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Iron-Catalyzed C–H Bond Activation

Laurean Ilies and Eiichi Nakamura

Abstract Iron-catalyzed C–H bond activation followed by C–C bond formation has received much attention in recent years, motivated by the environmental and economical merits of iron, as well as the scientific challenge in controlling and understanding the reactivity of iron species. This review describes the utilization of iron as a catalyst for directed C–H bond activation, followed by C–C bond formation. Catalytic activation of $C(sp^2)$-H and $C(sp^3$-H) bonds, followed by oxidative reaction with nucleophiles, or reaction with electrophiles is described. Reactions of substrates possessing a directing group are mainly discussed, but other substrates are also presented. Carbon–heteroatom bond formation is also briefly discussed.

Keywords C–C bond formation · C–H bond activation · Iron

Contents

L. Ilies (✉) and E. Nakamura (✉)
Department of Chemistry, The University of Tokyo, School of Science, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan
e-mail: laur@chem.s.u-tokyo.ac.jp; nakamura@chem.s.u-tokyo.ac.jp

1 Introduction

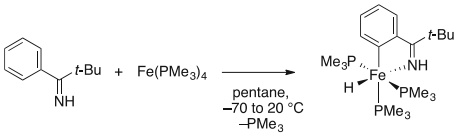
Transition-metal-catalyzed carbon–hydrogen (C–H) activation followed by carbon–carbon (C–C) bond formation has become one of the most active research topics in recent synthetic chemistry, because it could enable the straightforward, step-efficient construction of the framework of target molecules [1–5]. However, there are serious challenges to overcome for the development of these reactions: the C–H bond is thermodynamically stable and difficult to cleave, especially in the presence of other functional groups, typically more labile; also, to differentiate between the many C–H bonds in an organic molecule is a formidable task. Utilization of a directing group, which coordinates the metal catalyst and cleaves the proximity C–H bond selectively in an intramolecular-like fashion, has been a popular strategy to overcome these problems. Late-transition metals such as Pd, Ru, Rh, Ir, etc. have been extensively investigated for this purpose, and versatile and efficient catalytic systems based on these metals have been achieved. However, economic and environmental incentives shifted the interest to first-row transition metals (base metals) for C–H bond activation [6]. Among these, iron is the most abundant transition metal, inexpensive, and nontoxic, and therefore, it has attracted special attention for catalysis [7, 8].

This review describes the utilization of iron as a catalyst for directed C–H bond activation, followed by C–C bond formation. Nondirected reactions, many of which proceed through radical pathways, are briefly discussed. Carbon–heteroatom bond formation is briefly discussed, and reactions where iron acts as a Lewis acid or simply as a radical initiator are outside the scope of this review. Several reviews or minireviews discussing iron-catalyzed C–H bond activation have been published recently [9–16].

2 Functionalization of C(sp^2)–H Bonds

2.1 Substrates Possessing a Directing Group

Cyclometalation reactions using iron complexes have been known for a long time [17–20]. Of special interest for the development of a catalytic reaction under mild conditions are the reports that iron(0) complexes can oxidatively add into the *ortho* C–H bond of an aromatic imine (Eq. 1), and alkyliron(II) complexes can cleave an *ortho* C–H bond with elimination of alkane (Eq. 2) [21, 22].



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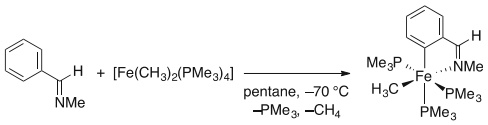

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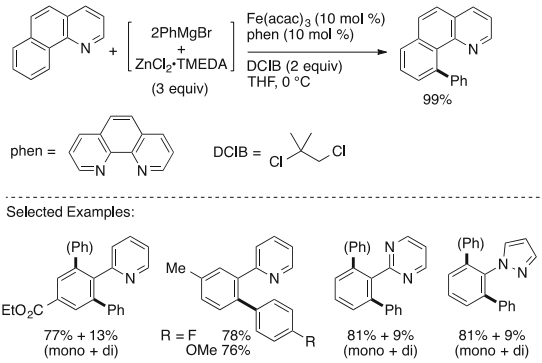
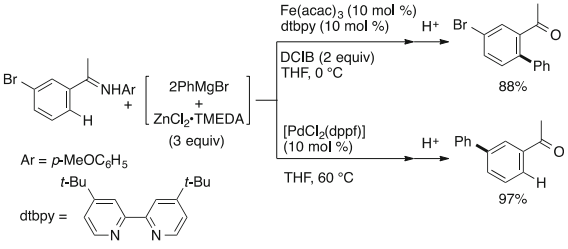
2.1.1 Catalytic Reactions with Nucleophilic Reagents

After the relatively numerous reports on cyclometalation reactions using iron complexes, the first example of a catalytic reaction was reported in 2008, when Nakamura and collaborators reported that arylpyridines and congeners can be arylated with diarylzinc generated in situ from a Grignard reagent and $ZnCl_2$·TMEDA in the presence of a catalytic amount of Fe(III) salt, a bipyridine-type ligand, and a dihaloalkane oxidant (Eq. 3) [23]. The reaction proceeded in high yield at 0°C, with selectivity for the monoarylated product.



(3)

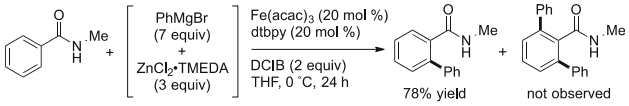
The same group reported 1 year later that aromatic imines can also be *ortho* arylated under similar conditions, and the resulting imine was hydrolyzed during acidic workup to the corresponding ketone (Eq. 4) [24]. The C–H bond was preferentially functionalized in the presence of a reactive bromide, triflate, or tosylate group, in contrast with palladium catalysis, where the halide reacts selectively (Eq. 5). Nakamura group also demonstrated that dioxygen can be used as an alternative oxidant, albeit the reaction efficiency decreased [25].



(4, 5)

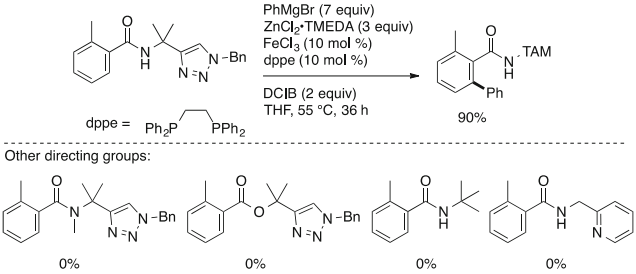
Under similar reaction conditions, *N*-methylbenzamides were *ortho* arylated with diarylzinc (Eq. 6) [26]. The reaction proceeded selectively and only the

monoarylated product was obtained, presumably because of the steric bias induced by the *ortho* substituent, which disturbs the cyclometalation step.



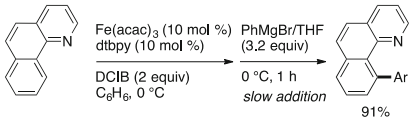
(6)

The oxidative reaction of amides with diarylzinc reagents was reported by Ackermann [27]. The use of a bidentate directing group containing a triazole moiety (TAM) was crucial for the efficiency of the reaction (Eq. 7).



(7)

The arylation of arylpyridines (Eq. 8) and aromatic amines (Eq. 9) can also be achieved using Grignard reagents [28]. For these reactions, the slow addition of the Grignard reagent proved crucial in order to prevent excessive homocoupling of the organometallic reagent [29, 30], and under the slow addition condition, the *ortho*-arylated compounds were obtained in high yield. DuBois used similar reaction conditions to investigate the arylation of various heterocyclic substrates such as pyridines, thiophenes, and furans (Eq. 10) [31].



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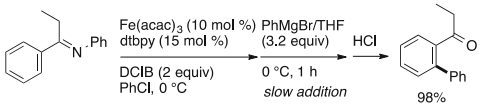


(9)

(10)

The mechanism of these reactions is largely unknown. Nakamura showed [28] that the reaction requires an oxidant for catalyst turnover and to accelerate reductive elimination, and the reaction with a stoichiometric amount of iron in the absence of an oxidant, followed by high deuterium incorporation upon quenching with

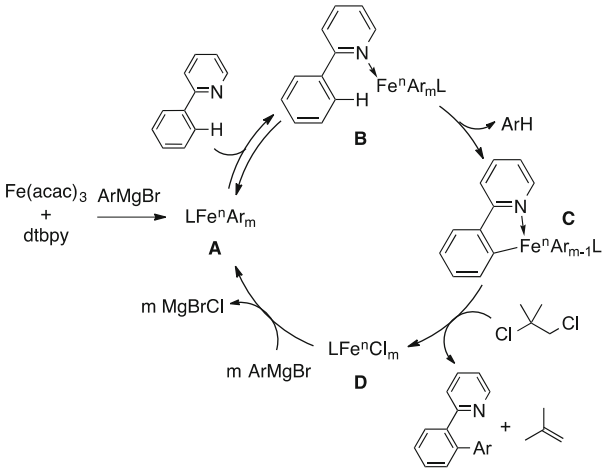
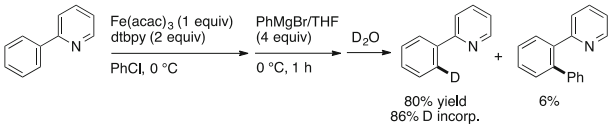


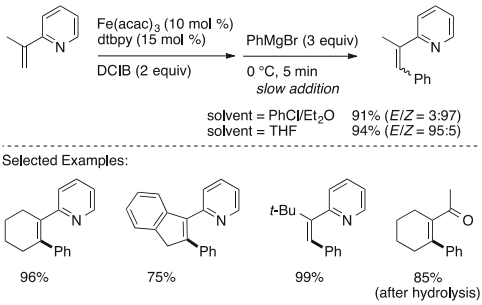
Fig. 1 A proposed catalytic cycle for the iron-catalyzed oxidative C–H functionalization with organometallic reagents

deuterium oxide (Eq. 11), suggested the intermediacy of a ferracycle. Kinetic isotope effect experiments showed a large value for the intermolecular (3.4) and intramolecular (3.1) competition, indicating that coordination of the pyridyl group to the iron catalyst takes place in a reversible manner and that the following C–H bond-cleavage step is the first irreversible step of the catalytic cycle [32]. Taking also into account the cyclometalation reaction with diorganoiron complexes depicted in Eq. 2, the authors proposed the catalytic cycle in Fig. 1. An organoiron species **A** generated from the iron(III) salt and the organometallic reagent [33] reversibly coordinates the substrate and then cleaves the *ortho* C–H bond to generate metallacycle **C**. This complex is stable in the absence of the oxidant as shown by the deuterium-labeling experiment but readily undergoes reductive elimination in the presence of a dichloroalkane oxidant to give the *ortho*-arylated product and regenerate the catalyst. The valence of iron during this catalytic cycle is unclear: formation of a homocoupling product (Ar–Ar) suggests that iron is reduced to a lower valence; however, subsequent work from Nakamura group (vide infra) showed that an iron(III) species is competent for C–H activation, and therefore, the reduction of iron may occur outside the catalytic cycle.



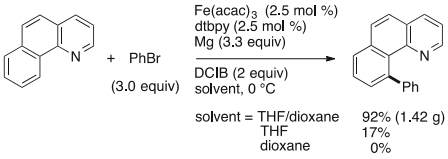
(11)

The group of Nakamura reported that an alkene possessing a pyridine or imine group can be arylated with Grignard reagents in a stereoselective fashion (Eq. 12) [34]. The reaction proceeded within 5 min at 0°C to give the *Z* product when chlorobenzene was used as a solvent or the *E* product when THF was used as a solvent. Control experiments showed that the *Z* product forms first and then isomerizes in the presence of THF.



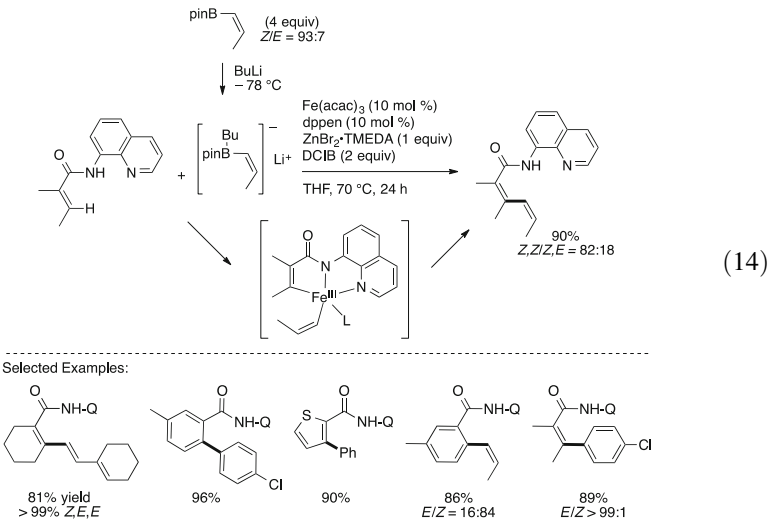
(12)

To circumvent the use of organometallic reagents, the group of Nakamura used aryl bromides in the presence of metallic magnesium for the *ortho* arylation of arylpyridines and aromatic imines (Eq. 13) [35]. It was assumed that a Grignard reagent is generated in situ, possibly facilitated by the iron catalyst [36–38]. Dioxane was used as a cosolvent in order to retard the generation rate of the Grignard reagent and its subsequent homocoupling, rather than to generate a diarylmagnesium reagent, which a control experiment showed to be low yielding.



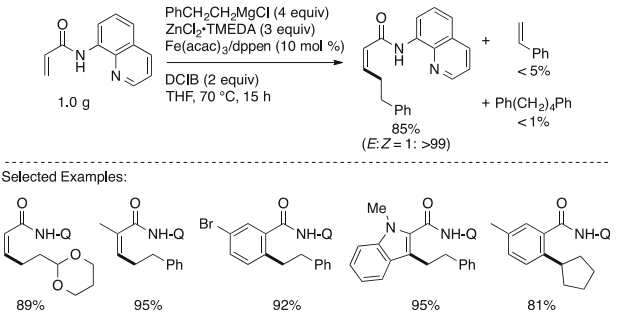
(13)

A common problem of these reactions was the rather restricted reaction scope and versatility. Because a significant amount of homocoupling of the organometallic reagent was observed and based on previous knowledge [33], it was assumed that iron was reduced to a lower-valent species (or a mixture of species) and combined with the use of a reactive organozinc or organomagnesium reagent, the reaction scope and functional group tolerance were poor. Ilies and Nakamura found a solution to this problem: if iron could be stabilized as an iron(III) species by the use of appropriate ligands and a milder organometallic reagent, a more versatile catalytic system was expected. And indeed, by using an organoborate as the organometallic reagent [39, 40] in the presence of an iron(III) salt, a diphosphine ligand, a zinc salt cocatalyst, and a dihalide oxidant, the coupling of a variety of aryl, heteroaryl, and alkenyl amides possessing a bidentate 8-quinolylamide group [41–43] with aryl and alkenyl boron reagents was achieved (Eq. 14) [44]. The stereospecific alkene–alkene coupling to produce (*Z*,*E*) or (*Z*,*Z*) dienes or trienes is especially noteworthy. The homocoupling of the organometallic reagent was observed in a trace amount for the catalytic reaction, and in small amount (13%) for the reaction using a stoichiometric amount of iron, demonstrating that the iron(III) species is not reduced by the organometallic reagent. Combined with the poor activity of an Fe(II) precursor, the authors concluded that an organoiron(III) species is responsible for cleaving the C–H bond. The zinc salt was considered to assist the transfer of the organic group from borate to iron [45, 46]. The authors also suggested the low-valent iron species that is generated after reductive elimination may be stabilized by spin delocalization over the diphosphine ligand and quinolylamine directing group [47].



(14)

Ilies and Nakamura recently reported the alkylation of alkene-, arene-, and heteroareneamides possessing the 8-aminoquinolyl group with alkylzinc halides (Eq. 15) [48]. The use of a bidentate directing group was crucial in order to prevent the β-hydride elimination of the alky liron intermediate; the reaction of a substrate possessing a monodentate directing group such as pyridine with phenethylzinc halide resulted in the recovery of the starting material together with formation of styrene. Notably, the homocoupling of the organometallic reagent was also suppressed, suggesting that an organoiron(III) species is the active species. The stereospecific reaction of acrylamide is especially noteworthy, because the reaction of this substrate is typically sluggish under C–H bond activation conditions.



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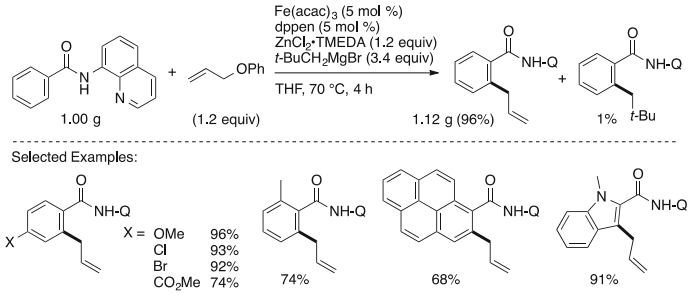
2.1.2 Catalytic Reactions with Electrophilic Reagents

The reactions described in the previous paragraph utilize an organometallic reagent as the reaction partner under oxidative conditions. From a practical point of view, the use of an electrophilic, neutral reagent as the reaction partner is more attractive. However, if an organometallic reagent is used as a base in the presence of an electrophile, the oxidative reaction between the C–H substrate and the

organometallic reagent and the reaction between the organometallic reagent and the electrophile compete with the desired reaction of the C–H substrate with the electrophile.

The first successful example of this type of reaction was reported by Ilies and Nakamura in 2013 (Eq. 16) [49]. They utilized a bidentate 8-quinolylamide directing group, a diphosphine ligand, and a bulky organozinc reagent as the base, to succeed in coupling an aromatic carboxamide with allyl phenyl ether in high yield, and with suppression of the oxidative reaction of the substrate with the organometallic reagent, or the cross-coupling between the allyl ether and the diorganozinc. Various aromatic carboxamides reacted well, but the scope of the allyl ether was limited. A deuterium-labeling experiment showed that the allylation reaction proceeds with γ-selectivity, and an intermolecular KIE experiment showed that the C–H bond activation step is not involved in the turnover-limiting step. The authors also showed that 1-arylpyrazoles and congeners can also be allylated with allyl phenyl ether using iron catalysis [50]. The authors also achieved an amination reaction under similar conditions, where an *N*-chloroamine was used as the electrophile (Eq. 17) [51].



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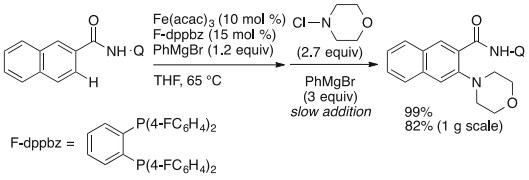
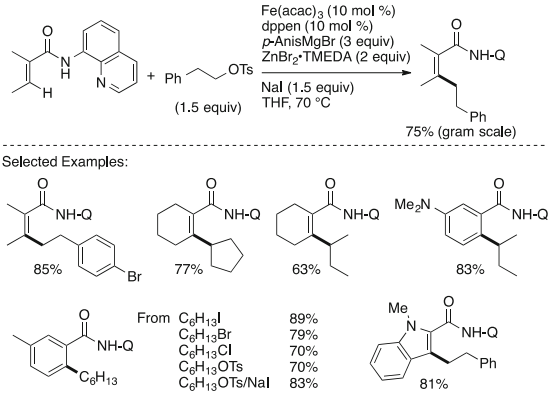


(17)

Iron-catalyzed alkylation of carboxamides possessing an 8-aminoquinolyl group with alkyl tosylates and halides was reported by Ilies and Nakamura [52], and at the same time the reaction of similar substrates with alkyl halides was reported by Cook [53, 54].

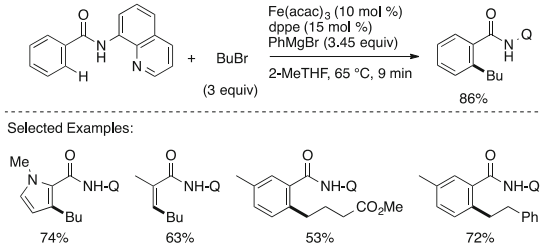
Ilies and Nakamura reported the iron/diphosphine-catalyzed reaction of arene-, heteroarene-, and alkeneamides with primary and secondary alkyl tosylates or halides (Eq. 18) [52]. The reaction of acyclic alkenes substrated proceeded stereoselectively, and acyclic secondary tosylates could be introduced without isomerization of the alkyl group to the linear one. A chiral alkyl center underwent isomerization, and a cyclopropylalkyl group reacted with the opening of the cyclopropyl ring, suggesting that the alkyl iron species has a radical character. Homocoupling of the organozinc halide that

was used as a base was not observed, suggesting that an organoiron(III) may be the active species. Control experiments showed that under the reaction conditions, alkyl tosylates and chlorides are converted into the corresponding bromides.



(18)

Cook reported the iron/diphosphine-catalyzed alkylation of arene-, heteroarene-, and alkeneamides with primary alkyl halides (Eq. 19) [53] and, shortly after, the alkylation of aromatic amides with benzyl chlorides and secondary alkyl bromides (Eq. 20) [54]. The reaction with primary alkyl bromides proceeded well for aromatic, heteroaromatic, and alkenyl amides; despite using phenylmagnesium bromide as a base, the reaction with benzyl chlorides proceeded well under air. As previously observed by Nakamura [28, 34], the slow addition of the Grignard reagent was crucial in order to achieve high yields, presumably because of the competing homocoupling [29]. Secondary alkyl bromides and iodides could be employed in the reaction with benzamides, but acyclic secondary alkyls underwent partial isomerization to the linear alkyl.



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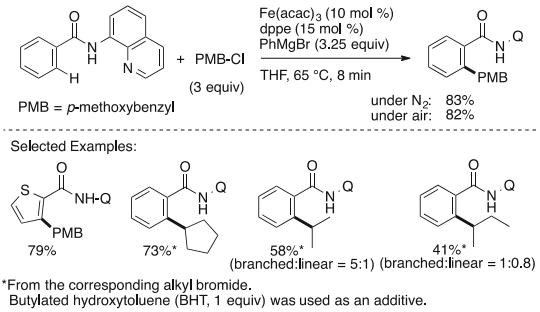
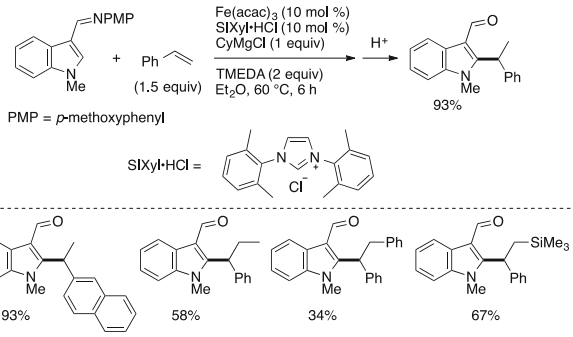


(20)

The iron-catalyzed directed C–H alkylation and alkenylation of indole derivatives possessing an imine group with alkenes and alkynes, respectively, was reported by Yoshikai (Eqs. 21 and 22) [55]. Inspired by an analogy with cobalt catalysis [56], they used an *N*-heterocyclic carbene as a ligand, cyclohexylmagnesium chloride as a base, and TMEDA as an essential additive for the reaction with alkenes, whereas phenylmagnesium bromide was the base of choice, and TMEDA was not necessary for the reaction with alkynes. The reaction with styrene derivatives proceeded regioselectively to give the branched product; however, other terminal alkenes such as 1-octene did not react. *β*-Substituted styrenes could also be employed in this reaction. Diaryl-, arylsilyl-, and alkylsilyl-substituted alkynes gave the (*E*)-alkenylated product, but in some cases isomerization was observed. A dialkylalkyne was much less reactive. Based on deuterium-labeling experiments, the authors proposed that the Grignard reagent reduces the iron precatalyst to a low-valent iron-NHC species, which after coordination to the imine directing group oxidatively adds the C–H bond. Next the alkene or alkyne undergoes migratory insertion into the iron hydride complex, followed by reductive elimination to give the product.



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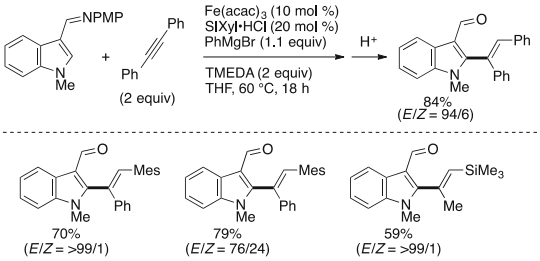

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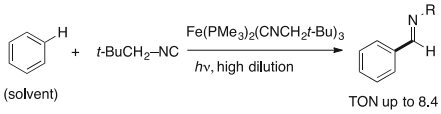
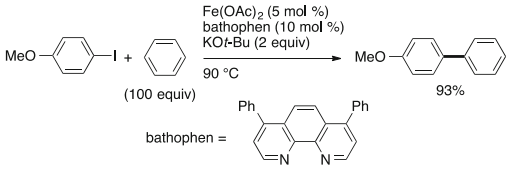
2.2 *Other Substrates*

It has been known from the 1970s that an iron complex can cleave the C–H bond of an arene [57, 58]. However, the exploitation of this reactivity for the development of a catalytic reaction has been largely neglected to date. An early attempt was described in 1987 [59], when Jones reported that an iron–isocyanide complex can insert the isocyanide group into the C–H bond of benzene upon irradiation with light, and in the presence of added isonitrile and high dilution, the reaction was catalytic in iron, albeit the turnover was low (Eq. 23).



(23)

In 2010, the groups of Charette and Lei independently reported an iron/diamine-catalyzed reaction of aryl iodides or bromides with a solvent amount of arene at 80–90°C (Eqs. 24 and 25) [60, 61]. A mixture of *ortho*-, *meta*-, and *para*-isomers was obtained when substituted arenes were used as the substrate, the *ortho*-isomer being the major product. The Charette group reported a KIE value of 1.04, while Lei group measured a KIE of 1.7. Based also on reaction inhibition by a radical scavenger, Charette suggested that radical processes are involved. Recent studies have revealed that cross-coupling of an aryl halide with an arene can proceed in the absence of a transition metal catalyst ([62] and references therein).



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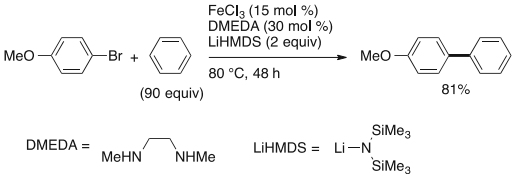
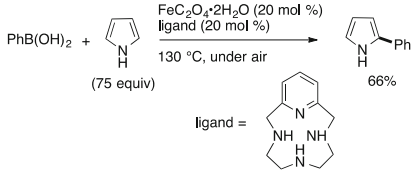


(25)

Hu and Yu reported an iron/macrocyclic polyamine-catalyzed reaction of arylboronic acids with a large excess of pyrrole or pyridine at 130°C under air (Eqs. 26 and 27) [63], based on their previous studies on iron-mediated reactions (initial report using a stoichiometric amount of iron: [64]). Pyrrole derivatives were arylated at 2-position in good yield (Eq. 26), but when pyridine was used as a substrate, the catalyst turnover was poor and 2-arylpyridine was obtained together with a small amount of 3-aryl- and 4-arylpyridine (Eq. 27). Because a catalytic amount of a radical scavenger did not inhibit the reaction, the authors proposed an oxoiron complex as the active species to activate the *ortho*-hydrogen of the heterocycle via σ-bond metathesis and also performed a DFT analysis of the mechanism. A related iron-catalyzed reaction of aryl boronic acids with heteroarenes was reported by Singh and Vishwakarma [65].



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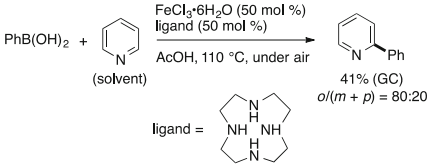
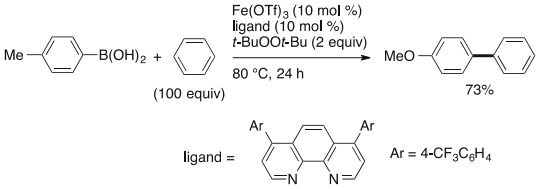


(27)

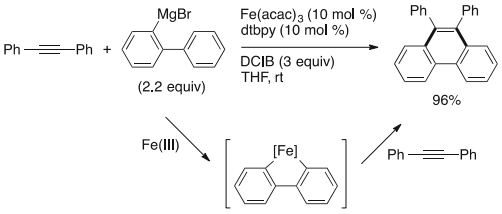
Shirakawa and Hayashi reported the iron-catalyzed oxidative coupling of arylboronic acids with arenes and heteroarenes (Eq. 28) [66]. They used iron(III) triflate, a bipyridine-type ligand, and a peroxide as an oxidant. For substituted arenes, a mixture of *ortho*-, *meta*-, and *para*-substituted compounds was obtained, with modest selectivity for the *ortho*-isomer. The authors propose that Fe(III) mediates generation of *t*-BuO radical from the peroxide, which oxidizes the arylboronic acid to generate an aryl radical that adds to the arene substrate.



(28)

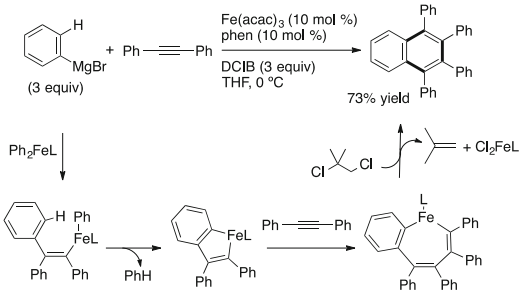
Nakamura reported that 2-biphenylmagnesium and congeners could be annulated with alkynes under mild reaction conditions in the presence of an iron catalyst and a dihalide oxidant to produce a variety of phenanthrene derivatives (Eq. 29) [67]. Based on deuterium-labeling experiments, the authors proposed the

intermediacy of a biphenyl metallacycle, formed through intramolecular activation of the *ortho*-hydrogen.



(29)

Nakamura group also reported the reaction of aryl Grignard reagents with two molecules of alkynes to produce polysubstituted naphthalenes (Eq. 30) [68]. Diarylalkynes reacted in good yield, but dialkylalkynes gave lower yield. A limitation of this reaction was the lack of regioselectivity when differently substituted substrates were used. The authors proposed that in situ-generated aryliron species carbometalate the alkyne [69–73], followed by C–H bond activation, insertion of a second molecule of alkyne, and finally reductive elimination to give the product.



(30)

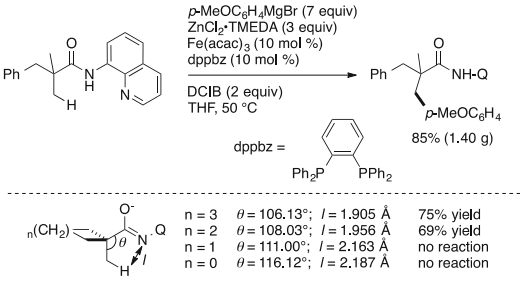
Iron-catalyzed silylation and borylation of a C–H bond has received much attention recently. Sunada and Nagashima reported that a disilaferracycle iron carbonyl complex can catalyze the C-3-selective silylation of indoles [74]. Ito and Nishiyama reported that a similar reaction can be catalyzed by a pincer iron complex containing a silyl ligand [75]. Ohki and Tatsumi reported that Cp*Fe complexes bearing imidazolium salts catalyze the borylation of furans and thiophenes [76]. The borylation of arenes catalyzed by nano-Fe2O3 was reported by Kuang and Wang [77]; a similar reaction was reported by Mankand, who used an iron–copper heterobimetallic complex under photochemical conditions [78], and by Bontemps, Sortais, Sabo-Etienne, and Darcel, who used a bis(diphosphine)iron complex under UV irradiation [79].

3 Functionalization of C(sp^3)–H Bonds

3.1 Substrates Possessing a Directing Group

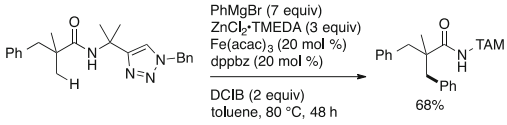
Directed activation of a C(sp^3)–H bond by an iron complex was much less investigated than the reaction of C(sp^2)–H bonds. Li reported the phosphine-directed C (sp^3)–H to form an iron pincer complex (e.g., [80]). Ohki and Tatsumi reported that Cp*Fe complexes bearing imidazolium salts undergo cyclometalation through C–H activation or can cleave the C–H bond of a heteroarene [81].

Nakamura reported the first iron-catalyzed directed functionalization of C(sp^3)–H bonds in 2013 (Eq. 31) [82]. Propionamides bearing a bidentate directing group could be arylated with diarylzinc reagents in the presence of an iron/diphosphine catalyst and a dichloroalkane oxidant. The nature of the directing group and of the diphosphine ligand was crucial for the success of this reaction, presumably because of stabilization of the putative organoiron intermediate. The reaction proceeded exclusive at the methyl C–H in the presence of a benzyl C–H, suggesting the intermediacy of organometallic species rather than a radical mechanism. The distance between the C–H bond and the directing group proved also important, and elongation of this distance resulted in shutting off the reaction.



(31)

Ackermann showed that a bidentate directing group containing a triazole moiety can also be used for this reaction, under otherwise very similar conditions (Eq. 32) [27].



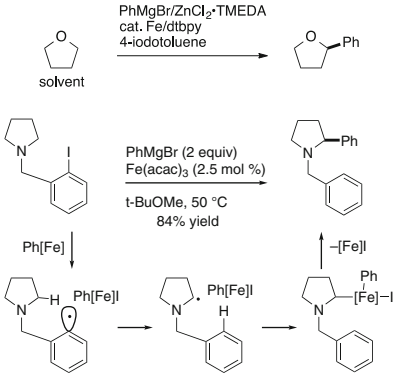
(32)

3.2 Other Substrates

Hartwig showed in 1997 that an iron boryl complex can cleave the C–H bond of a simple alkane under photochemical conditions [83, 84], but this reactivity was not exploited for C–C bond formation to date.

Nakamura observed the α-arylation of THF by an diorganozinc reagent in the presence of an iron/bipyridine-type ligand and 4-iodotoluene that presumably acted

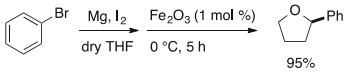
as an oxidant (Eq. 33) [85]. Based on this initial lead, a reaction that combines radical and organometallic reactivity of iron to achieve α-functionalization of aliphatic amines through 1,5-hydrogen transfer was designed (Eq. 34).



(33)

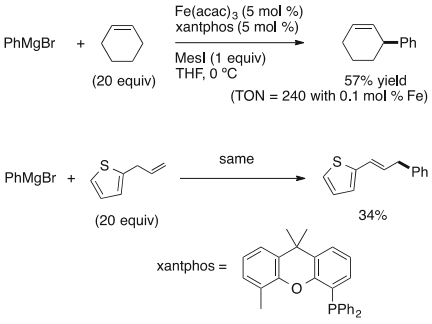
(34)

The α-arylation of ethers was further developed by Vishwakarma [86, 87], who reported that in situ-prepared Grignard reagents react with THF to give the corresponding 2-arylated compounds (Eq. 35). Despite its low solubility, iron oxide was the catalyst of choice, and high yields were reported.



(35)

The arylation of cyclic and acyclic alkenes at the allylic position with Grignard reagents was accomplished by Nakamura by using an iron/xantphos catalyst and mesityl iodide as an oxidant (Eqs. 36 and 37) [88]. The alkene was used in large excess, and the TON of the reaction reached 240. Control experiments supported the intermediacy of a π-allyliron rather than a Heck-type mechanism.



(36, 37)

A large number of cross-dehydrogenative couplings using iron catalysis under oxidative conditions have been reported [89, 90]. The coupling of sp^3–sp^3, sp^3–sp^2, and sp^3–sp bonds has been achieved. These reactions proceed through iron-mediated electron-transfer processes and are outside the scope of this review.

4 Conclusion

Iron-catalyzed C–H bond activation followed by C–C bond formation has received much attention in recent years, motivated by the environmental and economical merits of iron, as well as the scientific challenge in controlling and understanding the reactivity of iron species. Robust catalytic systems have been developed for directed C–H bond functionalization with organometallic reagents or with electrophiles, and in some cases versatility and efficiency rivaling precious metal catalysis have been achieved. Several examples of directed $C(sp^3)$–H activation have also been reported. Nondirected reactions have mostly relied on electron-transfer processes, especially the reactions of $C(sp^3)$–H bonds. While the pace of recent developments is impressive, it can be said that the potential of iron catalysis for C–H bond functionalization is far from being fulfilled. The repertoire of reactions is still limited, as is the variety of substrates available; many of these reactions use reactive organometallics as a base, and in many cases functional group tolerance or product selectivity is unsatisfactory. Two of the biggest obstacles in the development of these reactions are the lack of mechanistic understanding and implicitly the lack of guidelines for controlling the reactivity of iron species. It is the belief of the authors that in the near future these challenges will be successfully addressed, and efficient iron catalysts for versatile C–H bond functionalization will be achieved.

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