitroolefins, allowing access to all-carbon quaternary centers in high ee. The iridium(III) complex functions completely as a nonbonding catalyst and can be applied in loadings as low as 0.5 mol%.

Review: E. B. Bauer *Chem. Soc. Rev.* **2012**, *41*, 3153–3167.

SYNFACTS Contributors: Mark Lautens, Christine M. Le
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Comment: Previously, the authors reported the synthesis of a structurally related chiral-at-metal iridium complex, which functions as a hydrogen bonding catalyst for the asymmetric transfer hydrogenation of nitroalkenes (*J. Am. Chem. Soc.* **2013**, *135*, 10598). In both catalyst designs, an amidopyrazole moiety serves to activate the nitroalkene component. In this report, nucleophilic activation is presumed to occur through a hydrogen bonding contact between the indole N–H bond and an amide group on the catalyst. Lower enantioselectivity was observed in the case of *N*-methyl indole, suggesting the importance of this single hydrogen bond in the enantiodetermining addition step.