

Abstracts

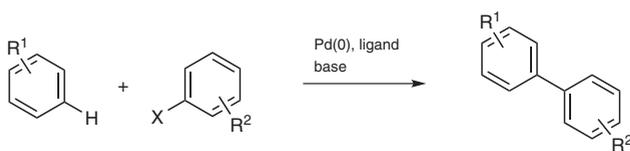
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1.1.1 Arylation Using a Palladium(0) Catalyst

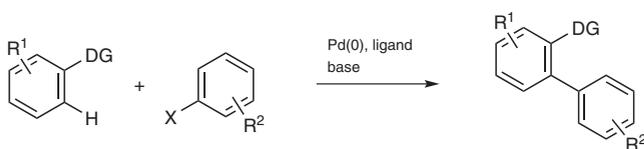
F. S. Melkonyan and V. Gevorgyan

The palladium(0)-catalyzed C–H arylation reaction is one of the pioneering transformations in C–H activation chemistry in general. In the past two decades, the method has been extensively developed and now represents a very powerful tool for the construction of C(sp²)–C(sp²) bonds. In this chapter, the palladium(0)-catalyzed C–H arylation of aromatic compounds is reviewed. The application of the method toward the synthesis of polycyclic aromatic hydrocarbons (PAHs), a variety of biaryl compounds, and natural products, with emphasis on the most practical and efficient protocols, are discussed.

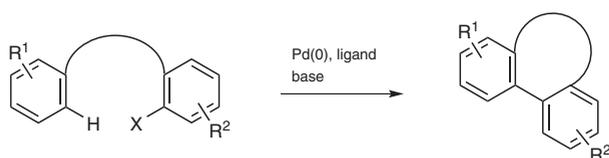
non-directed C–H arylation



directed C–H arylation



intramolecular C–H arylation



X = halogen, sulfonate; DG = directing group

Keywords: C–H activation · palladium catalysts · arylation · arenes · polycyclic compounds · biaryls · natural products

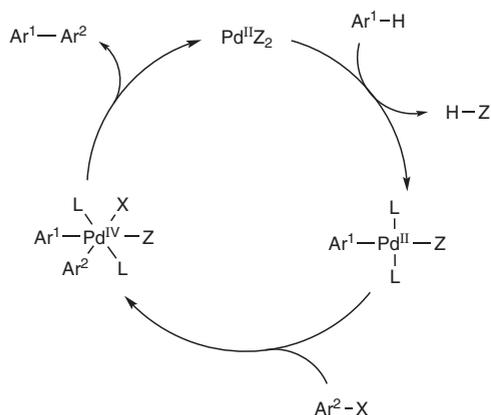
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1.1.2 Arylation Using a Palladium(II)/Palladium(IV) Catalyst System

P. Gandeepan and C.-H. Cheng

Aryl–aryl bonds are important structural motifs that are found in many natural products, bioactive compounds, and functional materials. Due to their application in various fields of organic and materials chemistry, continuous efforts have been made to develop attractive methods for their synthesis. In particular, aryl–aryl bond formation involving a palladium(II)/palladium(IV) catalyst system has received much attention in recent years. Compared to the traditional cross-coupling reactions and C–H arylation involving palladium(II)/palladium(0), biaryl formation via a palladium(IV) intermediate has high potential for application due to its insensitivity toward air and moisture, tolerance of various

functional groups, lack of ligand requirement, and the very mild reaction temperature. In this chapter, arylation reactions using a palladium(II)/palladium(IV) catalyst system are reviewed.



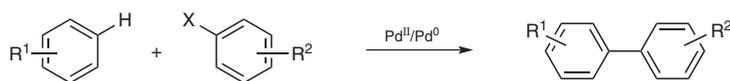
Keywords: palladium · arylation · C–H activation · biaryls · catalysis · chelation · palladium(IV) · oxidative coupling

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1.1.3 Arylation Using a Palladium(II) Catalyst

M. Zhang and W. Su

This chapter focuses on the synthesis of biaryl C–C bonds via palladium(II)-catalyzed direct arylation of arenes with aryltin, arylboron, and arylsilicon reagents and aromatic carboxylic acids. Due to the ubiquity of C–H bonds in organic molecules, these methods represent an efficient and straightforward approach to biaryl C–C bonds. The chapter is organized based on the type of arylating reagent used.



$\text{X} = \text{SnR}^3_3, \text{B}(\text{OR}^3)_3, \text{SiR}^3_3, \text{CO}_2\text{H}$

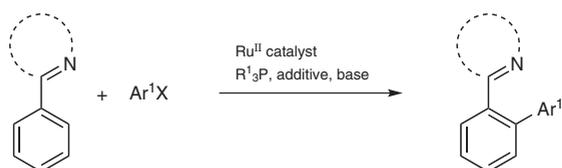
Keywords: C–H activation · arenes · arylation · biaryls · cross-coupling reactions · carboxylic acids · organometallic reagents · palladium catalysis

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1.1.4 Arylation Using a Ruthenium(II) Catalyst

M. Seki

The C–H arylation of α -functionalized benzenes proceeds smoothly in the presence of a ruthenium(II) catalyst. Key factors which control the reaction (catalyst, leaving group, additive, phosphine ligand, and base) are thoroughly discussed in terms of the efficiency and practicality of the process. Of particular interest is the synthesis of biaryls by means of C–H arylation, as these constitute a key feature of some important pharmaceutical compounds.



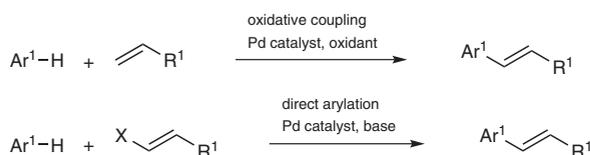
Keywords: arylation · biaryls · C–C bond formation · C–H activation · dihydroimidazoles · dihydrooxazoles · imidazoles · pyrazoles · pyridines · ruthenium(II) catalysis · tetrazoles · triazoles

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1.1.5 Vinylation Using a Palladium Catalyst

P. K. Dornan and V. M. Dong

This chapter covers methods for the vinylation of non-heteroaromatic arene C–H bonds with palladium catalysts. Both oxidative methods (dehydrogenative coupling of an arene with an alkene) and direct arylation methods (coupling of an arene with a vinyl halide or equivalent) are discussed. In many cases, directing groups are used to enhance reactivity and ensure site-selective vinylation. Examples of non-directed cases are also discussed. These vinylation methods are advantageous over other cross-coupling methods since pre-activation of the arene component (via an aryl halide or arylmetal species) is not necessary.



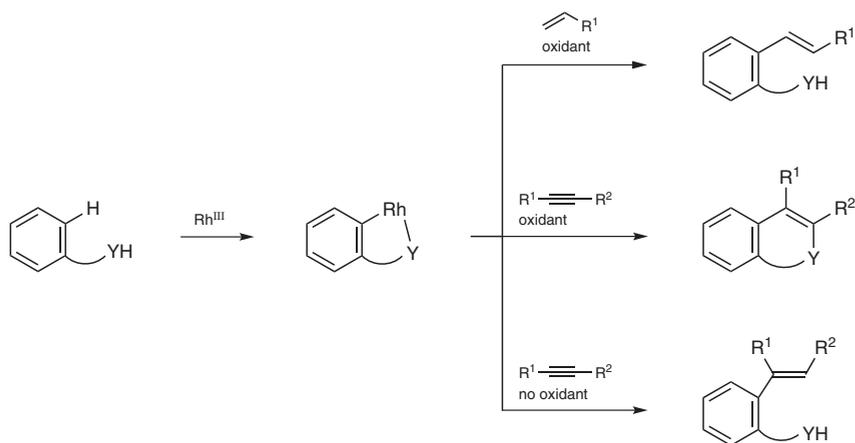
Keywords: C–H activation · C–H functionalization · styrenes · acrylates · palladium catalysts · vinylation · alkenylation · cross coupling · catalysis · oxidation · oxidative coupling · direct arylation

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1.1.6 Vinylation Using a Rhodium(III) Catalyst

T. Satoh and M. Miura

Rhodium(III)-catalyzed oxidative and non-oxidative couplings of a wide range of arenes possessing a directing group with alkenes and alkynes are summarized in this chapter. The reaction takes place regioselectively at the *ortho* position to give rise to the corresponding *ortho*-vinyolated arenes or benzannulated products.



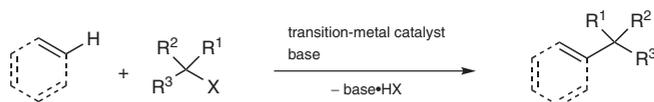
Keywords: alkenylation · annulation · C–C coupling · C–H bond cleavage · dehydrogenation · fused heterocycles · oxidative coupling · rhodium catalysts · vinylarenes · vinylation

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1.1.7 Metal-Catalyzed C–H Alkylation Using RX Compounds

C. S. Yi

This review covers transition-metal-catalyzed C(sp²)–H alkylation methods via carbon–heteroatom bond cleavage. The first part of the review delineates catalytic C(sp²)–H alkylation methods for arene and alkene substrates using various alkyl halides. Subsequently, alkylation by cleavage of C–B, C–Si, and C–Sn bonds is described. Finally, C(sp²)–H alkylation via C–O and C–S bond cleavage is reviewed.



X = Cl, Br, I, B(OR⁴)₂, SiR⁴₃, OR⁴, SR⁴

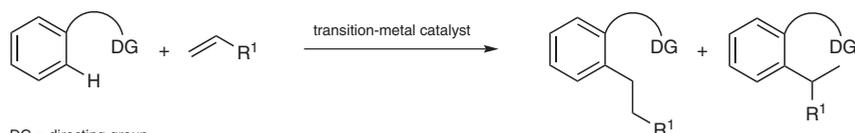
Keywords: alkylation · C–H activation · arenes · alkenes · transition-metal catalysts

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1.1.8 Metal-Catalyzed Alkylation Using Alkenes

T. Shibata and K. Tsuchikama

This review summarizes metal-catalyzed arene C–H bond activation using alkenes as alkylating reagents. Inter- and intramolecular reactions are covered, with examples leading selectively to either linear or branched products described.



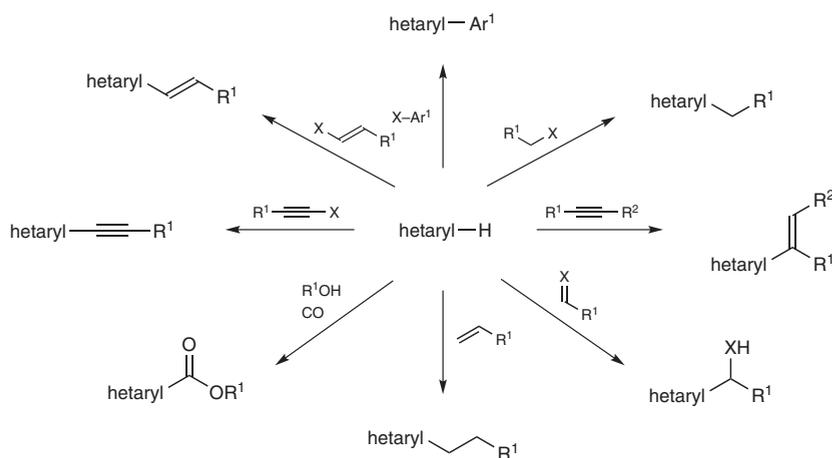
DG = directing group

Keywords: C–H activation · arenes · alkenes · alkylation · cobalt catalysts · iridium catalysts · rhenium catalysts · rhodium catalysts · ruthenium catalysts · scandium catalysts · styrenes · vinylsilanes · yttrium catalysts

1.2 C—C Bond Formation by Heterene C—H Activation

Y. Nakao

Heteroaromatic compounds play key roles in pharmaceuticals, agrochemicals, and materials, and the development of efficient synthetic methods to access differently substituted heterarenes is therefore an important issue in organic synthesis. To circumvent the limitations associated with classical protocols to form hetaryl—carbon bonds, metal-catalyzed heterene C—H activation followed by C—C bond-forming reactions has been developed extensively in recent decades. These transformations allow the construction of C—C bonds between hetaryl moieties and all the three differently hybridized carbons to result in alkylation, alkenylation, acylation, alkynylation, etc. of a diverse range of heterarenes irrespective of their electronic characters. This chapter deals with C—C bond formation by heterene C—H activation achieved by transition-metal catalysis.



Keywords: heterarenes · alkylation · alkenylation · arylation · acylation · alkynylation · cyanation