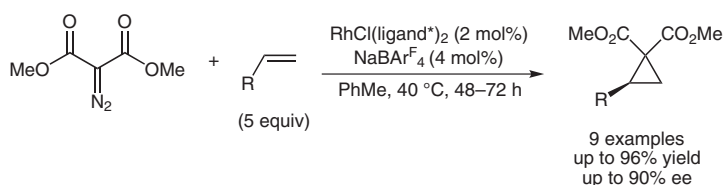


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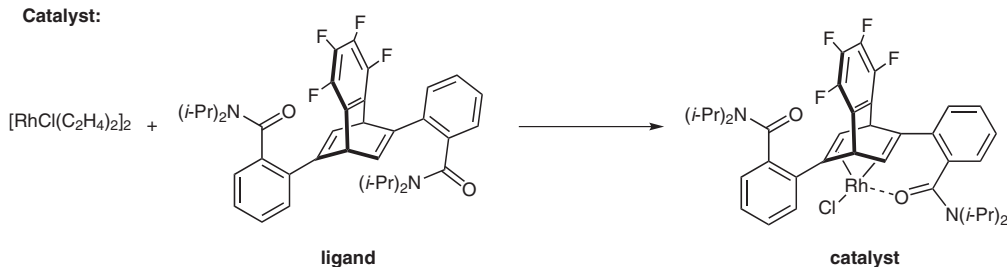
Asymmetric Cyclopropanation of Alkenes with Dimethyl Diazomalonate Catalyzed by Chiral Diene–Rhodium Complexes

Angew. Chem. Int. Ed. 2010, 49, 7324–7327.

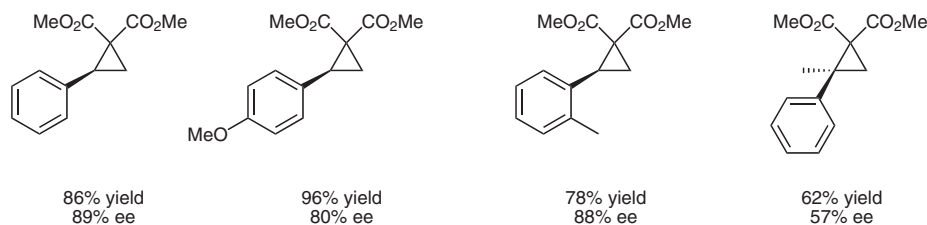
Asymmetric Cyclopropanation Using Dimethyl Diazomalonate



Catalyst:



Selected examples:



Significance: Many well-developed dirhodium(II) carboxamidates and carboxylates exist for highly enantioselective cyclopropanations of alkenes with diazo compounds (see Review below). Due to often low reactivity and enantioselectivity no highly asymmetric cyclopropanation using diazomalonates exists. The authors discovered that chiral cyclopropane *gem*-diesters can be prepared in good yields and enantioselectivities by using a cationic chiral rhodium–diene complex.

Review: H. Pellissier *Tetrahedron* 2008, 64, 7041–7095.

Comment: The authors screened a number of existing ligands for the title transformation, but an effective catalyst was not found. By placing amide groups on the *ortho* position of their previously developed tetrafluorobenzobarrelene ligands, good yields and enantioselectivities were obtained. X-ray crystallographic analyses of the complexes show a coordination of one of the amide oxygens to rhodium in the neutral complex, and both amide oxygens coordinating in the in situ formed cationic species. This structural feature is proposed to be crucial for the high reactivity.

SYNFACTS Contributors: Mark Lautens, Stephen G. Newman
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Category

Metal-Catalyzed
Asymmetric
Synthesis and
Stereoselective
Reactions

Key words

chiral dienes
cyclopropanation
rhodium

SYNFACTS
of the month