

Abstracts

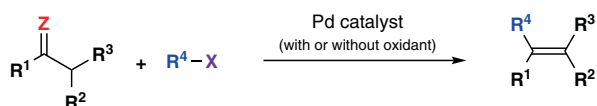
New

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47.1.1.4.12 **Synthesis of Alkenes by Palladium-Catalyzed Cross-Coupling Reactions with Carbene Precursors**

K. Wang¹ and J. Wang²

This review describes the synthesis of multisubstituted alkenes through palladium-catalyzed cross-coupling reactions with carbene precursors. In the past decade, transition-metal-catalyzed cross couplings involving carbenes have witnessed remarkable development, including those that form alkenes as the products. These palladium-catalyzed coupling reactions are summarized here, according to the type of cross-coupling partners and the carbene precursors.



Z = N₂, NNHTs

R⁴ = aryl, benzyl, alkynyl, etc.

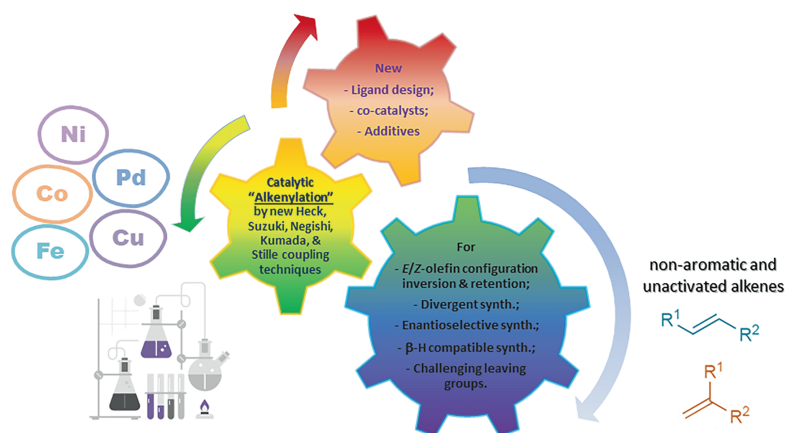
X = B(OH)₂, halogen, H, etc.

Keywords: cross coupling · palladium catalysts · carbenes · diazo compounds · tosylhydrazones · olefins · alkenes

47.1.2.1.5 **Synthesis of Alkenes by Cross-Coupling and Heck Reactions**

C.-Y. Ho and D. Raja

Since their discovery, Heck and cross-coupling reactions have become essential for catalytic alkene synthesis. Selected homogeneous methods for non-aromatic and unactivated alkene synthesis by catalytic alkenylation are reviewed herein (ca. 2008–2020). By using new combinations of ligands, additives, co-catalysts, and transition metals, significant advances and new mechanistic insights have been revealed recently. New strategies for accessing a broader substrate scope, milder reaction conditions, higher functional-group compatibility, and highly stereoselective synthesis are highlighted.



Keywords: alkenes · cross-coupling reactions · transition-metal catalysis · alkenylation · stereoselective olefin synthesis · stereodivergent olefin synthesis · enantioselective olefin synthesis · oxidative addition · transmetalation · alkene insertion · reductive elimination · Heck reaction · Suzuki–Miyaura coupling · Corriu–Kumada–Tamao coupling · Kosugi–Migita–Stille coupling · Hiyama coupling

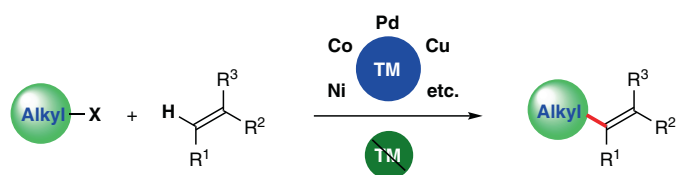
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47.1.2.1.6 Alkyl-Mizoroki–Heck-Type Reactions

A. Lei¹ and S. Tang²

Substituted alkenes are basic structural motifs in a large number of organic molecules and their synthesis has received continuous attention from synthetic chemists. One of the most straightforward methods for constructing substituted alkenes is the Mizoroki–Heck reaction. Generally, this transformation is catalyzed by palladium and mainly deals with the synthesis of substituted alkenes from aryl or vinyl electrophiles. In sharp contrast, the Mizoroki–Heck reaction of alkyl electrophiles has long been considered a challenging transformation due to the decreased rates of oxidative addition and subsequent facile β -hydride elimination. To address this limitation in traditional Mizoroki–Heck reactions, radical processes have been introduced to achieve the alkenylation of alkyl electrophiles. This review provides an overview of the recent developments in alkyl-Mizoroki–Heck-type reactions. Particular attention is paid to the intermolecular Mizoroki–Heck-type reaction between alkyl radicals and terminal alkenes. The limitations and advantages of using different catalytic methods are discussed and compared.



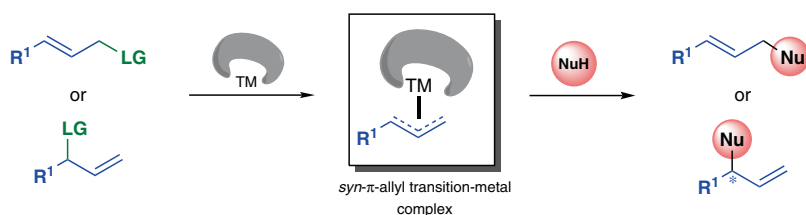
Keywords: alkenes · Mizoroki–Heck-type reaction · cross coupling · radicals · alkyl electrophiles · transition-metal catalysis · radical addition · light-induced

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47.1.2.3.3 Asymmetric π -Allyl Substitution ReactionsR. Jiang¹, P. Yang, and S.-L. You²

Asymmetric allylic substitution reactions catalyzed by transition-metal complexes, namely, the Tsuji–Trost-type reaction, can be used for constructing stereochemically defined carbon–carbon and carbon–heteroatom bonds. In this review, asymmetric allylic substitution reactions catalyzed by different transition-metal complexes, including those based on palladium, iridium, rhodium, and earth-abundant metals, are discussed. These reactions are categorized by the type of nucleophiles or transition-metal catalysts employed.



Keywords: alkenes · allylic substitution · asymmetric catalysis · dual catalysis · earth-abundant metals · enantioselectivity · iridium · palladium · rhodium · stereoselectivity · transition metals

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Updated Section ·

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Completely Revised Contributions ·

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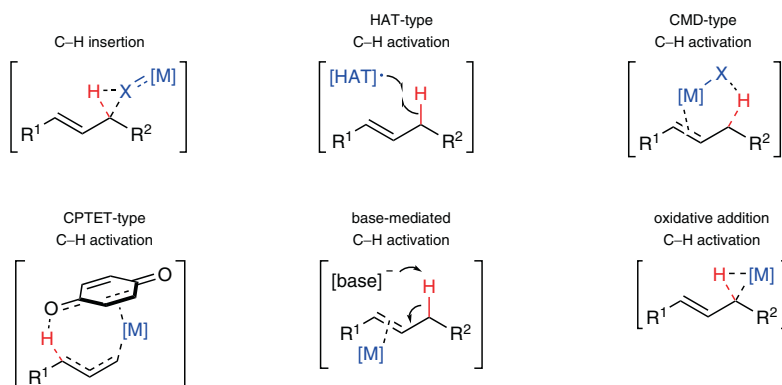
New Contributions

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47.1.2.5 **Allylic C–H Functionalization**P.-S. Wang^{1b}, M. Sayed^{1b}, and L.-Z. Gong^{1b}

The direct functionalization of allylic C(sp³)–H bonds allows alkenes to serve as versatile allylating agents capable of undergoing diverse bond-forming reactions, thereby enabling rapid access to alkene-bearing structural complexity from readily accessible feedstocks. In this review, representative reports on allylic C–H functionalization reactions published since 2013 are summarized by describing six types of allylic C–H activation modes: C–H insertion, hydrogen-atom transfer, concerted metalation/deprotonation (CMD), concerted proton and two-electron transfer (CPTET), base-mediated C–H activation, and oxidative addition to C–H bonds.



Keywords: alkenes · C–H activation · allyl compounds · allylic substitution · transition-metal catalysis · asymmetric catalysis

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47.1.4.11 **Synthesis of Alkenes by α,β -Dehydrogenation**

X. Jie and W. Su

This review describes methods for the synthesis of alkenes by elimination, with a specific focus on α,β -dehydrogenation reactions. It covers the literature published in the period 2011 to early 2020, providing an overview of recently developed transition-metal-catalyzed methods for α,β -desaturation of carbonyl compounds (e.g., ketones, aldehydes, esters, amides, etc.) as well as other functional groups. Key methods covered include palladium-catalyzed dehydrogenation via β -hydride elimination and copper-catalyzed desaturation via a radical pathway, as well as other miscellaneous methods. These approaches provide efficient access to α,β -unsaturated carbonyl compounds, which are important intermediates in the synthesis of diverse valuable organic molecules.



X = H, C, O, N, etc.; TM = Pd, Cu, Pt, Ir, Ni

Keywords: α,β -dehydrogenation · alkenes · α,β -unsaturated compounds · enones · enals · carbonyl compounds · transition-metal catalysis · palladium · copper · β -hydride elimination · radical processes

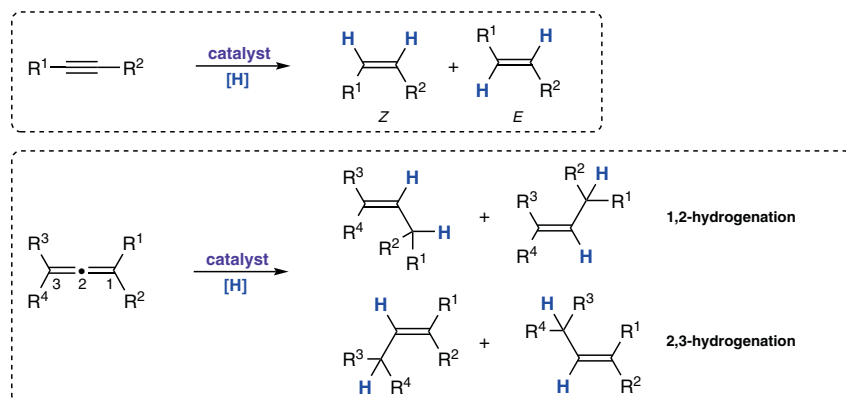
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47.1.5.2.3 **Synthesis of Alkenes via Hydrogenation of Alkynes and Allenes**

X. Liu, B. Liu, and Q. Liu

This review is an update to the earlier *Science of Synthesis* contribution describing methods for the synthesis of alkenes by (transfer) hydrogenation of alkynes and allenes, with a focus on catalytic methods reported since 2010. Representative methodologies for the selective preparation of terminal alkenes and *Z*- or *E*-alkenes are summarized, with the discussion divided into methods based on heterogeneous or homogeneous catalysis; these sections are then subdivided into hydrogenation or transfer-hydrogenation processes.



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Updated Section ·

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Completely Revised Contributions ·

New

New Contributions

Keywords: alkenes · alkynes · allenes · hydrogenation · transfer hydrogenation · heterogeneous catalysis · homogeneous catalysis · transition metals · base-metal catalysis · precious-metal catalysis · stereoselectivity

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47.1.5.5 **Synthesis of Alkenes via Metal-Catalyzed Hydrofunctionalizations**

Z. Cheng, Y. Zheng, and Z. Lu^{1b}

Alkenes bearing a functional group directly connected to the alkenyl moiety and functionalized allylic alkenes are important compounds. This review covers the synthesis of certain such alkenes via metal-catalyzed hydrofunctionalizations of alkynes and allenes. This update mainly summarizes protocols, reported in the period 2010–2020, that allow efficient access to various functional-group-tethered alkenes with high chemo-, regio-, and stereoselectivities.



FG = functional group = [B], [Si], Ar¹, R¹, SR¹, [P]

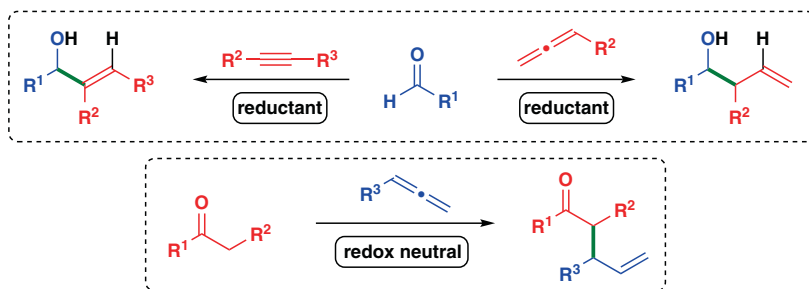
Keywords: alkenes · metal catalysis · hydrofunctionalization · alkynes · allenes · earth-abundant metals · transition-metal catalysis · hydrosilylation · hydroboration · hydroarylation · hydroalkylation · hydrothiolation · hydrophosphination · hydrophosphinylation · hydrophosphonylation

New

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47.1.5.6 **Synthesis of Functionalized Alkenes by Metal-Catalyzed Coupling of Carbonyls with Alkynes/Allenes***Z. Lin, R. Tao, and Y. Zhao*

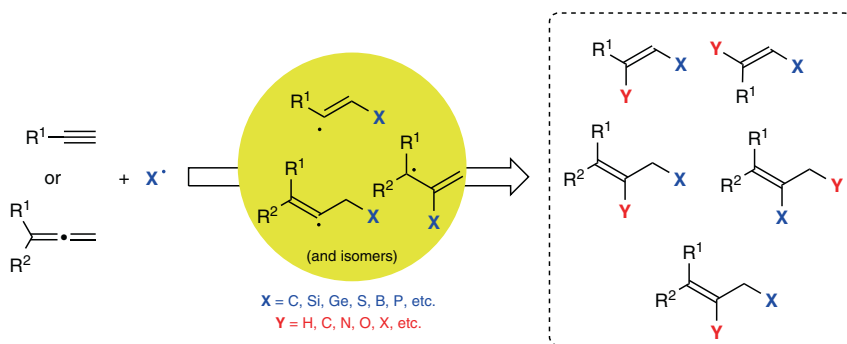
In this review, different coupling methodologies between carbonyls and alkynes or allenes affording highly functionalized alkenes are summarized. Two main strategies are discussed in detail: In the first one, electrophilic carbonyl species are utilized in metal-catalyzed reductive coupling reactions assisted by various reductants such as boranes, silanes, and hydrogen gas. In the second one, nucleophilic carbonyl species are employed in coupling reactions with electrophilic π -allyl intermediates generated in situ, resulting in a formal α -allylation of carbonyls. Various representative examples serve to demonstrate the high versatility of these two general strategies, including applications in the total synthesis of complex natural products. High regio- and stereocontrol can be achieved with excellent yields for most of the selected examples. Reports of decarboxylative coupling and metal-free coupling are also included.



Keywords: alkenes · alkynes · allenes · aldehydes · ketones · transition-metal catalysis · cross coupling · reductive coupling · π -allyl intermediates · enantioselectivity · regioselectivity

47.1.5.7 **Synthesis of Alkenes via Radical Addition Reactions***P. Chen and G. Liu*

The functionalization of alkynes and allenes involving radical processes is an efficient strategy for the synthesis of functionalized alkenes, and has experienced rapid growth over the past ten years with the development of photocatalysis and transition-metal catalysis. This review focuses on alkene synthesis initiated by radical addition to alkynes or allenes, with a particular focus on intermolecular reactions. Various radical species, including those based on carbon or heteroatoms (Si, Ge, S, B, etc.), can successfully add to alkynes and allenes to generate vinyl radicals or allyl radicals; these can react further via an assortment of processes, such as traditional radical atom transfer, oxidation to cationic species, or trapping by metal catalysts, to give functionalized alkenes.



Keywords: alkenes · alkynes · allenes · radical addition · vinyl radicals · allyl radicals · photocatalysis · transition-metal catalysis