

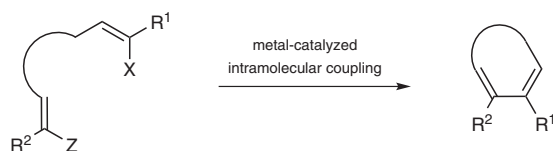
Abstracts

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1.1 Metal-Catalyzed Intramolecular Coupling Reactions

S. Gao and D. Wang

This chapter presents metal-catalyzed or -promoted intramolecular cross-coupling reactions for C–C bond formation in the preparation of cyclic compounds. Examples of synthetic applications in natural products syntheses are discussed to illustrate the potential of these methodologies.



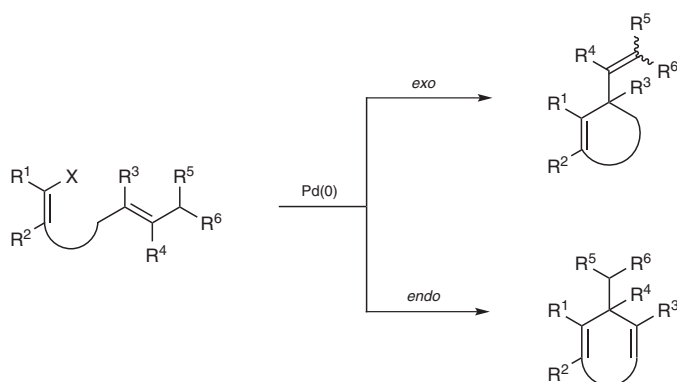
Keywords: cross coupling • reductive coupling • intramolecular coupling • C–C bond formation • palladium • chromium • copper • nickel • Suzuki–Miyaura coupling • Stille coupling • Negishi coupling • Sonogashira coupling • Hiyama coupling • dehydrogenative coupling • Nozaki–Hiyama–Kishi coupling • ene–yne coupling

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1.2 Intramolecular Heck Reactions

S. Jammi, C. Nottingham, and P. J. Guiry

This chapter presents the best methods for non-enantioselective and enantioselective intramolecular Heck reactions to form cyclic molecules.

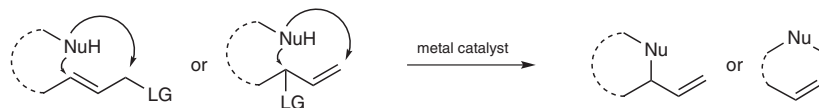


Keywords: intramolecular Heck cyclization • non-enantioselective • enantioselective • chiral • cross coupling • palladium(0) • halide • pseudohalide • alkene

1.3 Metal-Catalyzed Intramolecular Allylic Substitution Reactions

X. Zhang and S.-L. You

Metal-catalyzed intramolecular allylic substitution reactions provide diverse carbocycles and heterocycles. Various types of nucleophiles such as carbon, nitrogen, and oxygen can be employed.



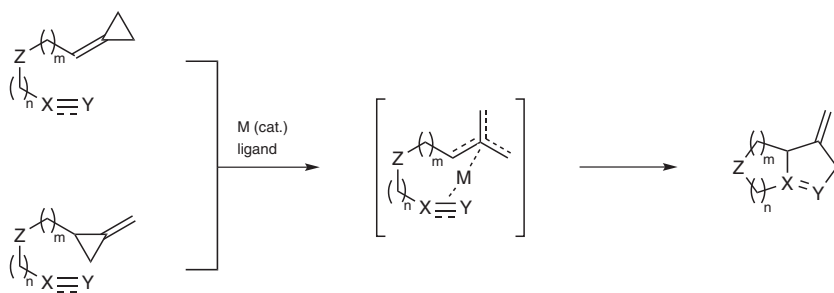
LG = leaving group; Nu = C, N, O

Keywords: allylic substitution • amines • gold • indoles • intramolecular reactions • iridium • palladium • phenols • ruthenium

1.4 Metal-Catalyzed Intramolecular Cyclizations Involving Cyclopropane and Cyclopropane Ring Opening

X. Tang and M. Shi

Due to the ring strain of cyclopropane rings, transition-metal catalysts can easily undergo an oxidative addition with the cyclopropane moiety of methylenecyclopropanes (MCPs) to give trimethylenemethane (TMM) intermediates. Subsequent intramolecular cyclization with unsaturated systems takes place to give cyclized products. Moreover, in the presence of a chiral ligand, high enantioselectivity can be achieved. The ring-fused products are versatile building blocks in organic synthesis.



Z = O, CR¹R², NR¹; n = m = 0, 1, 2; M = Pd, Ni, Rh, Ru

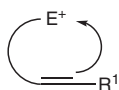
Keywords: cyclopropanes • methylenecyclopropanes • ring-opening reactions • cyclization • alkenes • alkynes • transition-metal catalysts • trimethylenemethanes • palladium • nickel • rhodium • ruthenium • chiral synthesis

1.5 Cyclization Reactions of Alkenes and Alkynes

L. Zhang

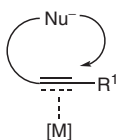
Discussed in this chapter are two classes of metal-catalyzed cyclization reactions of alkenes and alkynes, namely one where unactivated carbon–carbon double or triple bonds act as nucleophiles to attack tethered electrophiles, and the other where the π -system is activated by a metal-based π -acid and is subsequently attacked by carbon nucleophiles. In the former scenario, the in situ generation of electrophiles is typically promoted by hard Lewis acid catalysts, which initiate Prins, aza-Prins, or carbonyl-ene reactions. In the latter scenario, the coordination of a carbon–carbon double or triple bond to a soft Lewis acidic metal catalyst lowers the energy of the π^* orbital and thereby enables attack by nucleophiles. A large array of cyclic structural motifs are accessible, many in a stereoselective manner, via such metal catalysis. These motifs, including tetrahydrofurans, tetrahydropyrans, cycloalkenes, dihydronaphthalenes, carbazoles, coumarins, quinolinones, benzopyrans, dihydroquinolines, and phenanthrenes, are essential components of various bioactive compounds and natural products. Exemplary applications of these methods in the syntheses of natural products and relevant structures are also discussed.

nucleophilic π -system



electrophile generated in situ
via metal catalysis

electrophilic π -system



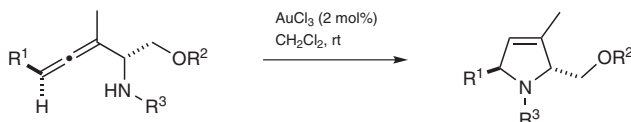
π -system activated by
metal catalyst

Keywords: cyclization · alkenes · alkynes · catalysis · Prins reaction · carbonucleophiles · gold · iron · mercury · palladium · natural products · tetrahydropyrans · dihydronaphthalenes · carbazoles · coumarins · quinolinones · benzopyrans · dihydroquinolines · phenanthrenes

1.6 Metal-Catalyzed Cyclization Reactions of Allenes

A. M. Phelps, J. M. Alderson, and J. M. Schomaker

Allenenes represent a unique scaffold for powerful cyclization reactions due to the ability to incorporate additional functionality into the newly formed ring. Metal-catalyzed cyclization reactions of allenenes represent a powerful strategy for the synthesis of highly functionalized heterocycles and carbocycles. A variety of metals can be used to facilitate cyclization; the nature of the metal influences which allene carbon is attacked by an internal nucleophile, leading to convenient access to multiple ring systems from a simple precursor. The unique axial chirality of allenenes can dictate the stereochemistry featured in the ring through axial-to-point chirality transfer.

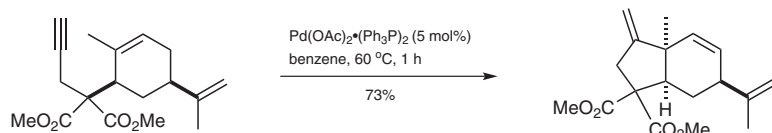


Keywords: allenenes · chirality transfer · carbocycles · heterocycles · pyrrolidines · benzocycles · cyclopropanes

1.7 Cycloisomerizations of Substrates with Multiple Unsaturated Bonds

Y. Yamamoto

Transition-metal complexes catalyze cycloisomerizations of substrates bearing multiple unsaturated carbon–carbon bonds. Carbo- and heterocycles are obtained via selective carbon–carbon bond formations with concomitant hydrogen-atom transfer under mild conditions.

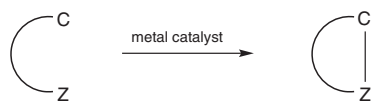


Keywords: transition-metal catalysts · cycloisomerization · alkynes · alkenes · allenes · 1,3-dienes · carbocycles · heterocycles · regioselectivity · enantioselectivity

1.8 Metal-Catalyzed Intramolecular C–N and C–O Bond Formation

E. M. Beccalli, A. Bonetti, and A. Mazza

Transition-metal-catalyzed intramolecular C–N and C–O bond formation using unsaturated alkene and alkyne systems containing tethered nitrogen nucleophiles (such as amines, amides, sulfonamides, amidines, azides, carbamates, guanidines, hydrazones, imines, and ureas) or oxygen nucleophiles (such as alcohols, ketones, phenols, hydroxylamines, and carboxylic acids) represents an efficient method for the preparation of heterocycles. Various reaction types may be involved, including amination, hydroamination, oxidative amination, carbamoylation, carboamination, alkoxylation, hydroalkoxylation, oxidative alkoxylation, hydroacyloxylation, carboalkoxylation, and alkoxy-carbonylation. Depending on the type of reaction, the choice of transition-metal complex to be used plays a fundamental role in obtaining a successful reaction.



Z = NR¹, O

Keywords: alkoxy-carbonylation · alkoxylation · amination · carbamoylation · carboalkoxylation · carboamination · hydroacyloxylation · hydroalkoxylation · hydroamination · intramolecular C–N bond formation · intramolecular C–O bond formation · oxidative amination · oxidative alkoxylation · transition-metal catalysis