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Copper-Mediated Intermolecular C–H/C–H and C–H/N–H Couplings via Aromatic C–H Cleavage

Koji Hirano and Masahiro Miura

Abstract Copper salts and complexes have recently received significant attention as less expensive and abundant alternatives to some noble transition metal catalysts such as palladium, rhodium, and ruthenium, in the research field of C–H activation. They not only replace the above precious metal catalysts in the known C–H transformations but also mediate unique, otherwise challenging, cross-coupling reactions involving C–H bond cleavage. This chapter mainly focuses on recent advances in the copper-mediated or copper-catalyzed intermolecular C–H/C–H and C–H/N–H aromatic couplings. Seminal mechanistic studies on the copper-mediated C–H functionalization are also discussed.

Keywords Aromatic compounds · C–C formation · C–N formation · Copper · Dehydrogenative coupling

Contents

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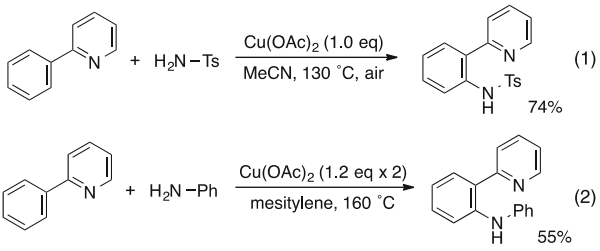
1 Introduction

Since the pioneering work on the ruthenium-catalyzed directed C–H alkylation by Murai and coworkers [1], the transition metal-mediated C–H functionalization has grown rapidly because of its possibility for transformation of ubiquitous C–H bonds to versatile functional groups in atom- and step-economical manners. While the second- and third-row transition metal catalysts such as palladium, rhodium, and ruthenium have initially been developed, for the realistic catalyst loading, many researchers then turned attention into less expensive and easy-to-handle first-row transition metals. Particularly, less toxic and abundant copper salts are attractive alternatives for the above noble metal catalysts and have great potential for ideal but greatly challenging intermolecular C–H/C–H and C–H/N–H couplings [2–6]. In 2006, two seminal examples for the C–H/N–H coupling were reported concurrently by Yu [7] and Chatani [8]. While not catalytic in copper, 2-phenylpyridine was found to undergo dehydrogenative amination with tosylamide or aniline without employing any precious metal catalysts (Eqs. 1 and 2). Since then, this research field has greatly progressed and is now one of the hottest areas in C–H functionalization. In this chapter, recent advances in the copper-mediated intermolecular dehydrogenative C–C and C–N aromatic couplings are summarized; the intramolecular version is not covered because the excellent review is now available [9]. Additionally, some related couplings with miscellaneous heteroatom nucleophiles and seminal mechanistic studies on the Cu-promoted C–H functionalization are also referred.



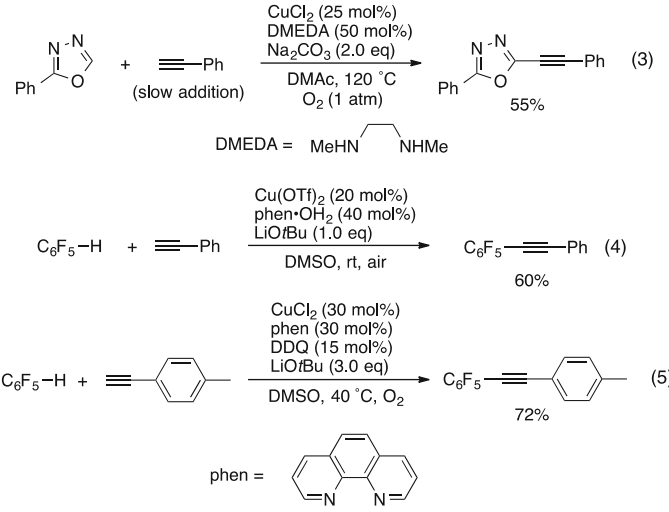
2 C–H/C–H Coupling

The transition metal-promoted C–C cross-coupling reaction ranks as the most important bond-forming strategy in modern organic synthesis. Traditionally, organic halides and organometallic reagents are employed as prefunctionalized starting materials [10–12]. On the other hand, the metal-mediated C–H activation can skip prefunctionalization steps such as halogenation and stoichiometric metalation. In particular, the dehydrogenative C–H/C–H coupling can be an ultimate C–C formation because no preactivation of both starting materials are needed. In this section, copper-mediated C–H/C–H aromatic couplings are divided into

three types of alkynylation, arylation, and alkylation, and their scope and limitations are described.

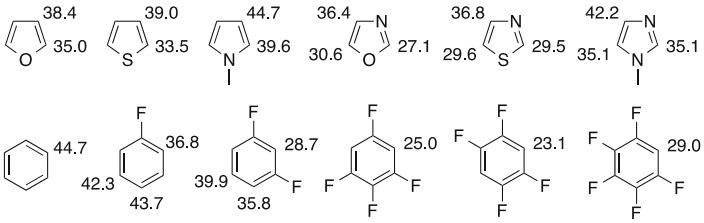
2.1 Alkynylation

Arylacetylenes are among the most fundamental and important π-conjugated systems in various areas of organic chemistry. A powerful and reliable approach to these molecules is the palladium/copper-catalyzed cross-coupling of aryl halides with terminal alkynes, also known as the Sonogashira coupling [13–16]. However, the stoichiometric halogenation of arenes is inevitable for the preparation of the starting halogenated arenes. Ultimately, the direct coupling between arenes and terminal alkynes via twofold C–H bond cleavage of both substrates is an ideal goal since no preactivation step is required. The first copper-mediated dehydrogenative alkynylation of aromatic compounds was reported by Miura and coworkers in 2010 (Eq. 3) [17]. The aromatic substrate is limited to some acidic 1,3-azoles, but preliminary attempts to apply catalytic conditions are also successful by using molecular oxygen as a terminal oxidant. Subsequently, the same group [18] and Su [19], independently, succeeded in the related direct alkynylation of polyfluoroarenes (Eqs. 4 and 5). A relatively strong base, LiO*t*Bu, is necessary, but the reaction proceeds well under mild conditions without special slow addition techniques.

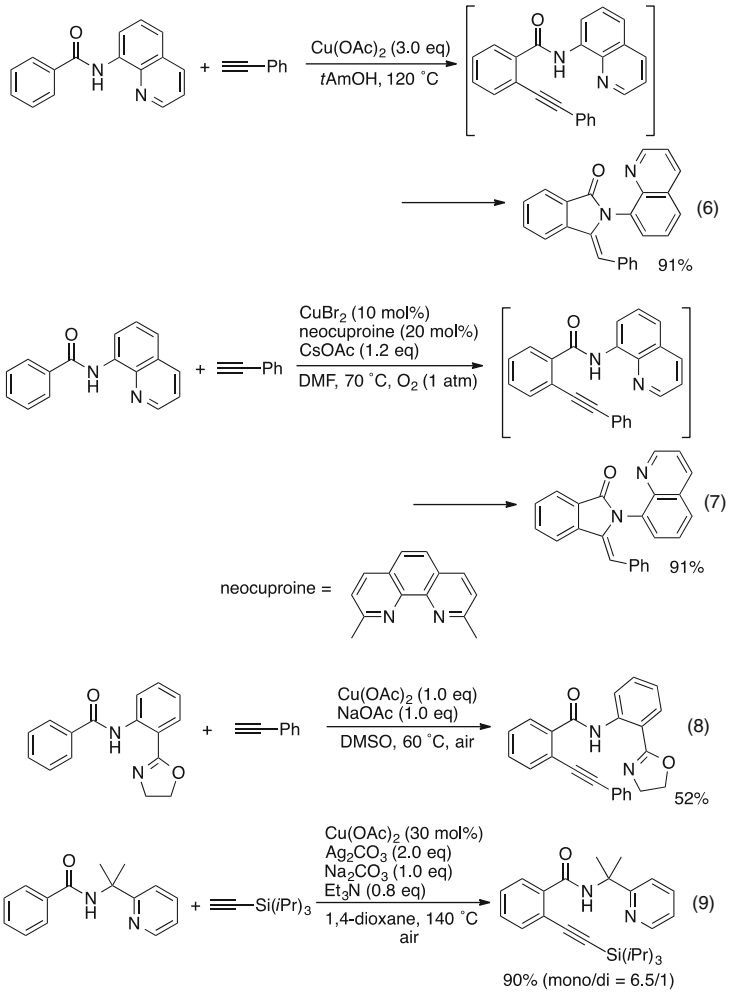


In the above leading work, the aromatic C–H cleavage step is apparently dependent on the acidity of aromatic C–H. The theoretical pK_a values of representative (hetero)aromatic compounds are shown in Table 1 [20].

Table 1 Theoretical pK_a values of some representative (hetero)aromatic compounds in DMSO

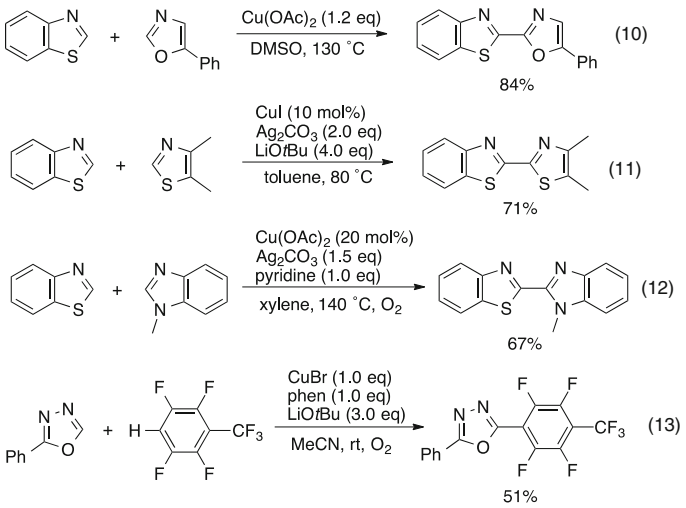


On the other hand, recent development of the bidentate coordination strategy [21, 22] successfully expands the substrate scope into the more general benzene derivatives. The first applicable directing group is the aminoquinoline-based *N*,*N*-bidentate amide, which was originally developed by Daugulis [23]. Although the dehydrogenative alkynylation occurs smoothly, probably because of the relatively high acidic nature of the aminoquinoline NH, the in situ generated alkynylated product spontaneously undergoes the subsequent annulation to provide the methylene isoindolinone skeleton (Eqs. 6 and 7) [24, 25]. More recently, Dai and Yu [26] and Shi [27] successfully suppress the undesired annulation by the oxazolinylaniline- and pyridinylpropylamine-modified coordinating moieties, respectively, and the desired alkynylated products were obtained in good yields (Eqs. 8 and 9). The latter two directing groups are easily removed under base-promoted hydrolysis conditions after the coupling reaction.

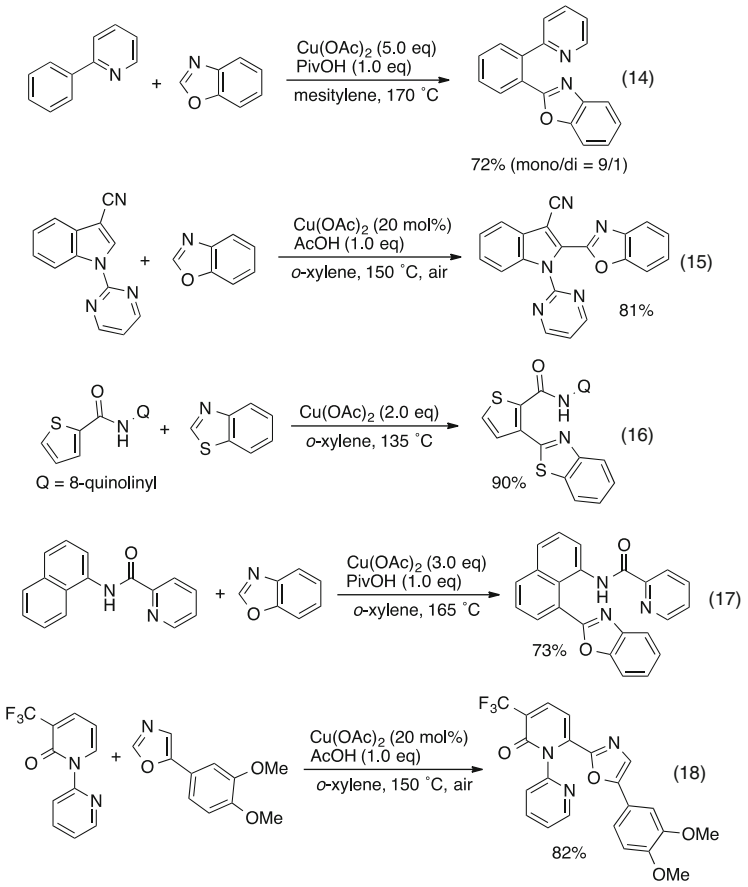


2.2 *Arylation*

Since the biaryl structures are prevalent cores in pharmaceutical targets and functional materials [28, 29], the dehydrogenative biaryl coupling of nonfunctionalized simple arenes has been extensively studied in recent years. Early successful examples with copper salts alone involve the cross-coupling reaction of relatively acidic 1,3-azoles and polyfluoroarenes (Eqs. 10–13) [30–33].



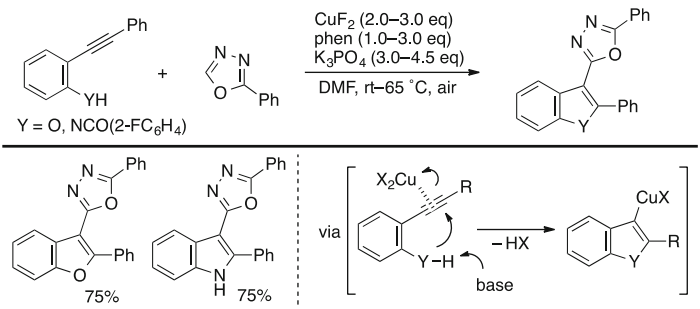
The application to less acidic, general arenes was first reported by the group of Hirano and Miura in 2011. Under $Cu(OAc)_2$/PivOH-promoted conditions, 2-phenylpyridine directly cross-couples with some 1,3-azoles (Eq. 14) [34]. The related dehydrogenative biaryl couplings of indoles, benzamides, and naphthylamines also proceed in the presence of $Cu(OAc)_2$, with the assistance of appropriate directing groups, to make the corresponding bi(hetero)aryl linkages efficiently (Eqs. 15–17) [35–37]. The directors except for the 2-phenylpyridine are readily attachable and detachable: 2-pyrimidyl (Eq. 16) and 8-aminoquinolinyl (Eq. 17) groups were removed smoothly by sodium alkoxide-mediated alcoholysis. Additionally, in some cases, the molecular oxygen renders the reaction catalytic in copper. The copper-based C–H/C–H coupling strategy can also be applicable to the regioselective direct heteroarylation of 2-pyridones at the C6 position (Eq. 18) [38].



The same research group also developed the formal dehydrogenative construction of benzofuran- and indole–azole conjugations via an annulative metalation of ortho-alkynylphenols and ortho-anilines (Scheme 1) [39, 40]. In the case of the aniline, the substituent on the nitrogen is spontaneously removed after the C–C formation to form the free NH indole exclusively. This protocol requires the alkyne and heteroatom functions in one coupling partner but can provide a unique approach to the biologically important bi(heteroaryl)s from nonhalogenated and nonmetalated starting materials.

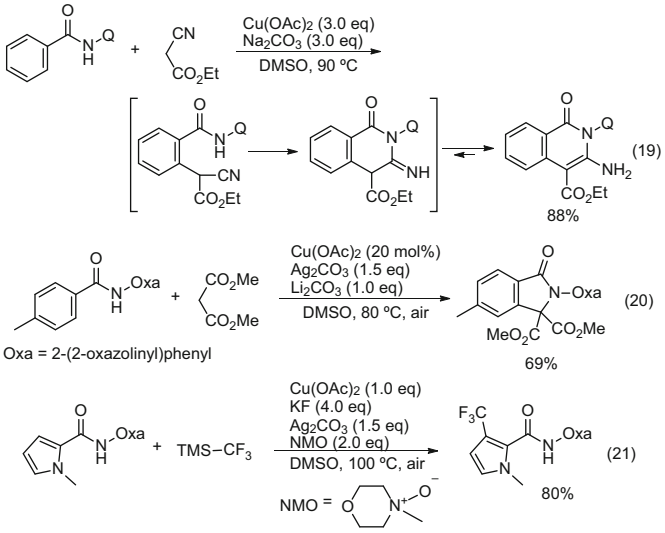
2.3 *Alkylation*

The copper-mediated dehydrogenative alkylation of aromatic compounds is less investigated, compared to the alkynylation and arylation in Sects. 2.1 and 2.2. The limited successful example includes the quinoline-containing benzamide and



Scheme 1 Formal dehydrogenative construction of bi(heteroaryl)s via annulative metalation

relatively acidic active methylene compound, namely, ethyl cyanoacetate (Eq. 19) [41]. An initially formed alkylated product undergoes the intramolecular nucleophilic addition/tautomerization sequence to furnish the formally annulated product, isoquinolinone, in a good yield. Very recently, Dai and Yu succeeded in the annulation reaction of benzamide with malonates by the action of the oxazolinylaniline auxiliary (Eq. 20) [42]. While not dehydrogenative, the oxidative C–H trifluoromethylation with TMS-CF_3 also appears (Eq. 21) [43].

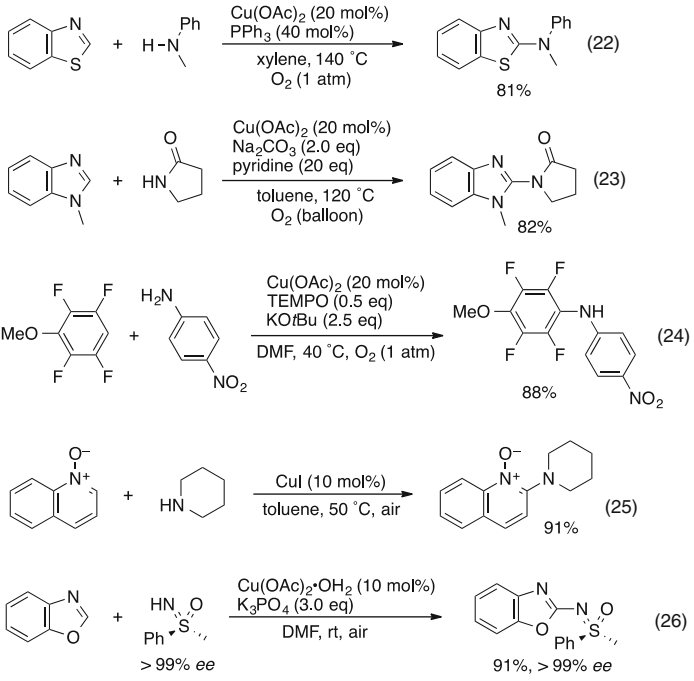


3 C–H/N–H Coupling

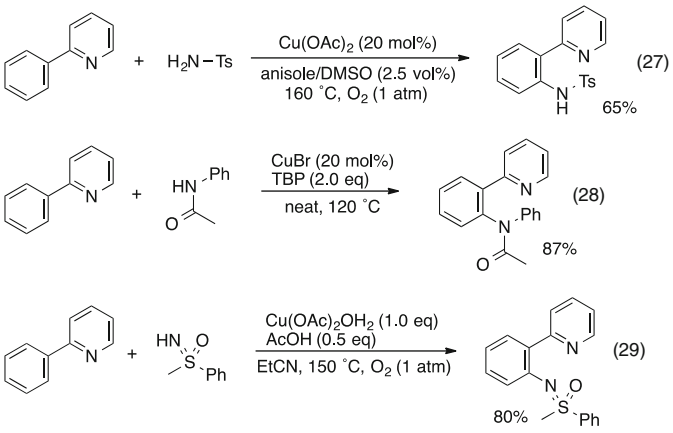
Due to the ubiquity of (hetero)arylamines in biologically active compounds, natural products, and organic functional materials, the aromatic C–N formation has been widely explored over the last two decades [44, 45]. Among them, the

dehydrogenative coupling with readily available (hetero)arenes and amines is ideal but difficult, particularly in an intermolecular manner, even with the noble transition metals such as palladium. The challenging aromatic C–H/N–H coupling has been recently achieved in copper-based systems.

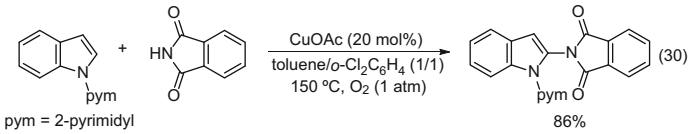
The first copper-*catalyzed* intermolecular C–H/N–H coupling was reported by Mori and Schreiber, independently, in 2009 (Eqs. 22 and 23) [46, 47]. Although the scope of the aromatic compound is limited to the acidic 1,3-azoles, the catalytic turnover of copper is realized by an ideal oxidant, molecular oxygen. Subsequently, similar aminations of polyfluoroarenes (Eq. 24) and pyridine *N*-oxides (Eq. 25) were developed by Su [48] and the groups of Li [49], Wu, and Cui [50], respectively. When the biologically important sulfoximine is employed as a nitrogen source, the reaction proceeds smoothly even under ambient conditions, and the enantiopure substrate is converted into the product without affecting the enantiomeric excess (Eq. 26) [51].



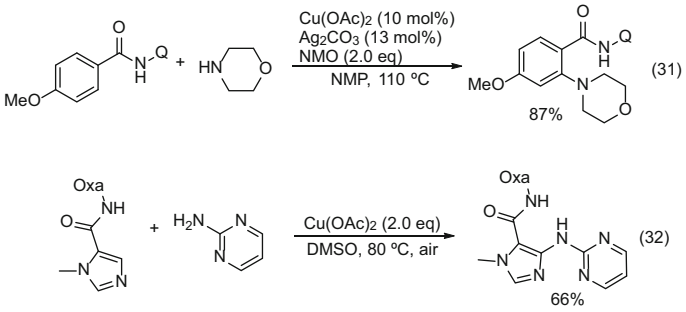
Meanwhile, Nicholas succeeded in the development of catalytic variants of work by Yu and Chatani in Eqs. (1) and (2). The key to the success is a careful choice of the solvent: an anisole/DMSO cosolvent system is essential for the good conversion (Eq. 27) [52]. Li and coworkers also reported the catalytic system with *tert*-butyl peroxide (TBP) as an oxidant (Eq. 28) [53]. In the latter case, an aminyl radical species might be involved in the C–N forming step [54], although the details are not clear. Additionally, the sulfoximine is also a promising coupling partner for 2-phenylpyridine, albeit with a stoichiometric amount of $Cu(OAc)_2$ (Eq. 29) [55].



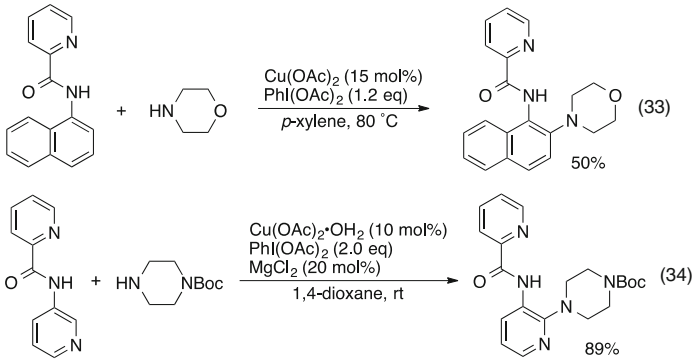
More general arenes and heteroarenes can be employed by the introduction of appropriate directing groups. Shen and coworkers reported the CuOAc/O_2-catalyzed C2-selective amination of *N*-(2-pyrimidyl)indoles with phthalimide (Eq. 30) [56].



Similar to the C–H/C–H coupling mentioned in Section 2, some *N*,*N*-bidentate coordinating groups also work well in the C–H/N–H coupling. Benzamides bearing the quinoline moiety are directly aminated under the copper/silver bimetallic catalyst system, although the exact role of the silver salt is not clear (Eq. 31) [57]. The oxazoline-based double coordination strategy allows the otherwise difficult dehydrogenative C–N coupling of various heteroarenes and heteroarylamines to afford heteroatom-rich diarylamines of pharmaceutical importance (Eq. 32) [58]. Intriguingly, the scope of amines is complementary: in the former case, strongly basic alkylamines are applicable whereas the latter conditions accommodate less basic arylamines and amides.



By using a picoline-type director, anilides can also couple with alkylamines in a dehydrogenative manner to form the corresponding 1,2-diaminobenzene derivatives (Eqs. 33 and 34) [59, 60]. The hypervalent I(III) reagent, $PhI(OAc)_2$ is a critical oxidant, and the reaction occurs under relatively mild conditions (rt–80 °C). The unique *ortho*-regioselectivity observed in the reaction of 1-naphthylamine and preliminary deuterium-labeling experiments suggests a single electron transfer (SET) mechanism, although the detailed pathway still remains obscure.

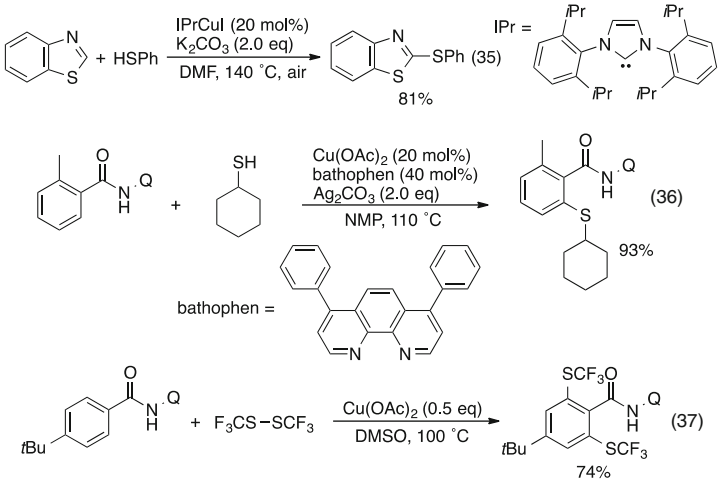


4 C–H/X–H Coupling with Other Heteroatom Nucleophiles

Some heteroatom nucleophiles other than amines also couples with aromatic C–H bonds under appropriate copper-based conditions to make the corresponding C–X bonds efficiently.

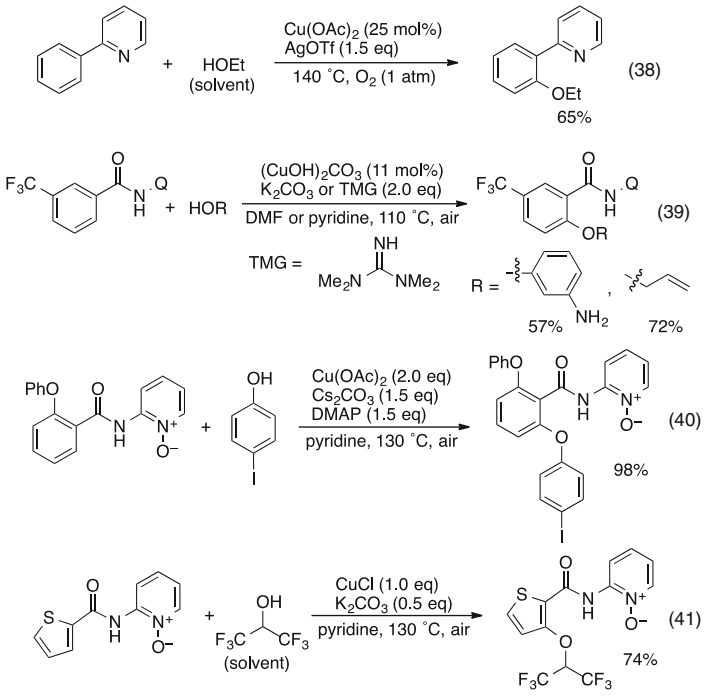
4.1 S-Nucleophiles

Several copper salts have been found to promote the dehydrogenative thiolation of 1,3-azoles with both aromatic and aliphatic thiols [61–66]. Especially, *N*-heterocyclic carbenes (NHCs)-ligated copper complexes show the high catalytic activity (Eq. 35) [66]. The thiolation of less acidic aromatic substrates is possible with the aid of Daugulis's quinoline-type bidentate coordinating group (Eq. 36) [67]. In this case, the corresponding disulfides, for example, $F_3CS–SCF_3$, are also effective thiolation reagents (Eq. 37) [68].



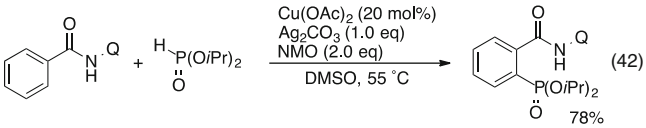
4.2 O-Nucleophiles

The C–H/O–H coupling of 2-phenylpyridine with primary and secondary aliphatic alcohols occurs in the presence of a $Cu(OAc)_2$ catalyst and $AgOTf/O_2$ dual oxidants (Eq. 38) [69]. Unfortunately, phenols in place of the alcohols result in no formation of the C–O coupling products, due to the dominant self-coupling under oxidative conditions. The use of the quinoline auxiliary overcomes this limitation, and phenol derivatives as well as easily-oxidizable allylic and benzylic alcohols can be employed (Eq. 39) [70]. Interestingly, with 3-aminophenol, the selective C–O formation over C–N formation is observed. Very recently, the group of Niu and Song introduced the unique *N,O*-bidentate directing group based on 2-aminopyridine *N*-oxide and succeeded in the copper-mediated dehydrogenative C–O coupling of aromatic compounds with both aromatic and aliphatic alcohols (Eqs. 40 and 41) [71, 72]. Unusual compatibility with aryl iodide as well as hexafluoro-2-propanol (HFIP) is observed.

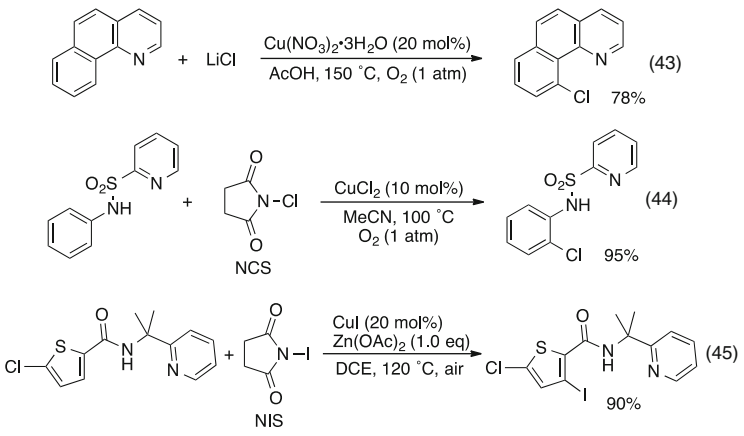


4.3 *Miscellaneous Nucleophiles*

The potential of P-based nucleophiles in the copper-promoted dehydrogenative aromatic coupling was reported by the research group of Chen and Yu (Eq. 42) [73]. With the assistance of the *N*,*N*-bidentate coordination of the aminoquinoline, the copper-catalyzed C–P formation of aromatics with dialkylphosphonates proceeds to produce the corresponding aryl phosphonates in good yields.



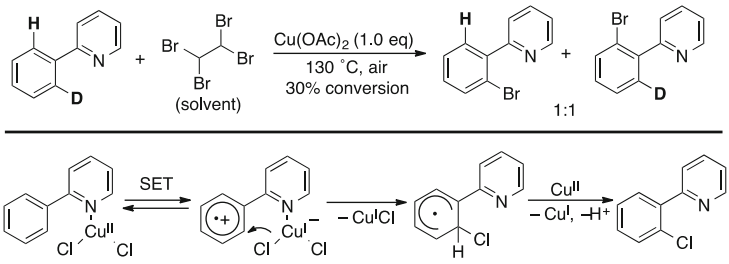
Some halogen sources, such as LiCl, NCS, and NIS, also couple with aromatic C–H bonds to form the corresponding C–halogen bonds under appropriate copper catalysis [7, 74–78]. Some representative examples are illustrated in Eqs. (43) to (45).



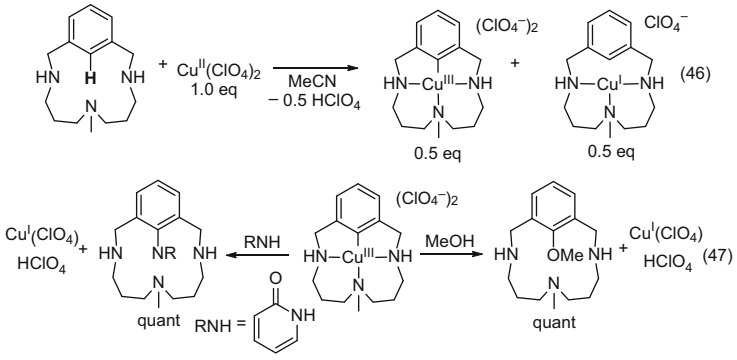
5 Mechanistic Studies

The detailed mechanism of copper-mediated dehydrogenative couplings mentioned above remains largely elusive because under oxidative conditions, copper complexes can have several oxidation states including Cu(0), Cu(I), Cu(II), and Cu(III). Despite such complications, seminal studies recently appear. In an early work by Yu in 2006 (Eq. 1) [7], a SET mechanism is proposed on the basis of deuterium-labeling experiments: no kinetic isotope effect (KIE) is observed in the intramolecular competition (Scheme 2). As exemplified by the chlorination, the pyridine directing group can coordinate to the Cu center to form ate-type complexes and induce the one-electron oxidation followed by ligand transfer regioselectively at the *ortho*-position. The second SET process by an additional Cu(II) species provides the observed C–H functionalized product.

On the other hand, a very unique redox system involving Cu(I)/Cu(II)/Cu(III) oxidation states was reported by Ribas, Stahl, and coworkers [79–81]. They extensively studied the reactivity of the triazamacrocyclic ligand with Cu(II) and successfully characterized C–H activated Ar–Cu(III) and Cu(I) complexes. The careful investigation of the reaction stoichiometry revealed that 0.5 eq of Ar–Cu(III) and 0.5 eq of Ar–Cu(I) are formed from 1.0 eq of Cu(II), thus suggesting an disproportionation of Cu(II) into Cu(III) and Cu(I) during the C–H activation event (Eq. 46). Upon treatment of the isolated Ar–Cu(III) complex with MeOH as an oxygen nucleophile, the C–H alkoxylated product and Cu(I) salt are obtained quantitatively (Eq. 47). A similar C–N bond formation occurs when NH pyridone is used as a nitrogen nucleophile.

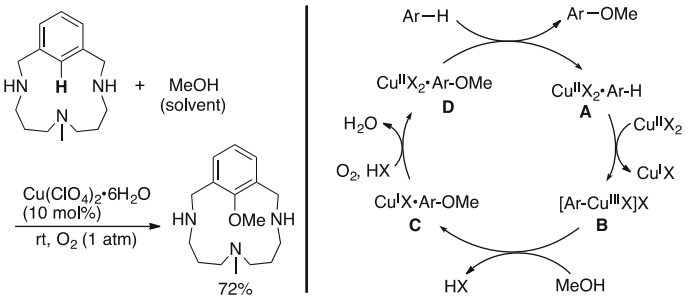


Scheme 2 A SET mechanism of Cu(II)-mediated C–H functionalization proposed by Yu

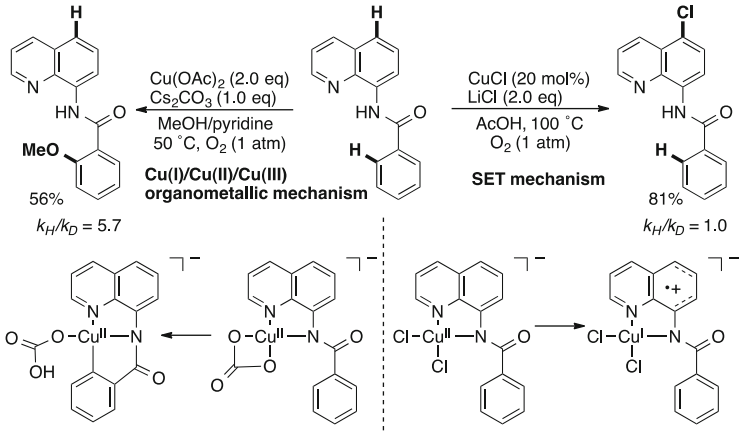


Based on the above outcomes, the mechanism of the Cu(II)/O_2-catalyzed C–H/O–H coupling of the macrocyclic arene with MeOH is proposed as shown in Scheme 3. An initial complexation of the arene with Cu(II) (**A**) is followed by C–H cupration with concomitant disproportionation by additional Cu(II) to form Ar–Cu(III) intermediate (**B**). Subsequent reaction with MeOH probably through reductive elimination furnish the C–O coupling product-ligated Cu(I) complex (**C**). The formed Cu(I) species is reoxidized by O_2 (**D**), and final ligand exchange with the starting arene liberates the product and regenerates the starting Cu(II) complex (**A**) to complete the catalytic cycle.

Additionally, the research group of Ertem and Stahl recently reported a condition-dependent, divergent mechanism in the Cu(II)-mediated C–H functionalization of the benzamide with Daugulis's auxiliary (Scheme 4) [82]. Under acidic chlorination conditions with a CuCl catalyst and LiCl in AcOH, the SET mechanism is operative, and the C–H chlorination occurs selectively at C5 position of the quinoline ring. A KIE value of 1.0 also supports the electron transfer system. In sharp contrast, under relatively basic conditions, the Cu$(OAc)_2$-mediated C–H/O–H coupling with MeOH proceeds exclusively at the *ortho*-position of the benzamide ring. A large KIE value of 5.7 as well as the observed site selectivity apparently indicates a different C–H activation mechanism. In the latter case, the reaction involves a Cu(I)/Cu(II)/Cu(III) organometallic pathway similar to that in Scheme 3. Particularly notable is the C–H activation at the Cu(II) center prior to the oxidation



Scheme 3 A unique one-electron redox mechanism in Cu(II)-mediated C–H/O–H coupling

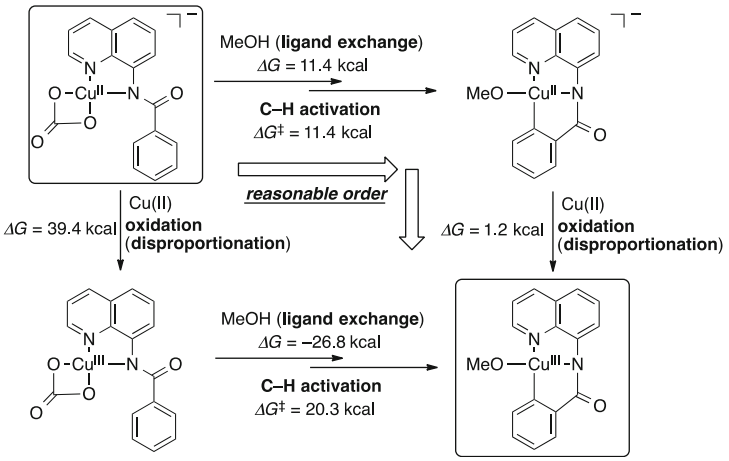


Scheme 4 A condition-dependent, divergent mechanism in Cu(II)-mediated C–H activation: SET vs organometallic pathway

(disproportionation) into the Cu(III), which is supported by DFT calculations (Scheme 5).

6 Conclusion

Over the last decade, the copper-mediated or copper-catalyzed C–H functionalization has been developed rapidly and greatly by significant efforts of many researchers, and cheap and abundant copper salts now can replace, to some extent, precedented noble transition metal catalysts such as Pd, Rh, and Ru. Moreover, some unique features of copper salts and complexes are observed. The intermolecular dehydrogenative cross-couplings mentioned in this chapter are such good examples, and they are otherwise challenging even under known noble transition metal catalysis. However, there is still a large room for further



Scheme 5 DFT calculations for C–H activation: Cu(II) vs Cu(III)

development: improvement of turnover number (or frequency), use of atmospheric oxygen as an ideal terminal oxidant, activation of even more challenging sp^3 C–H bonds [83–85], and application to asymmetric catalysis. The clarification of detailed mechanisms and design of new Cu-based catalysis can address these problems and open a door to truly useful and practical synthetic transformation based on C–H activation chemistry.

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