ORGANIC SEMINAR

Catalytic Stereocontrolled Carbene and Vinylidene Transfer Reactions

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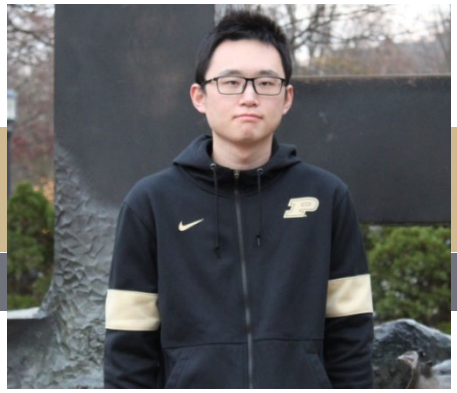
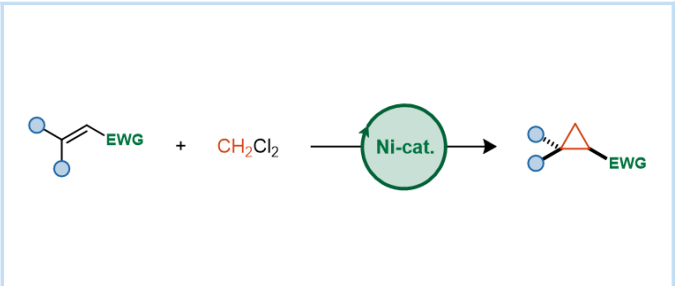


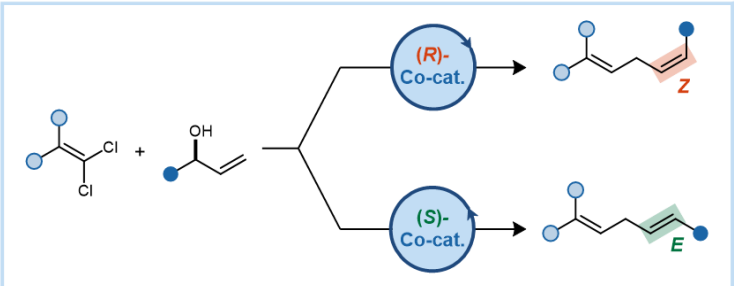
Carbenes are useful C1 synthons in a variety of cycloaddition and bond insertion reactions. *gem*-Dihaloalkanes are an emerging class of carbene precursors that are readily available and do not require stabilizing groups. A (PyBox)Ni catalyst is able to activate CH_2Cl_2 to generate a nucleophilic nickel carbene, which is used in cyclopropanation reactions of a wide range of electron-deficient alkenes. By using a chiral PyBox ligand, asymmetric cyclopropanations can be carried out for the synthesis of arylcyclopropyl esters, which are important pharmaceutical intermediates. Mechanistic studies indicate that a triplet nickel carbene reacts with the alkene substrate in a stepwise [2 + 2]-cycloaddition/C–C reductive elimination pathway. The absolute stereochemistry of the reaction can be rationalized by DFT models.

A (PyBox)Co catalyst activates 1,1-dichloroalkenes to generate a cobalt vinylidene species, which reacts with a chiral allylic alcohol to give a 1,4-diene product through a [2 + 2]-cycloaddition/*anti*-β-O elimination pathway. The *E* and *Z* isomers of the 1,4-diene can be selectively prepared by using different enantiomers of the PyBox ligand. This strategy can be used in the synthesis of bioactive molecules that contain the 1,4-diene moiety.

Nickel Catalyzed Nucleophilic Cyclopropanations with CH_2Cl_2



Cobalt Catalyzed Stereodivergent Synthesis of 1,4-Dienes



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PURDUE UNIVERSITY | James Tarpo Jr. and Margaret Tarpo Department of Chemistry