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Digest paper

Recent advances on catalytic asymmetric difunctionalization of 1,3-dienes

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ABSTRACT

1,3-Dienes and derivatives are either feedstock chemicals or easily available materials. Catalytic difunctionalization of 1,3-diene is one of the most powerful methods for carbon—carbon bond formation with rapid increase of the molecular complexity and synthetic value in an atom economic way. By choosing proper metals and chiral ligands, a variety of catalytic asymmetric difunctionalization of conjugated dienes in a highly regioselective fashion have been reported. In this digest review, we will summarize recent advances on this topic based on different metals. We will also introduce unique phenomena that include reversal of regio- and diastereoselectivity.

Contents

Introduction

Selective functionalization of 1,3-dienes are important reactions in organic synthesis, because 1,3-dienes are feedstock chemicals and especially butadiene is produced in more than 10 million tons per year worldwide.[1] Concerted cycloadditions may be the most widely used method for diene reactions, stepwise catalytic enantioselective reactions exhibit high synthetic potentials, but still limited in number and classes.[2] In recent years, electrophilic addition of a organometal species to diene leading to a monofuncationalized π-allylic intermediate followed by a nucleophilic attack at one of the allylic carbons leads to a 1,2- or 1,4-addition is an active research field.[3] It is of importance while challenge to control the regioselectivity toward 1,2- or 1,4-addition and a mixtures of 1,2- and 1,4-regioisomers are often produced.[4] In contrast to the employment of classical electrophilic reagent, with the use of proper transition metals, highly regioselective additions to

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conjugated dienes can be obtained.[5] From a synthetic point of view, it is of more importance if these additions are asymmetric by using proper chiral ligands. Converting the feed stock chemicals to optically pure fine chemicals would greatly enhance the synthetic values of the methods. Currently, several excellent reviews and articles have been published which include palladium-catalyzed additions to conjugated dienes.[6] This review introduces different metal-catalyzed reactions leading to enantioselective difunctionalization in the 1,2- or 1,4 positions of 1,3-dienes. Eight metal catalysts are arranged by the number of frequency, beginning with 8 examples for Pd, followed by 4 examples for Cu, and 4 examples for Ni, and so on.

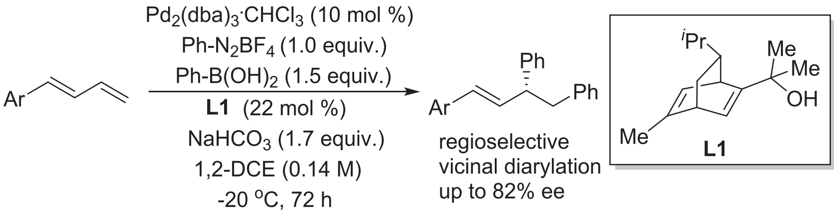
Palladium-catalyzed asymmetric difunctionalization of 1,3-dienes

Palladium(II) salts are the most studied metals to activate carbon—carbon double bonds toward nucleophilic attack.[7] And this is the basis for the Wacker process for industrial oxidation of ethylene to acetaldehyde. Nonetheless, reaction parameters have to be carefully tuned in order to achieve high selectivity in difunctionalization of 1,3-dienes. In 2014, Sigman and co-workers established a Pd(0)-catalyzed intermolecular vicinal diarylation of terminal 1,3-dienes using aryldiazonium tetrafluoroborates and arylboronic acids. Using this strategy, two different arenes are regioselectively introduced in a vicinal fashion across the terminal alkene of a variety of terminal 1,3-dienes at ambient temperature. In the presence of a chiral bicyclo[2.2.2]octadiene ligand **L1** at −20 °C, good enantioselectivity has also been achieved, albeit at the cost of yield. This study open new possibilities to asymmetric difunctionalization of 1,3-dienes using palladium catalyst (Scheme 1).[8]

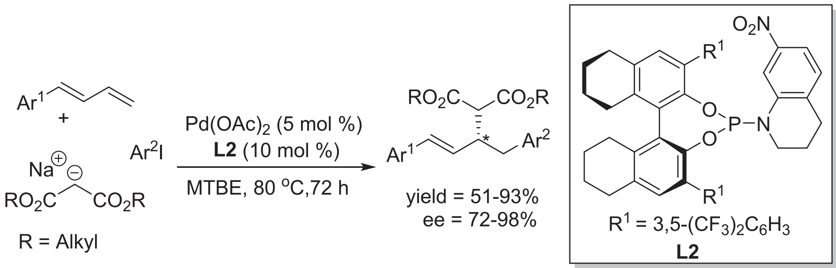
In 2015, Gong and co-workers advanced a highly efficient Pd-catalyzed enantioselective three-component coupling of 1,3-dienes with aryl iodines and stabilized carbon nucleophiles (sodium dialkyl malonates). BINOL-based phosphoramidite ligand **L2** was established to be the most effective chiral ligand for this chemistry, which not only provides high catalytic activity but also is able to efficiently control the regio and stereoselectivity (Scheme 2). The reaction is proposed to proceed via a Pd-catalyzed cascade arylation and asymmetric allylic alkylation involving two different types of π-allyl-Pd intermediates. A broad scope of substrates, including 1,3-dienes and iodoaryl compounds are tolerated.[9]

The asymmetric allylation reaction of carbonyl compounds (mainly aldehydes) with allylic reagents is one of the most important reactions, affording synthetically useful homoallylic alcohols which can undergo further transformations due to the presence of a double bond.[10] Considerable efforts have been devoted to the development of enantioselective allylation of carbonyl compounds.[11] In 2016, Gong and coworkers developed a highly selective multicomponent carbonyl allylation reaction of 1,3-dienes, aryldiazonium tetrafluoroborates, and aldehydes enabled by a dual catalysis of palladium acetate and chiral anion phase transfer agent. Interestingly, chiral phosphoric acid **L3** is sole chiral element to control the stereoselectivity including the *Z*-configuration and high levels of enantioselectivity (Scheme 3). The reaction tolerates a wide range of substrates leading to enantioenriched homoallylic alcohols with high structural diversity.[12]

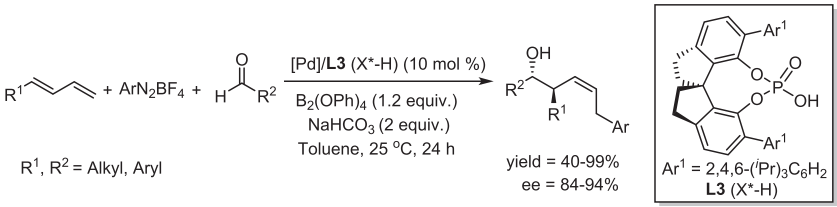
Relying on a novel aminal activation for further elaboration strategy developed by the same group,[13] in 2016, Huang and coworkers reported a highly enantioselective aminomethylamination of conjugated dienes with aminals catalyzed by a palladium in



Scheme 1. Pd-catalyzed asymmetric diarylation of 1,3-dienes.



Scheme 2. Pd-catalyzed asymmetric allylic alkylation of 1,3-diene.



Scheme 3. Pd-catalyzed multicomponent carbonyl allylation reaction of 1,3-dienes.