

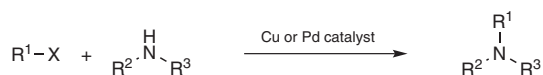
Abstracts

p 9

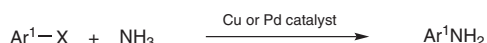
2.1.1.1 Alkylamines with Aryl and Alkenyl Electrophiles

M. Tomás-Gamasa

This review covers selected efficient synthetic methods for metal-catalyzed cross-coupling reactions that can directly convert simple substrates, such as aryl halides or arylboronic reagents and alkylamines or ammonia, into a range of *N*-alkylaniline derivatives under mild conditions. Emphasis is placed on copper- and palladium-catalyzed amination reactions, which are described in the first and second parts of the chapter, respectively.



R¹ = aryl, alkenyl; R² = alkyl; R³ = H, alkyl; X = Cl, Br, I, B(OR⁴)₂



X = Cl, Br, I

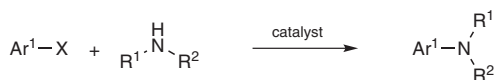
Keywords: amination · C–N bond formation · copper catalysis · palladium catalysis · Ullmann reaction · Chan–Lam–Evans reaction · *N*-arylation · alkylamines · aryl halides · ammonia · boronic acid derivatives

p 43

2.1.1.2 Alkylamines with Hetaryl Electrophiles

U. Scholz, W. Dong, J. Feng, and W. Shi

Methods for cross-coupling reactions to form C–N bonds between hetaryl electrophiles and alkylamines are reviewed. The methods described focus mainly on reactions using palladium or copper catalysts. However, methods employing other metal catalysts are also summarized.



Ar¹ = hetaryl; R¹ = R² = H, alkyl; X = Cl, Br, I, OTf, OTs

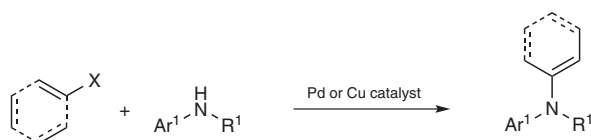
Keywords: cross coupling · amination · hetaryl electrophiles · alkylamines · palladium catalysts · copper catalysts · nickel catalysts · cobalt catalysts · phosphorus ligands

p 107

2.1.2.1 Aryl- and Hetarylaminates with Aryl and Alkenyl Electrophiles

M. B. Hay and J. D. Hicks

Palladium and copper complexes catalyze the formation of C–N bonds between aryl- or hetarylaminates and aryl and alkenyl halides/pseudohalides. Recent work in this area has resulted in the development of highly active catalysts, which have improved substrate scope and allow reactions to be carried out under milder conditions.



Keywords: C–N bonds · palladium catalysis · copper catalysis · anilines · arylation

— p 173 —

2.1.2.2 Aryl- and Hetaryl Amines with Hetaryl Electrophiles

Q. Shen, F. Guo, and J. F. Hartwig

The recent progress in palladium- and copper-catalyzed cross coupling of hetaryl electrophiles with aryl and hetaryl amines is reviewed. Significant advances in this area have been achieved, and many of these advances have been driven by the development of new ligands and by careful evaluation of reactions conditions. Some of the challenges confronted by coupling reactions that form C–N bonds with different classes of heterocyclic electrophiles and nucleophiles are described.



Ar¹ = hetaryl; Ar² = aryl, hetaryl; R¹ = H, alkyl, aryl, hetaryl

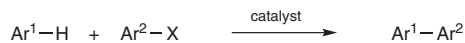
Keywords: hetarenes · hetaryl amines · palladium · copper · cross coupling

— p 195 —

2.1.3 C–N Bond-Forming Reactions of Hetarenes

O. K. Ahmad and M. Movassaghi

Azaheterocycles are important substructures in a large number of natural products, pharmaceuticals, and fine chemicals. The synthesis of highly substituted hetarenes remains an important synthetic challenge in synthetic organic chemistry. Recent advances in transition-metal-catalyzed coupling reactions have led to the development of a wide range of methods for C–N bond-forming reactions of azaheterocyclic compounds. This account reviews the N-arylation and N-vinylation of hetarenes and is organized according to the metal used to catalyze the C–N bond formation.



Ar¹ = hetaryl; Ar² = aryl, hetaryl

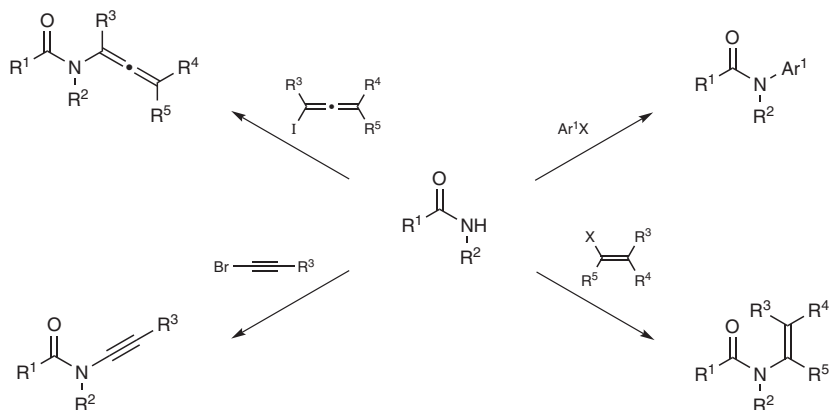
Keywords: amination · amines · aza compounds · carbon–heteroatom bonds · C–N bonds · copper catalysts · imidazoles · indoles · nitrogen heterocycles · nitrogen ligands · palladium catalysts · pyrroles

— p 215 —

2.1.4 C–N Bond-Forming Reactions of Amides and Carbamates

A. Klapars

Arylation and alkenylation reactions of amides and carbamates using copper and palladium catalysts are reviewed. The complementarity of the palladium- and copper-catalyzed amidation methods is emphasized and the substrate scope is outlined.



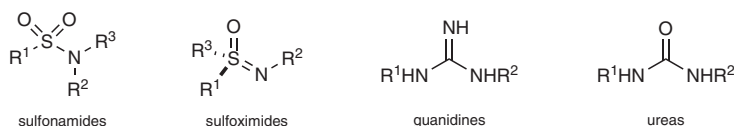
Keywords: C–N bond formation · arylation · aryl amidation · alkenyl amidation · alkynyl amidation · intramolecular amidation · arylboronic acids · amides · carbamates · oxazol-idinones · palladium catalysts · copper catalysts

p 255

2.1.5 C–N Bond-Forming Reactions of Sulfonamides, Sulfoximides, and Other Nitrogen Nucleophiles

J. Duan, H. Chen, X. Hong, and M. Harmata

Sulfonamides, sulfoximides, guanidines, and ureas are highly important classes of compounds for the pharmaceutical industry and have been of enormous interest to synthetic chemists. This review presents the state of the art of C–N bond-forming reactions of sulfonamides, sulfoximides, and other nitrogen nucleophiles.



Keywords: sulfonamides · sulfoximides · sulfamides · sulfonimidamides · guanidines · ureas · C–N bond formation

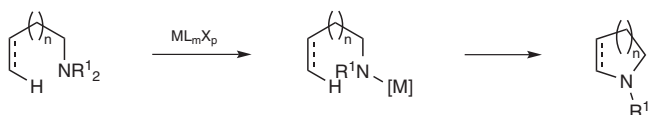
p 283

2.1.6 C–N Bond-Forming Reactions of C–H Electrophiles

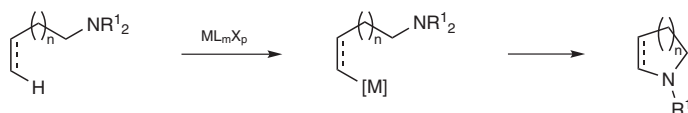
T. G. Driver

Recent transition-metal-mediated methods to construct C(sp²)–N and C(sp³)–N bonds from C–H bonds are examined within this chapter. These C–H bond aminations can be categorized into two different strategies: metal activation of the nitrogen atom or metal activation of the C–H bond. This chapter presents both the scope and challenges of the currently available methods and is organized according to the source of the nitrogen atom.

Nitrogen-Atom Activation



C–H Bond Activation



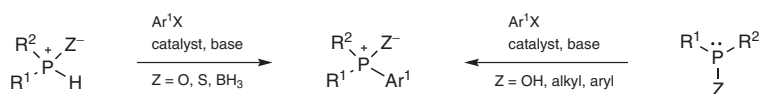
Keywords: metals · catalysis · amination · C–H activation · nitrenes · heterocycles · amines

p 331

2.2 C–P Bond-Forming Reactions

C. Petit and J.-L. Montchamp

This section covers the formation of C–P bonds via metal-catalyzed cross coupling, with particular focus placed upon the reactivity of aromatic sp^2 -carbon-containing electrophiles. The literature is reviewed up to the summer of 2011, and a discussion of all major phosphorus functional groups is included.



$R^1 = R^2 = \text{H, alkyl, aryl, alkoxy}$

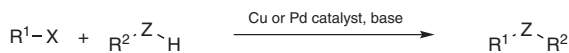
Keywords: copper catalysis · C–P bond formation · cross coupling · homogeneous catalysis · nickel catalysis · palladium catalysis · *H*-phosphinates · phosphine oxides · phosphines · phosphinic acids · phosphites · phosphonates · phosphonium salts · phosphorus compounds · silylphosphines

p 363

2.3.1 C–O and C–S Bond-Forming Reactions of C–X Electrophiles

C. C. Eichman and J. P. Stambuli

Various late transition metals catalyze the formation of C–O or C–S bonds in a general manner. These metal-catalyzed cross-coupling reactions proceed in high yields with proper ligand choice, and this section details the most efficient methods available for such bond formation.



X = halide; Z = O, S

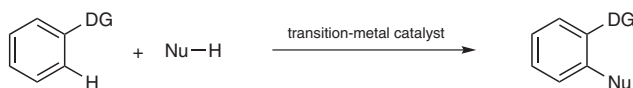
Keywords: C–O bond formation · copper catalysis · cross-coupling reactions · C–S bond formation · etherification · ethers · palladium catalysis · sulfides · thioetherification · thioethers

p 395

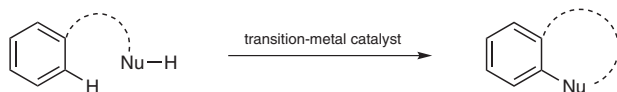
2.3.2 C–O and C–S Bond-Forming Reactions of C–H Electrophiles

K. Inamoto

The formation of C–O and C–S bonds through transition-metal-catalyzed (or -mediated) C–H bond functionalization is described. Most examples employ a palladium catalyst, and both intermolecular and intramolecular processes are possible.



DG = directing group



Nu-H = O- or S-atom-based nucleophile

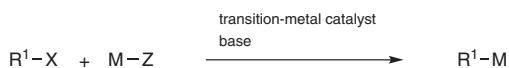
Keywords: C–H activation · carbon–heteroatom bonds · C–H bonds · C–N bonds · C–S bonds · copper catalysts · heterocycles · oxidative coupling · oxygen heterocycles · palladium catalysts · sulfur heterocycles

— p 439 —

2.4.1 C–B and C–Si Bond-Forming Reactions of C–X Electrophiles

M. Murata

Metal-catalyzed cross-coupling reactions of M–M or M–H compounds (M = B, Si) provide a direct method for conversion of C–X bonds into C–M bonds. Tetraalkoxydiboron and dialkoxyboron species are excellent boron nucleophiles in the borylation of aryl, alk-1-enyl, allyl, and benzyl halides or pseudohalides. Catalytic silylation of aryl halides with disilanes has been significantly improved and, furthermore, hydrosilanes such as trialkoxy-silanes and trialkylsilanes can be used as silicon nucleophiles. These reactions tolerate a wide variety of functional groups and proceed with excellent yields, thereby allowing the simple, convenient, and elegant preparation of functionalized C–M compounds.



M = B(OR²)₂, SiR²₃, Si(OR²)₃; Z = M, H; R¹ = alkyl, alk-1-enyl

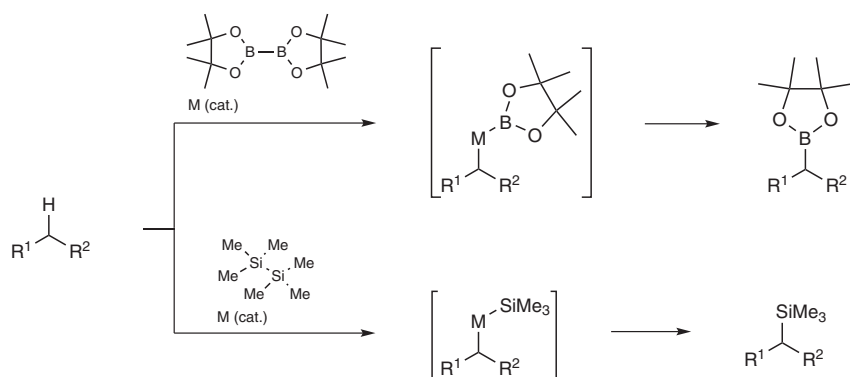
Keywords: coupling reactions · borylation · silylation · chemoselectivity · C–B bonds · C–Si bonds · palladium catalysts · nickel catalysts · rhodium catalysts · arylboranes · vinylboranes · arylsilanes · vinylsilanes

— p 485 —

2.4.2 C–B and C–Si Bond-Forming Reactions by C–H Functionalization

K. J. Szabó

Catalytic borylation and silylation based on C–H functionalization are very important tools for the synthesis of new organic reagents. This review covers the recent developments in this field, including the C–H borylation and silylation of aromatics and vinylic and allylic alkenes, and some examples of alkane functionalization. The performance and catalytic activity of iridium, rhodium, ruthenium, palladium, and other metal catalysts are reviewed, and particular attention is directed to the selectivity issues of C–H bond functionalization and to the mechanistic aspects of the reactions.



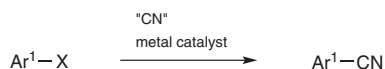
Keywords: C–B bond formation · C–H bond functionalization · C–Si bond formation · homogeneous catalysis · iridium catalysis · organoboronates · organosilanes · rhodium catalysis · ruthenium catalysis · palladium catalysis

p 523

2.5 C–CN Bond-Forming Reactions

G. Yan, Y. Zhang, and Jianbo Wang

The development of methodology for the preparation of nitriles is of significant interest to organic chemists. In the past few decades, numerous methods for the synthesis of nitriles have been developed. Among them, the transition-metal-catalyzed cyanation reaction has been a powerful tool for the straightforward construction of C–CN bonds in modern organic synthesis. In this chapter, some efficient transition-metal-catalyzed cyanation reactions are summarized.



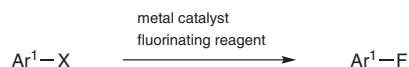
Keywords: nitriles · transition-metal catalysis · cyanation · green chemistry · halides · boronic acids · alkenes · alkynes · alcohols · thiols · C–H activation

p 551

2.6 C–F Bond-Forming Reactions

K. B. McMurtrey and M. S. Sanford

This chapter describes both metal-mediated and metal-catalyzed procedures for converting aryl–X reagents (X = boronic acid, silyl, stannyl, hydrogen, or trifluoromethylsulfonyl) into aryl fluorides. Fluorination is accomplished using electrophilic or nucleophilic fluorinating reagents, and the metal catalysts are typically palladium or silver complexes.



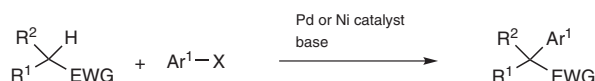
X = H, B, Si, Sn, OTf

Keywords: fluorination · palladium · silver · boronic acids · silanes · stannanes · C–H activation

2.7.1 C–C Cross-Coupling Reactions of Acidic C–H Nucleophiles with One Activating Group

S. P. Marsden

Nucleophiles generated by deprotonation of activated C–H positions undergo cross coupling with aryl halides and pseudohalides under palladium or nickel catalysis. The range of activating groups includes aldehydes, ketones, esters, amides, nitriles, sulfonyl, and nitro groups.



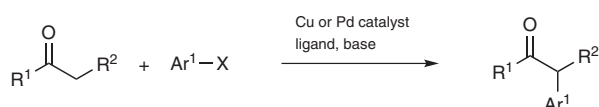
EWG = CHO, COR³, CO₂R³, CONR³R⁴, CN, SO₂R³, NO₂; X = I, Br, Cl, OTf

Keywords: arylation · aryl compounds · asymmetric catalysis · C–C bonds · C–C coupling · enolates · nickel catalysts · palladium catalysts

2.7.2 C–C Cross-Coupling Reactions of Acidic C–H Nucleophiles with Two Activating Groups

Y. Wu, Jun Wang, and F. Y. Kwong

This chapter describes the recent advances in C–C cross-coupling reactions of acidic C–H nucleophiles with two neighboring activating groups. Both copper- and palladium-catalyzed protocols are reviewed, focusing predominantly on the literature published in the period 1990–2011.



R¹ = alkyl, aryl, OR³; R² = CO₂R⁴, COR⁴, CN, NO₂, SO₂Ar²; X = I, Br, Cl, OSO₂Ph

Keywords: arylation · carbonyl compounds · copper catalysis · cross-coupling reactions · malonates · C–H nucleophiles · palladium catalysis