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Asymmetric Catalysis with an Inert Chiral-at-Metal Iridium Complex
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Asymmetric Transfer Hydrogenation of Nitroalkenes by an Iridium Complex

Category

Metal-Catalyzed
Asymmetric
Synthesis and
Stereoselective
Reactions

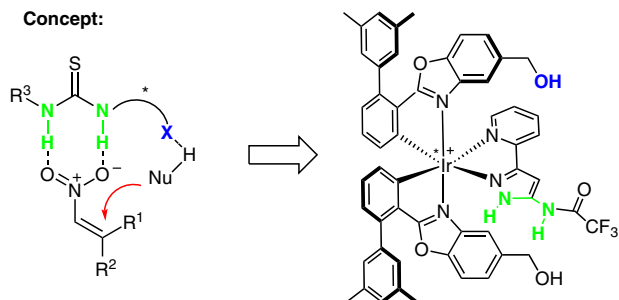
Key words

asymmetric
hydrogenation

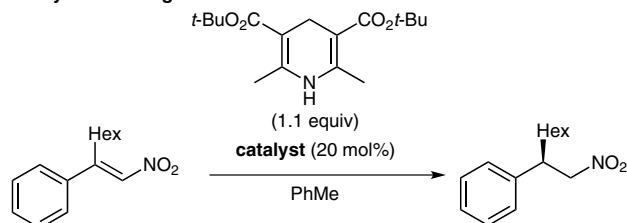
non-covalent
catalysis

iridium

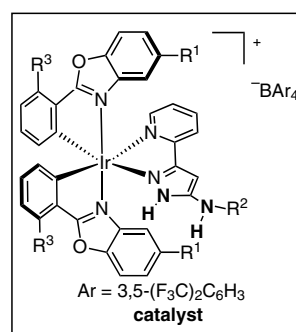
Concept:



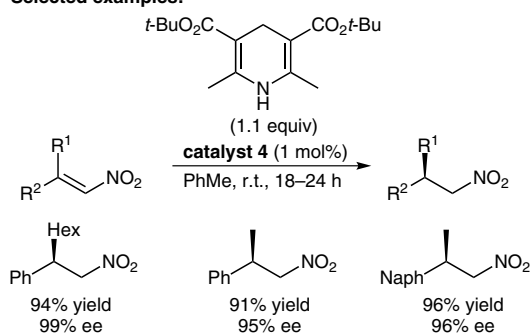
Catalyst screening:



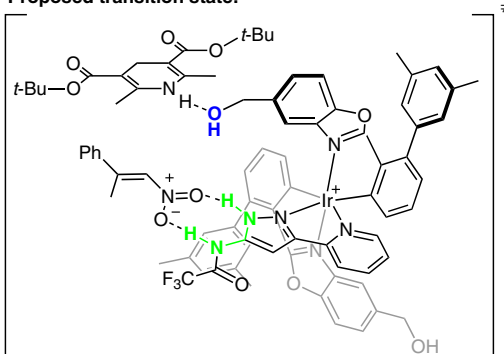
cat. 1 ($R^1 = \text{CH}_2\text{OH}$, $R^2 = \text{H}$, $R^3 = \text{H}$) 63% ee
cat. 2 ($R^1 = \text{CH}_2\text{OH}$, $R^2 = \text{Ph}$, $R^3 = \text{H}$) 84% ee
cat. 3 ($R^1 = \text{CH}_2\text{OH}$, $R^2 = \text{COCF}_3$, $R^3 = \text{H}$) 90% ee
cat. 4 ($R^1 = \text{CH}_2\text{OH}$, $R^2 = \text{COCF}_3$, $R^3 = 3,5\text{-Me}_2\text{C}_6\text{H}_3$) 99% ee
cat. 5 ($R^1 = \text{H}$, $R^2 = \text{Ph}$, $R^3 = \text{H}$) 0% ee



Selected examples:



Proposed transition state:



Significance: The authors reported a highly efficient asymmetric transfer hydrogenation of nitroalkenes by a bis-cyclometalated iridium complex. This catalyst exceeds the performance of most organocatalysts with respect to enantiomeric excess (up to 99% ee) and catalyst loading (down to 0.1 mol%).

SYNFACTS Contributors: Hisashi Yamamoto, Masahiro Sai
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Comment: Inspired by the design of non-covalent organocatalysts, the authors prepared a substitutionally inert bis-cyclometalated iridium complex. In the catalyst, the pyrazole moiety acts as a double hydrogen-bond donor for the nitroalkene, whereas a hydroxy group serves as a hydrogen-bond acceptor for the Hantzsch ester.