

Exploration of Earth-Abundant Transition Metals (Fe, Co, and Ni) as Catalysts in Unreactive Chemical Bond Activations

Published as part of the *Accounts of Chemical Research* special issue "Earth Abundant Metals in Homogeneous Catalysis".

Bo Su,[†] Zhi-Chao Cao,[†] and Zhang-Jie Shi^{†,‡,*}

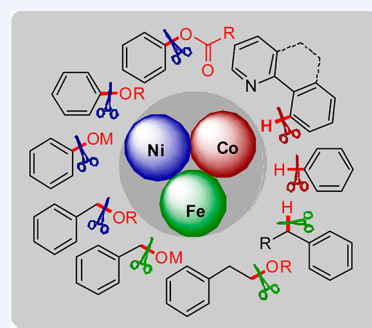
[†]Beijing National Laboratory of Molecular Sciences (BNLMS) and Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

[‡]State Key Laboratory of Organometallic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

CONSPECTUS: Activation of inert chemical bonds, such as C–H, C–O, C–C, and so on, is a very important area, to which has been drawn much attention by chemists for a long time and which is viewed as one of the most ideal ways to produce valuable chemicals. Under modern chemical bond activation logic, many conventionally viewed "inert" chemical bonds that were intact under traditional conditions can be reconsidered as *novel functionalities*, which not only avoids the tedious synthetic procedures for prefunctionalizations and the emission of undesirable wastes but also inspires chemists to create novel synthetic strategies in completely different manners.

Although activation of "inert" chemical bonds using stoichiometric amounts of transition metals has been reported in the past, much more attractive and challenging catalytic transformations began to blossom decades ago. Compared with the broad application of late and noble transition metals in this field, the earth-abundant first-row transition-metals, such as Fe, Co, and Ni, have become much more attractive, due to their obvious advantages, including high abundance on earth, low price, low or no toxicity, and unique catalytic characteristics.

In this Account, we summarize our recent efforts toward Fe, Co, and Ni catalyzed "inert" chemical bond activation. Our research first unveiled the unique catalytic ability of iron catalysts in C–O bond activation of both carboxylates and benzyl alcohols in the presence of Grignard reagents. The benzylic C–H functionalization was also developed via Fe catalysis with different nucleophiles, including both electron-rich arenes and 1-aryl-vinyl acetates. Cobalt catalysts also showed their uniqueness in both aromatic C–H activation and C–O activation in the presence of Grignard reagents. We reported the first cobalt-catalyzed sp^2 C–H activation/arylation and alkylation of benzo[*h*]quinoline and phenylpyridine, in which a new catalytic pathway via an oxidative addition process was demonstrated to be much preferable. Another interesting discovery was the Co-catalyzed magnesiation of benzylic alcohols in the presence of different Grignard reagents, which proceeded via Co-mediated selective C–O bond activation. In C–O activation, Ni catalysts were found to be most powerful, showing the high efficacy in different kinds of couplings starting from "inert" O-based electrophiles. In addition, Ni catalysts exhibited their power in C–H and C–C activation, which have been proven by us and pioneers in this field. Notably, our developments indicated that the catalytic efficacy in cross coupling between aryl bromides and arenes under mild conditions was not the privilege of several noble metals; most of the transition metals exhibited credible catalytic ability, including Fe, Co, and Ni. We hope our studies inspire more interest in the development of first row transition metal-catalyzed inert chemical bond functionalization.



1. INTRODUCTION

C–H, C–O, and C–C bonds are the most fundamental structural units in organic compounds. The *inertness* of these chemical bonds brings many disadvantages if chemists plan on functionalizing them. Taking the transition metal-catalyzed functionalization of arenes for example (Figure 1), in conventional organic transformations, the *inert* C–H or C–O bond must be first converted to the corresponding activated C–X (X = I, Br, Cl) or C–OR (R = Tf, Ts, Ms, etc.) functionalities, lengthening the synthetic routes and invariably resulting in the emission of wastes. Therefore, in modern chemistry, transition metal-catalyzed highly selective C–H, C–O, and C–C functionalization is more attractive.^{1–11} Under this logic,

unreactive chemical bonds can be reconsidered as *functionalities*, inspiring chemists to revolutionize the chemical synthesis by creating completely new synthetic strategies.¹

In the past several decades, late and noble transition metals, which are usually not abundant on earth, played key roles in "inert" bond activations. From an industrial point of view, expensive prices and high toxicity limit their broad applications. Comparably, the first-row transition metals, such as Fe, Co, and Ni, are much more abundant on earth, inexpensive, and more environmentally friendly. For example, the natural abundance of

Received: September 19, 2014

Published: February 13, 2015

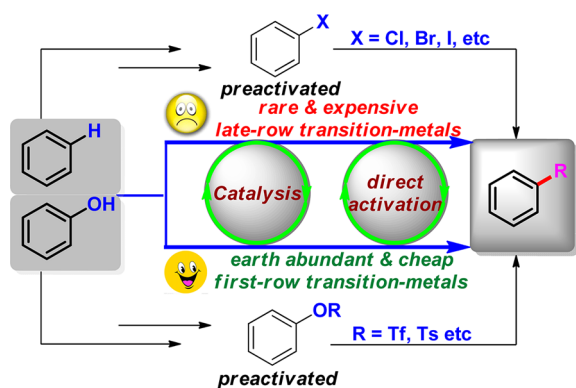


Figure 1. Inert chemical bond activation logic.

Fe, Ni, and Co on earth is about 32%, 1.8% and 0.88%, respectively. On the other hand, the first row transition-metal based catalysts usually display totally different or complementary catalytic reactivities owing to their unique d-electron structures. However, the investigation of first-row transition-metal catalyzed “inert” bond activation was recently unveiled. In this Account, we summarize our recent progress on Fe, Co, and Ni catalyzed “inert” chemical bond activation.

2. Fe CATALYSIS

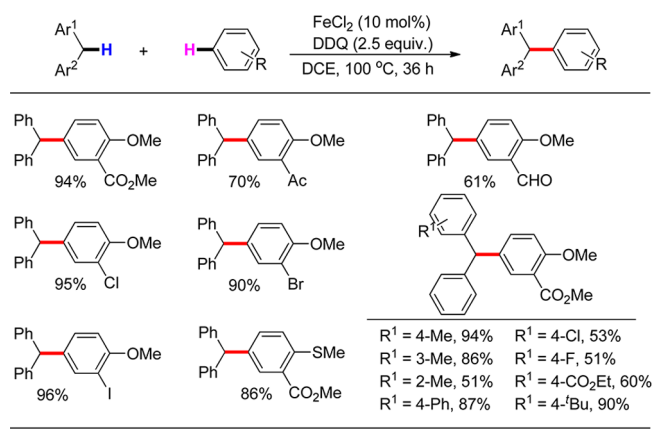
Fe is the most abundant transition metal on earth and plays important roles in nature. Indeed, Fe was also one of the metals early and successfully used in chemical synthesis. Although iron-catalyzed organic transformations, including nucleophilic additions, substitutions, reductions, oxidations, hydrogenations, cycloadditions, isomerizations, and rearrangements, as well as polymerizations, have been well studied,^{3,4} its application in “inert” chemical bond activation had been less investigated compared with that of late transition-metals. Aiming at exploring more environmentally friendly, practical, and conceptually novel organic transformations, we explored the catalytic application of Fe catalysis in C–O and C–H bond activations.

2.1. Fe-Catalyzed C–H Activation

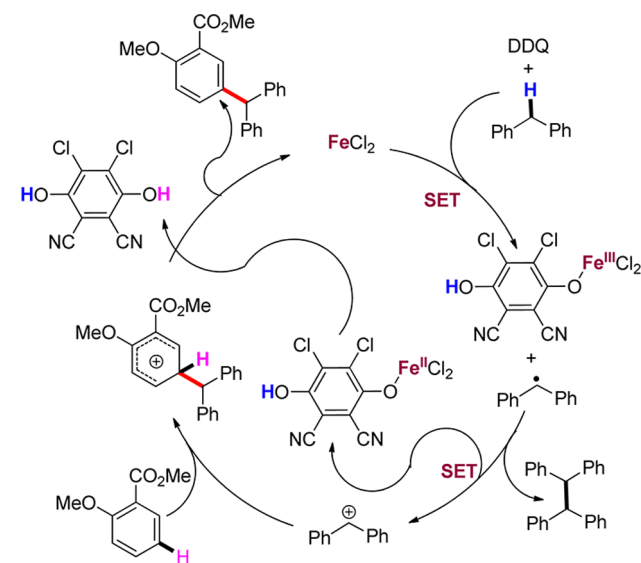
Although much progress has been made in direct C–H functionalization in the last decades, Fe has been rarely applied in this field. To pursue more ideal catalytic processes, much effort has been made to carry out the Fe-catalyzed C–H activation in the past several years. Nakamura extensively investigated Fe-catalyzed C–H activation and subsequent transformations and did much elegant work.^{12–18} In the past several years, stimulated by Fe-catalyzed cross dehydrogenative coupling (CDC reaction),^{2,19} our studies were focused on direct functionalization of benzylic C–H bonds. We demonstrated an unprecedented oxidative cross-coupling of a benzylic sp^3 C–H bond and an sp^2 C–H bond, in which two types of C–H bonds were transformed in one reaction.²⁰ $FeCl_2$ was found to be the optimal catalyst, and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was the best oxidant (Table 1). Other transition metal catalysts, such as cobalt, nickel, copper, and palladium, did not accelerate the reaction as remarkably as iron. Mechanistic studies indicated that the reaction might proceed via a double single electron transfer (SET) process, followed by C–C bond formation via Friedel–Crafts alkylation, and cleavage of the benzylic C–H bond was involved in the rate-determining step (Scheme 1).

With the understanding of the pathway, we then explored C–C bond formation through Fe-catalyzed benzylic sp^3 C–H functionalization with 1-aryl-vinyl acetates as nucleophiles. Di-

Table 1. Fe-Catalyzed Cross-Coupling of sp^3 C–H Bonds with Arenes

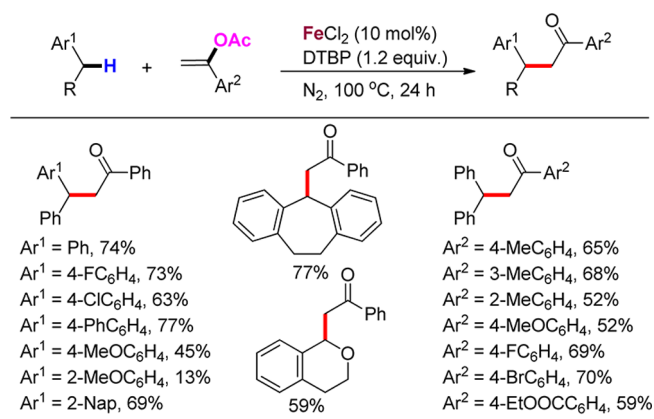


Scheme 1. Proposed Mechanism of Fe-Catalyzed Cross-Coupling of sp^3 C–H Bonds with Arenes



tert-butyl peroxide (DTBP) was indispensable for this reaction (Table 2).²¹

Table 2. Fe-Catalyzed Cross-Coupling of sp^3 C–H Bonds with Alkenes



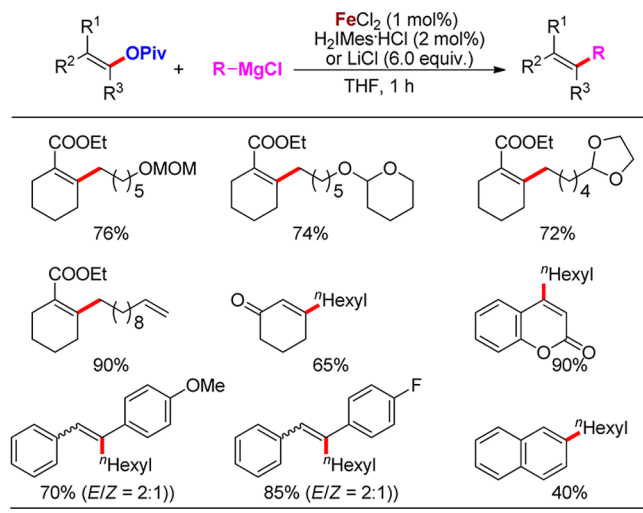
2.2. Fe-Catalyzed C–O Activation

Initially, phenols and ketones must be transformed to active sulfonates and phosphates to participate in coupling reactions.²² However, other common O-containing compounds, including ethers, esters, carboxylates, and unreactivated phenols and alcohols, have rarely been used as coupling partners directly. Undoubtedly, C–O activation to improve the reactivity of these O-containing chemicals is highly appealing. However, due to the inherent inertness of these C–O bonds, application of these compounds via C–O bonds was very challenging.

With the advances in Fe catalysis, beautiful examples have been demonstrated in traditional cross coupling reactions, especially with sulfonates as electrophiles.²³ As one of the major goals to investigate the O-based electrophiles through C–O activation, we also explored Fe catalysis in Kumada coupling with alkenyl carboxylates.

In Fürstner's beautiful examples, highly reactive Fe⁰ (maybe Fe²⁻) species generated in the presence of Grignard reagents can catalyze the cross-coupling with various substrates.²⁴ We envisaged such an active species could play vital roles in cross coupling of various O-based electrophiles. After extensive investigation, we achieved the first Fe-catalyzed cross-coupling of alkenyl pivalates and alkenyl Grignard reagents.⁶ A combination of FeCl₂ and H₂IMes proved to be highly efficient, allowing the coupling reaction to proceed efficiently with 1.0 mol % iron catalyst at 0 °C (Table 3). Under the reaction conditions,

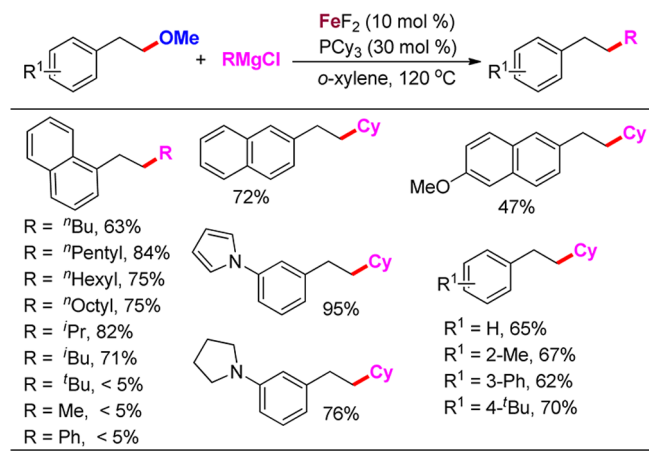
Table 3. Fe-Catalyzed Selective C–O Activation of Alkenyl Carboxylates



aryl pivalates and aryl carbamates also showed good reactivity, which lead to our further investigation. After this discovery, Garg and others further extended this chemistry to aryl derivatives.^{5,25} Today, this chemistry has become a standard procedure to synthesize polysubstituted olefins.

Among various C–O bonds, the two sp³ C–O bonds in dialkyl ethers are chemically and energetically similar and thus are more challenging to differentiate. Kakiuchi and Kochi showed the beauty to discriminate two sp³ C–O bonds in Ru-catalyzed cross coupling by linking an N-containing group at one side.²⁶ We first reported the Fe-catalyzed alkylation of homobenzylic ethers using Grignard reagents as a coupling partner (Table 4).²⁷ Mechanistic investigation unveiled that the coupling might go through a dehydroalkoxylation, carboferrocation, and protonation sequence. The key carbometalation intermediate was

Table 4. Fe-Catalyzed sp³ C–O Activation of Homobenzylic Ethers



further proven by quenching the reaction with different electrophiles, which was also consistent with the addition reaction reported by Nakamura et al.²⁸ Notably, this observation might offer an opportunity to develop new methodology to pursue bifunctionalization of alkenes, especially styrene.

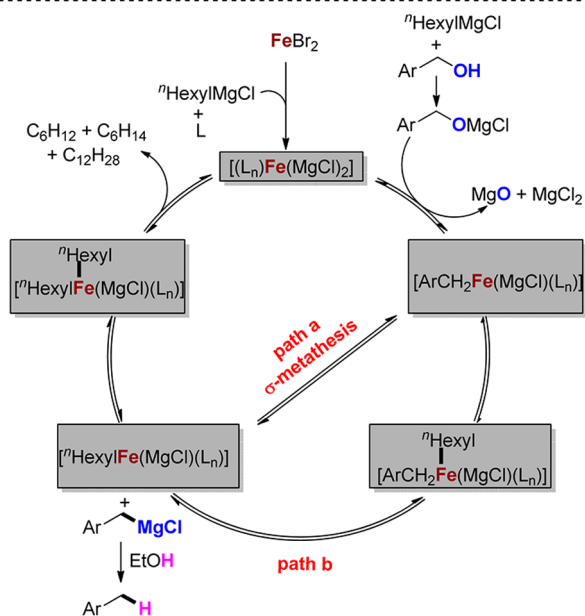
One of our major goals in C–O activation was to utilize common alcohols as coupling partners. When we explore benzylic alcohols in cross coupling with Grignard reagents via Fe catalysis, only a trace amount of desired coupling product was detected, while reductively deoxygenative toluene derivatives were always observed. Although a similar reaction via late transition-metal catalysts was reported,^{29–31} iron catalysts had never shown such a catalytic ability. Indeed, various iron catalysts exhibited good reactivity in the presence of ⁿhexylMgCl. When the iron catalyst was replaced with copper salts, very low efficiency was observed, which excluded that the copper contaminant catalyzed process. Many functional groups, including C–F, C–OMe, and C–N, were tolerated (Scheme 2). It is important to note that detailed isotope-labeling experiment investigation showed that the new introduced “H” came from protic solvent. Beside protons, carbon-based electrophiles (e.g., BnBr) were also used to trap the in situ generated intermediate. These results strongly supported the formation of BnMgX. Although formation of new Grignard reagents via transition metal-catalyzed hydromagnesiation or carbomagnesiation of alkynes and alkenes has been disclosed,^{32–35} to the best of our knowledge, this was the first example of transition metal-catalyzed magnesiation of alcohol.

3. Co CATALYSIS

As neighbors in the periodic table, Co and Fe share some of similar advantages (e.g., cheap, abundant, etc.). To some extent, Co catalysts may exhibit a higher reactivity in many reactions. In fact, some unique characteristics and interesting modes of action have made it very attractive recently.^{36–38} However, compared with Fe-catalyzed inert chemical bond activation, Co catalysis lagged greatly.

3.1. Co-Catalyzed C–H Activation

Although transition metal-catalyzed C–H activation has made great progress in the past two decades, catalytic direct C–H transformation mediated by cobalt was very rare. In 2010, Yoshikai and co-workers reported an elegant Co-catalyzed directing group assisted C–H activation/alkenylation reaction.³⁹

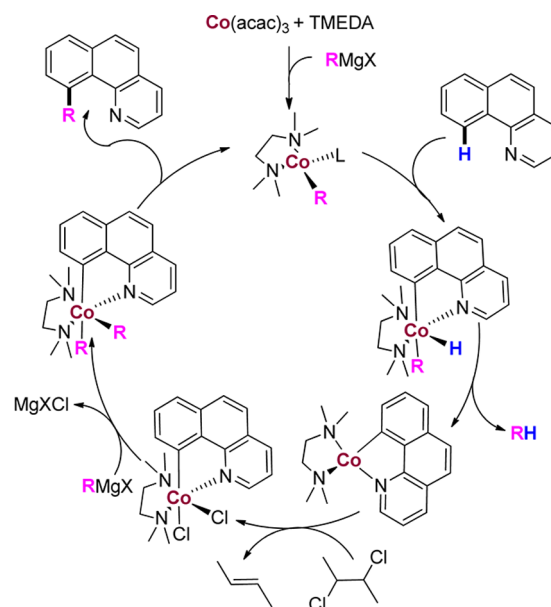
Scheme 2. Fe-Catalyzed Magnesiumation of Benzylic Alcohol via sp^3 C–O Bond Activation


Inspired by the Fe-catalyzed cross-coupling of C–H and Grignard reagents,^{12–14} we attempted to investigate cobalt as a candidate to execute such chemistry.

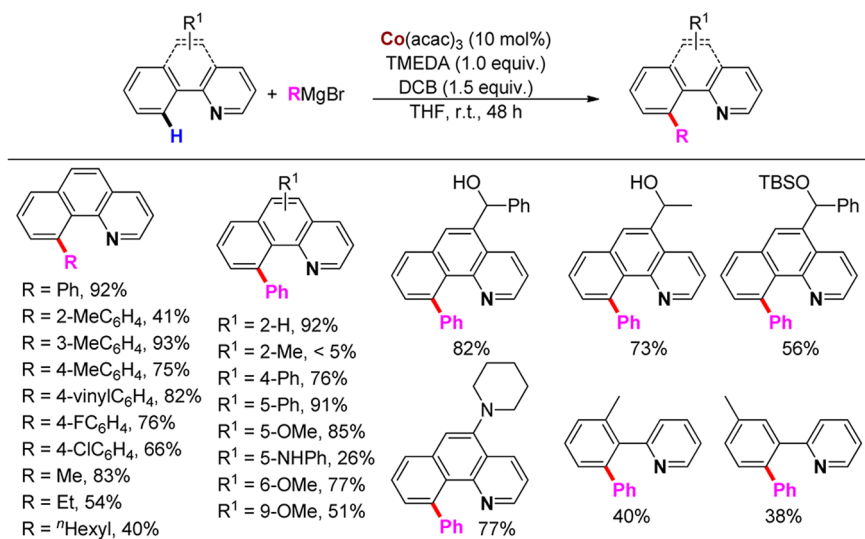
Benzo[*h*]quinoline was initially selected as standard substrate due to its directing ability and stability.⁴⁰ Actually, direct nucleophilic attack to pyridine derivatives at the 2-position by Grignard reagents was a big challenge. By introducing a suitable transition-metal catalyst and lowering the reaction temperature, the reactivity of RMgBr can be reduced, thus reducing the possibility of the undesired nucleophilic addition. The cross-coupling reaction was successfully achieved with $\text{Co}(\text{acac})_3$ as a catalyst in the presence of TMEDA (*N,N,N',N'*-tetramethylethylenediamine) and DCB (2,3-dichlorobutane) in THF at room

temperature (Table 5). Various benzo[*h*]quinolines and 2-phenylpyridines with alkyl, aryl, free hydroxyl, *sec*- and *tert*-amine, OTS, etc. were suitable substrates. Besides aryl Grignard reagents, alkyl reagents were also applicable.

From the mechanistic studies, a proposed catalytic cycle is shown in Scheme 3. In the presence of TMEDA and Grignard

Scheme 3. Proposed Catalytic Cycle of the Direct C–H/Grignard Reagent Cross-coupling


reagents, a catalytically active Co(I) species was generated, which further underwent oxidative addition with benzo[*h*]quinoline to generate a Co(III) intermediate. After reductive elimination, a new Co(I) together with the byproduct RH was generated. The newly formed Co(I) species was reoxidized to Co(III) by DCB (2,3-dichlorobutane), which furnished the coupling product after double transmetalations and subsequent reductive elimination. Almost at the same time, Nakamura and co-workers reported Co-catalyzed amide directed C–H activation/alkylation, where they utilized alkyl chloride as coupling partner.⁴¹ Later on,

Table 5. Co-Catalyzed Direct C–H/Grignard Reagent Cross-Coupling


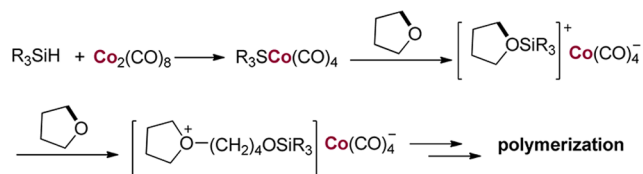
Nakamura and Yoshikai developed various different Co-catalyzed alkylations using different alkylating reagents.^{42–45}

3.2. Co-Catalyzed C–O Activation

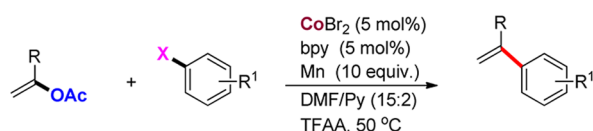
Comparatively, Co catalysts have rarely been used to activate C–O bonds. An early example of Co-catalyzed C–O cleavage was reported by Chalk in 1970 (Scheme 4a).⁴⁶ In the presence of

Scheme 4. Co-Catalyzed C–O Activation

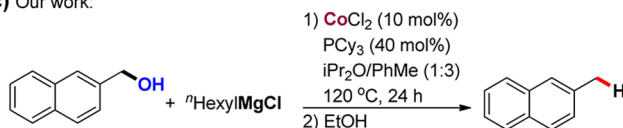
(a) Chalk *et al.* :



(b) Gosmini *et al.* :



(c) Our work:



R_3SiH and $Co_2(CO)_8$, the in situ formed $R_3SiCo(CO)_4$ promoted the ring-opening of tetrahydrofuran and the following polymerization. Subsequently, Murai and co-workers demonstrated a $Co_2(CO)_8$ -catalyzed ring opening of THF to generate aldehydes or vinyl silyl ethers in the presence of excess $HSiEt_2Me$ and Co .⁴⁷

Another beautiful example was reported by Gosmini (Scheme 4b).⁴⁸ The reductive coupling of vinyl acetates and aryl halides underwent smoothly under Co catalysis in the presence of Mn as reductant. Low-valent $Co^{0/I}$ was proposed to be active species during this reaction.

During our studies in C–O activation, we also observed the credible reactivity of Co catalysts in different transformations. For example, the deoxygenative reduction of benzylic alcohol can also be catalyzed by Co catalysts (Scheme 4c).⁷ Although the efficiency is not comparable to other metal catalysts, this result implied the potential of cobalt catalysts in this field.

4. Ni CATALYSIS

Standing in the same d^{10} group, Ni (\$1/g) is much cheaper than Pd (\$183/g) and Pt (\$483/g). Both Pd and Pt exhibited “magic” catalytic reactivity in both homogeneous and heterogeneous catalysis. Compared with its counterparts in group 10, Ni might be more attractive from the perspectives of not only economics but also its unveiled unique characteristics. For example, Ni is usually found not only in 0 and +2 but also +1 and +3 oxidation states, while Pd is typically observed in 0 and +2 oxidation states (in some cases +3 and +4), and Pt more readily accesses +4 oxidation states. On the other hand, different from the oxidative insertion of Pd(0) to organohalides, the oxidative addition of low-valent Ni (Ni(0) or Ni(I)) prefers the SET process. In addition, owing to its smaller size located in the third row, Ni is more nucleophilic. Therefore, Ni was found to be powerful in inert C–O, C–H, and C–C activation.

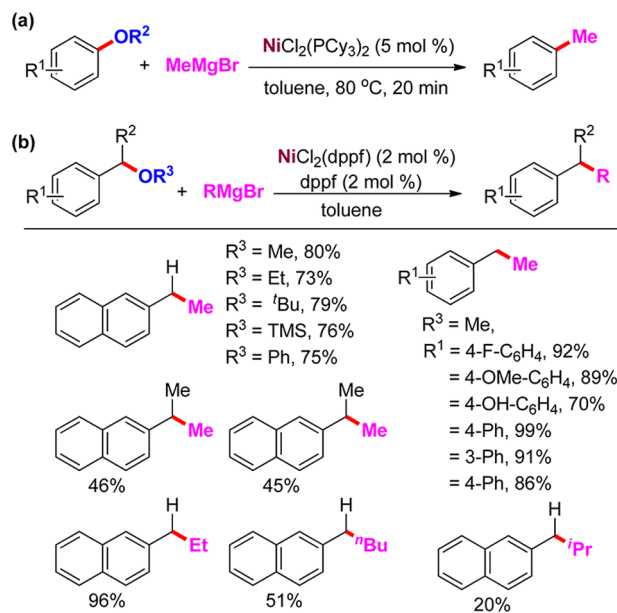
4.1. Ni Catalysis in C–O Activation

As mentioned above, the initial work used O-based sulfonates and phosphates as electrophiles in cross coupling. In these coupling reactions, Pd catalyst was still a key player, although in some cases Ni showed credible reactivity. After comprehensive review of the literature in this field, it was found that Ni catalysts showed remarkable reactivity, probably arising from the above-mentioned uniqueness of the Ni element. In fact, Ni is now the best metal to induce the C–O cleavage of various O-based nucleophiles.

4.1.1. Ni-Catalyzed Etheric C–O Activation. As one of the major organic compounds, ethers always showed extremely inertness under common conditions and were rarely used as starting materials. Ni-catalyzed Kumada–Tamao–Corriu coupling with aryl/alkenyl ethers can be traced to 1979 by Wenkert.⁴⁹ However, such an important study was neglected until Dankwardt picked it up in 2004.⁵⁰ These important studies unveiled the essence of Ni-catalyzed C–O activation. In this field, Chatani and co-workers are major players in the activation of aryl ethers and upgraded the reactions in this field.⁵¹ We initiated the C–O bond activation of ethers in late 2004 and first focused on the Ni-catalyzed methylation of aryl alkyl ethers since both Wenkert and Dankwardt omitted the methylation in their studies.^{49,50}

After extensive screening of reaction conditions, it was found that ligand sets had a great influence on the efficiency, and PCy_3 proved to be the best choice (Scheme 5a),⁵² as was similar to the

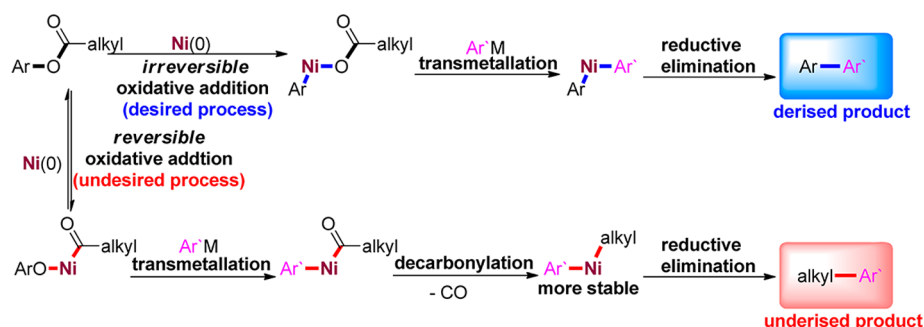
Scheme 5. Ni-Catalyzed Etheric C–O Activation



Dankwardt’s results. The magic role of PCy_3 toward Ni catalysis probably arose from the match of both electronic and steric properties of PCy_3 with the Ni center. Unfortunately, other alkyl Grignard reagents could not be utilized as nucleophile.

Later on, we first successfully developed the Ni-catalyzed alkylation of benzyl alkyl ethers with alkyl Grignard reagents (Scheme 5b).⁵³ Here dppf gave the best results. Different benzyl alkyl ethers with many functional groups tolerated gave the desired alkylated products in good to excellent yields. Later on, Jarvo and Watson developed the stereoselective version of this

Scheme 6. Rational Design of Selective C–O Activation of Carboxylate

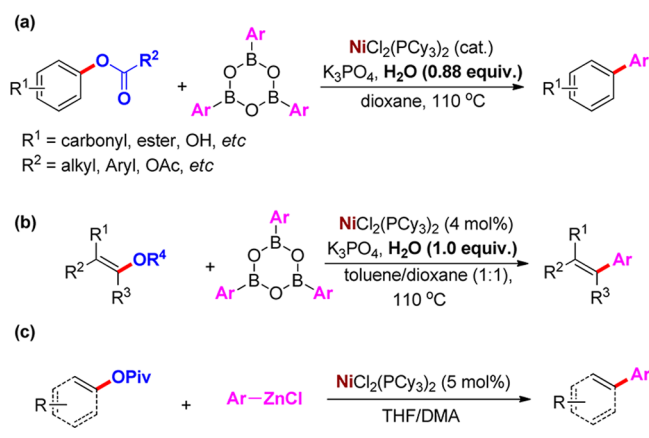


transformation, highly extending the potential application of this method.^{54–56}

4.1.2. Ni-Catalyzed Esteric C–O Activation. Due to the lability of the acyl C–O bond, carboxylates, though readily available, have rarely been used as coupling partners to date, except allylic and benzylic carboxylates. Murai and Kakiuki reported beautiful examples via Ru catalysis through a directing strategy.⁵⁷ In 2009, Garg and our group simultaneously reported the first example of aryl carboxylates with aryl boronic acid derivatives.^{8,58} As reported, a competitive oxidative addition of Ni(0) occurs reversibly at the acyl C–O bond and potentially at the aryl C–O bond. In Yamamoto's studies, the former case terminated the catalytic cycle by formation of stable alkyl–Ni species through decarbonylation (Scheme 6).⁵⁹ In our design, enhancement of the transmetalation of the aryl–Ni species and inhibition of the decarbonylation of the acyl–Ni complex were essential, which can be tuned by a proper ligand set. This suspension was further proved by DFT calculation by Liu and co-workers.⁶⁰

With rational design, 2-naphthyl acetate was selected as model substrate to explore Ni-catalyzed cross coupling. Actually, coupling proceeded smoothly when NiCl₂(PCy₃)₂ was used as catalyst and K₃PO₄ as base (Scheme 7a).⁵⁸ It was noteworthy

Scheme 7. Ni-Catalyzed Selective C–O Activation of Aryl Carboxylates



that the critical amount of water was essential, which was considered to improve the reactivity of boron reagents while it did not enhance the hydrolysis of the esters.

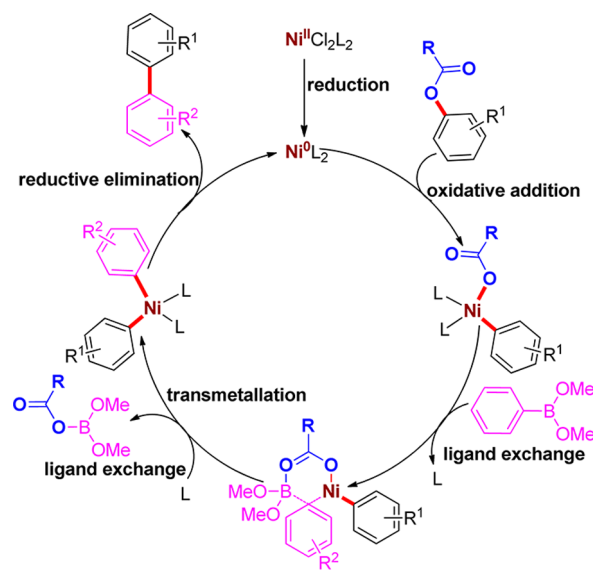
Although the cross-coupling reaction of phenyl acetate failed under the above reaction conditions, steric hindered phenyl pivalates are suitable. These results were supported by Garg.⁸ This system can be further extended to vinyl acetate via Ni

catalysis, thus highly expanding its potential applications (Scheme 7b).⁶¹

In the above-mentioned reaction, fairly harsh reaction conditions such as high temperature and high catalyst loading are required, thus limiting their potential applications. Therefore, more active organozinc reagents were applied to allow milder reaction conditions.⁶² Unfortunately, naphthyl acetate was not suitable, and most of the starting material was hydrolyzed to naphthol. It is understandable since arylzinc reagents are more nucleophilic. By increasing the steric hindrance at carbonyl group with pivalates, the desired products were obtained in good yield under mild conditions (Scheme 7c).

The aforementioned reactions ran through a similar pathway (Scheme 8). First, active catalyst species Ni(0) was generated in

Scheme 8. Tentative Mechanism of the Ni-Catalyzed Selective C–O Activation of Aryl Carboxylates

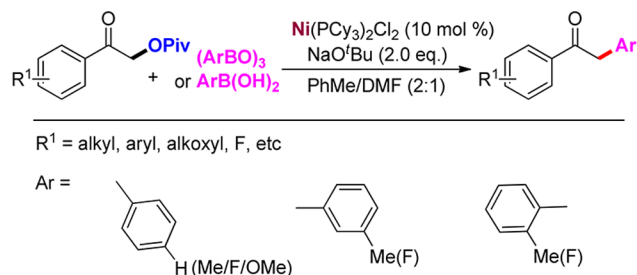


the presence of organometallic reagents, followed by oxidative addition to afford an aryl Ni(II) intermediate. After ligand exchange and transmetalation, the newly formed diaryl Ni(II) intermediate underwent reductive elimination to furnish biaryls and regenerate the Ni(0) catalyst.

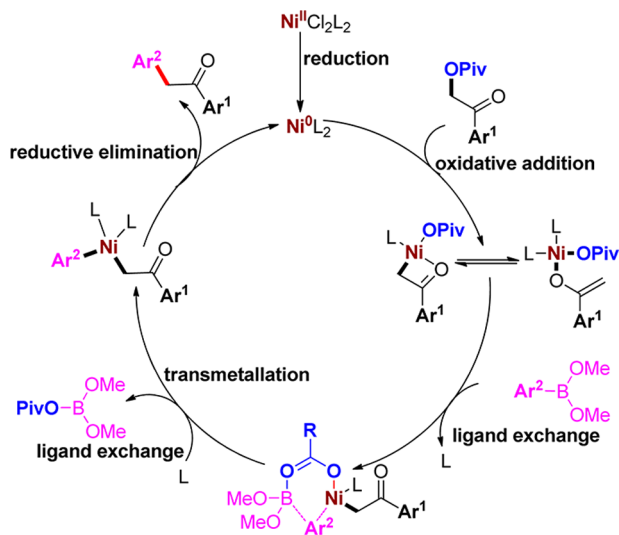
As a continuation of sp² C–O activation of aryl and alkenyl carboxylates, we moved to investigate Ni-catalyzed sp³ C–O activation. The successful cross-coupling of α -pivaloxyl ketones and aryl boronic acids or boroxines was developed via Ni-catalyzed sp³ C–O activation.⁶³ In comparison, the coupling of α -pivaloxyl ketones with boronic acid derivatives needed relative

high catalyst loading (10%) and strong base (NaO^tBu) (Scheme 9). A tentative mechanism involving a Ni(0)/Ni(II) catalytic cycle was proposed as shown in Scheme 10.

Scheme 9. Ni-Catalyzed sp³ C–O Activation of α -Pivaloxyl Ketones



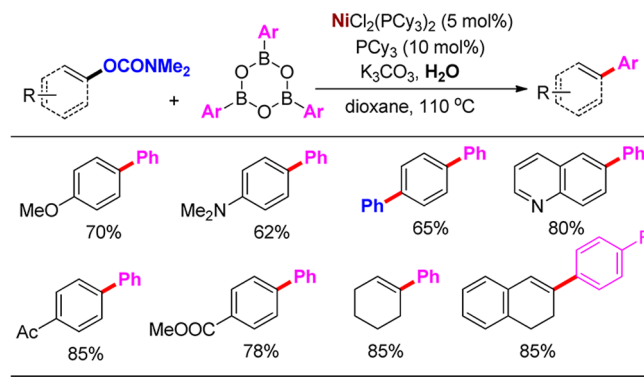
Scheme 10. Proposed Mechanism of the Ni-Catalyzed sp³ C–O Activation of α -Pivaloxyl Ketones



4.1.3. Ni-Catalyzed C–O Activation of Aryl/Alkenyl Carbamates. In Garg's studies, the corresponding carbamates were more stable and good alternatives for cross coupling with arylboronic acids.⁹ Later on, Snieckus's investigation gave further support for Ni catalysis.⁶⁴ Notably, ethyl carbamate was also a directing group for directed orthometalation Directed ortho metalation (DoM) to carry out further transformations. We also planned to extend the Ni-catalyzed cross-coupling of aryl/alkenyl carbamates with boroxines almost at the same time as Garg and Snieckus.^{9,64} The coupling of *N,N*-dimethylamino-substituted phenylcarbamates with phenylboroxine underwent smoothly when 5 mol % NiCl₂(PCy₃)₂ was used (Table 6).⁶⁵

4.1.4. Ni-Catalyzed C–O Bond Activation of Phenolates. Direct cleavage of the C–O bond of phenols is quite ideal in organic transformations. However, the intrinsic properties of phenol hampered such a design, for example, (1) high bond dissociation energy of C–OH or C–OM indicated the difficulty of direct cleavage of the C–O bond and (2) phenolate also acts as good ligand to bind the metals, further impeding the cleavage of the C–O bond. In Wenkert's studies, little product was produced by cross-coupling of magnesium naphthoxide and Grignard reagents,^{49,66} However, they also claimed it was impossible to promote the efficiency of such transformations.

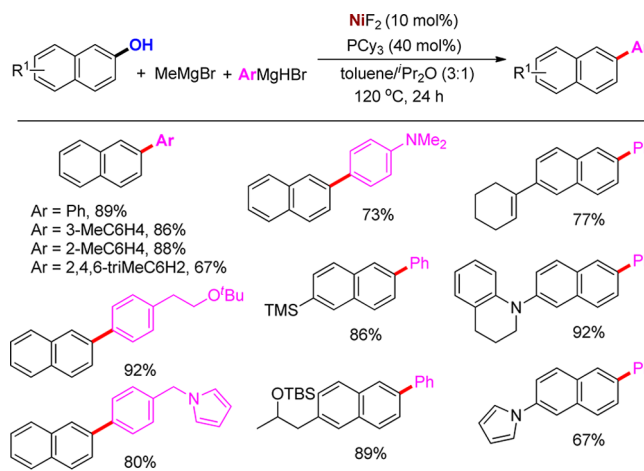
Table 6. Ni-Catalyzed Selective sp³ C–O Activation of Aryl/Alkenyl Carbamates



We envisioned that the metal ion in the naphtholate might act as an electron-withdrawing group by coordination to change the electronic features of the phenolic C–O bond. Thus, we transformed 2-naphthol to magnesium naphtholate. The crystal structure of 2-NaphOMgBr showed that it existed as a dimer, and the length of the C–O bond of magnesium naphtholate was the same as that of naphthol, demonstrating at least that the formation of the magnesium salt did not strengthen the C–O bonds and providing the potential for the C–O transformation.

In fact, 2-NaphOMgBr and (2-NaphO)Mg showed higher reactivity in cross coupling with Grignard reagents beyond sodium and potassium salts.⁶⁷ The combination of NiF₂ and PCy₃ in a mixture of toluene and diisopropyl ether proved to be optimal (Table 7).

Table 7. Ni-Catalyzed C–O Activation of Magnesium Naphtholates

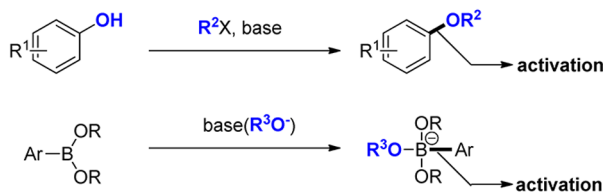


In comparison, organoboronic acid derivatives are much better electron deficient Lewis acids to some extent. Thus, ideally, the formation of aryl borate could better activate the C–O bond of phenolate while simultaneously activating the C–B bond by the formation of borate, thus called “mutual activation” (Scheme 11). The advantage of this concept is that both coupling partners activate each other, thus avoiding the need for preactivation and the addition of extra base as traditional activation models.

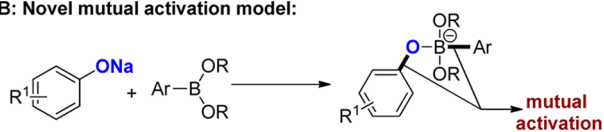
To demonstrate our design, various 2-naphtholates with different metal ions and phenylboroxine were subjected to the nickel catalyst system. It was found that although magnesium naphtholate gave no desired product, and lithium, potassium,

Scheme 11. Rational Design of the New Mutual Activation Concept

A: Traditional activation models:

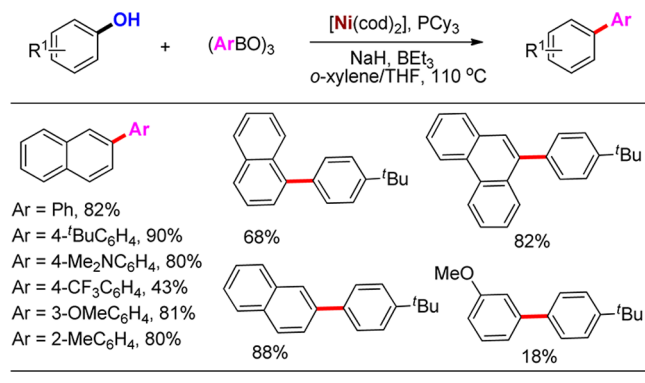


B: Novel mutual activation model:



and zinc naphtholates only give trace amounts of coupling product, sodium naphtholate showed good reactivity. It was worth noting that addition of weak Lewis acid BEt_3 highly promoted the transformation. Further screening indicated that combination of $[\text{Ni}(\text{cod})_2]$ and PCy_3 was the best choice (Table 8).⁶⁸

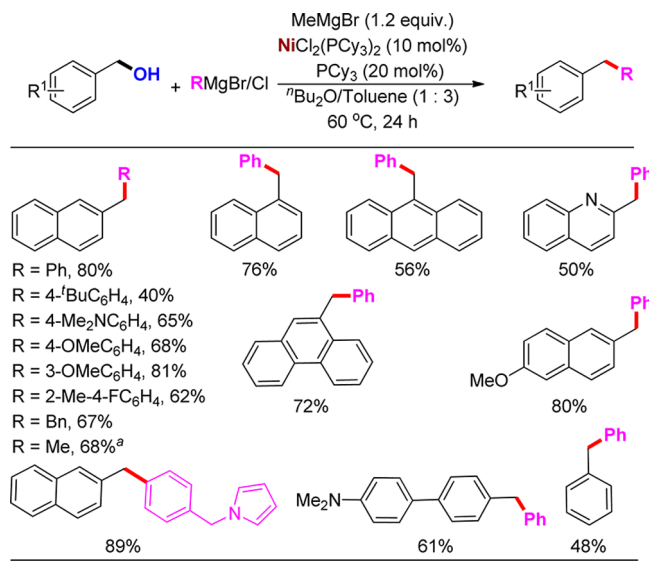
Table 8. Ni-Catalyzed C–O Activation of Sodium Naphtholates



After detailed mechanistic studies, our proposed mutual activation model was strongly supported via a pathway involving a Lewis acid assisted Lewis acid effect as shown in Figure 2B, which was demonstrated by both ^{11}B NMR spectrum and X-ray structure of key intermediate.

4.1.5. Ni-Catalyzed C–O Activation of Benzylic Alcohols. As mentioned, benzylic alcohol can be reduced via Fe catalysis. Ni also showed credible reactivity.⁷ To our interest, in the presence of aryl, methyl, or benzyl Grignard reagents, the coupling reaction took place with Ni catalysts in high efficacy (Table 9).⁷ However, with Fe and Co as catalysts, the efficiency was dramatically decreased although the desired product was observed in some cases.

Table 9. Ni-Catalyzed sp^3 C–O Bond Activation of Benzylic Alcohols



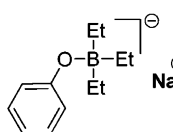
4.2. Ni-Catalyzed C–C Activation

When we studied the Suzuki–Miyaura type coupling with aryl carboxylates as electrophiles,⁶⁵ we found that the CN group could not survive and some of the unexpected cross coupling product according to the Ar–CN cleavage was isolated, indicating that C–CN bond could be a potential partner in Suzuki–Miyaura coupling. Indeed, the Ni-catalyzed C–CN cleavage and their application have been well studied.^{10,11} Hiyama and Nakao made the significant contributions in this field.⁶⁹ However, the cross coupling reaction based on such a C–C cleavage remained elusive. After extensive investigation, it was found that the cross-coupling of aryl nitriles and boronic esters proceeded well when *t*-BuOK was used as base and CuF_2 as an additive. Various nitriles and a wide range of boronic esters were subject to these reaction conditions, giving desired products in moderate to good yields (Scheme 12a).⁷⁰ Due to the relative inertness of C–CN, selective and sequential cross-couplings are easily achieved, practical potential application of which was demonstrated in the synthesis of polyarenes (Scheme 12b).

5. CONCLUSION AND PERSPECTIVE

In the past 10 years, we have devoted ourselves in the field of inert bond activation. This Account mainly examined our recent efforts on the Fe-, Co-, and Ni-catalyzed C–O, C–H, and C–C bond activations. Starting from ethers, carboxylates, carbamates, and naphthol and benzyl alcohols, we intensively studied the catalytic ability of earth abundant transition metals, including Fe, Co, and Ni, in C–O activation of these compounds. With the different features of Fe and Co, we also tested their catalytic ability in oxidative coupling of aryl and benzyl C–H bonds with different nucleophiles. Occasionally, we also tested the catalytic

A) Direct activation of the C–O bond



B) Mutual activation model

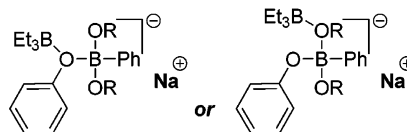
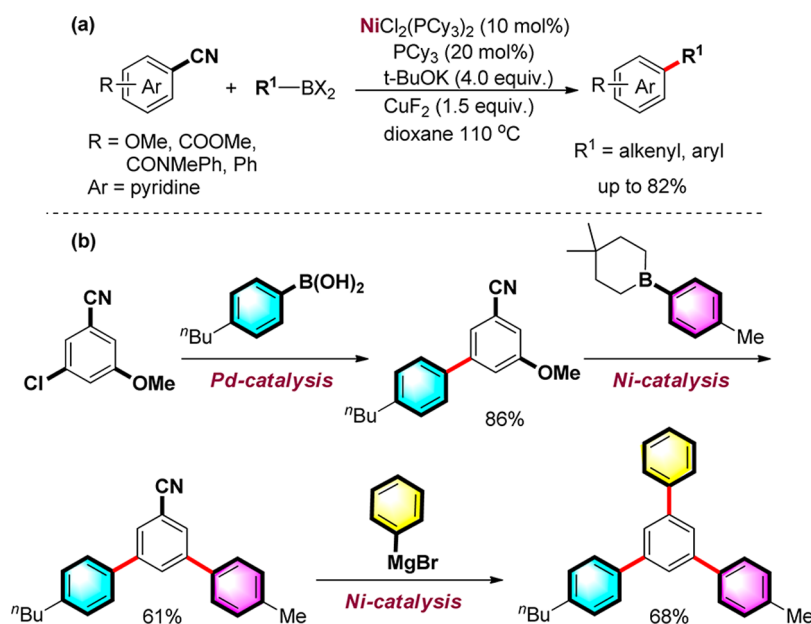


Figure 2. Possible Role of Et_3B in the Mutual Activation.

Scheme 12. Ni-Catalyzed C–C Bond Activation of Aryl Nitriles



ability of Ni catalysts in cleavage of Ar–CN and the following Suzuki–Miyaura coupling. These studies broadly extended the catalytic ability of these earth abundant, cheap, easily available, and lower toxicity or nontoxic (but not least) transition metals. With these developments, we also expand the electrophiles from O-based leaving group to C-based leaving group in cross coupling reactions, as well as the ideal cross dehydrogenative arylations (CDA) from two different types of C–H bonds. From the current studies, the miscellaneous catalytic abilities of Fe, Co, and Ni have been demonstrated. They have also shown their magic abilities and power in other fields, for example, aliphatic C–H transformations. With their intrinsic features different from the broadly used late transition-metal catalysts, it is just the start for the application of these metals in catalysis, which will have broad applications in old catalytic systems, new transformations, and heterogeneous catalysis. Designing new ligand sets to fit for their features, discovering their new transformations, and unveiling the relationship between their structures and their reactivity are highly needed. Undoubtedly, development of more efficient and robust catalyst systems is highly desirable. We believe that the blossoming of the field of earth abundant transition-metal catalysis will promote the life of the human being with the release of the burden of chemical production.

AUTHOR INFORMATION

Corresponding Author

*E-mail: zshi@pku.edu.cn.

Funding

Financial support by MOST (2015CB856600 and 2013CB228102), NSFC (Nos. 21332001 and 21431008), China Postdoctoral Science Foundation (No. 2014M560841) and MSD China Postdoctoral Fellowship is gratefully acknowledged.

Notes

The authors declare no competing financial interest.

Biographies

Bo Su was born in 1984 in Henan, China. He obtained his B.S. at Zhengzhou University in 2008 and Ph.D. with Professor Qingmin Wang in Nankai University in 2013. He then joined the Shi group at Peking University for his postdoctoral research. His current research interests include inert chemical bond activation, development of novel synthetic methodology, and total synthesis of natural products.

Zhi-Chao Cao was born in 1991 in Anhui, China. He received his B.S. from Anhui Normal University in 2012. He is currently a third-year graduate student with Professor Shi at Peking University. His current research interests focus on transition-metal-catalyzed inert C–O bond activation.

Zhang-Jie Shi was born in 1974 in Anhui, China. He obtained his B.S. at East China Normal University in 1996 and Ph.D. with Professor Shengming Ma in Shanghai Institute of Organic Chemistry (SIOC) in 2001. After his postdoctoral work with Professors Gregory L. Verdine at Harvard University and Chuan He at the University of Chicago, he joined the chemistry faculty of Peking University in 2004, where he was promoted to a full Professor in 2008. Prof. Shi received the Tetrahedron Young Investigator Award in 2012, the OMCOS Award, and the Second Rank National Award of Natural Sciences in 2013. His current research interests focus on transition-metal-catalyzed C–O bond, C–H bond, and C–C bond activations and the fixation of CO₂ and N₂.

REFERENCES

- (1) Yamaguchi, J.; Yamaguchi, A. D.; Itami, K. C–H Bond Functionalization: Emerging Synthetic Tools for Natural Products and Pharmaceuticals. *Angew. Chem., Int. Ed.* **2012**, *51*, 8960–9009.
- (2) Li, C.-J. Cross-Dehydrogenative Coupling (CDC): Exploring C–C Bond Formations beyond Functional Group Transformations. *Acc. Chem. Res.* **2008**, *42*, 335–344.
- (3) Sun, C.-L.; Li, B.-J.; Shi, Z.-J. Direct C–H Transformation via Iron Catalysis. *Chem. Rev.* **2011**, *111*, 1293–1314.
- (4) Bolm, C.; Legros, J.; Le Pailh, J.; Zani, L. Iron-Catalyzed Reactions in Organic Synthesis. *Chem. Rev.* **2004**, *104*, 6217–6254.
- (5) Mesganaw, T.; Garg, N. K. Ni- and Fe-Catalyzed Cross-Coupling Reactions of Phenol Derivatives. *Org. Process Res. Dev.* **2012**, *17*, 29–39.
- (6) Li, B.-J.; Xu, L.; Wu, Z.-H.; Guan, B.-T.; Sun, C.-L.; Wang, B.-Q.; Shi, Z.-J. Cross-Coupling of Alkenyl/Aryl Carboxylates with Grignard

Reagent via Fe-Catalyzed C–O Bond Activation. *J. Am. Chem. Soc.* **2009**, *131*, 14656–14657.

(7) Yu, D. G.; Wang, X.; Zhu, R. Y.; Luo, S.; Zhang, X. B.; Wang, B. Q.; Wang, L.; Shi, Z. J. Direct Arylation/Alkylation/Magnesium of Benzyl Alcohols in the Presence of Grignard Reagents via Ni-, Fe-, or Co-Catalyzed sp^3 C–O Bond Activation. *J. Am. Chem. Soc.* **2012**, *134*, 14638–14641.

(8) Quasdorf, K. W.; Tian, X.; Garg, N. K. Cross-Coupling Reactions of Aryl Pivalates with Boronic Acids. *J. Am. Chem. Soc.* **2008**, *130*, 14422–14423.

(9) Quasdorf, K. W.; Riener, M.; Petrova, K. V.; Garg, N. K. Suzuki–Miyaura Coupling of Aryl Carbamates, Carbonates, and Sulfamates. *J. Am. Chem. Soc.* **2009**, *131*, 17748–17749.

(10) Miller, J. A. C–C Bond Activation with Selective Functionalization: Preparation of Unsymmetrical Biaryls from Benzonitriles. *Tetrahedron Lett.* **2001**, *42*, 6991–6993.

(11) Miller, J. A.; Dankwardt, J. W. Nickel Catalyzed Cross-Coupling of Modified Alkyl and Alkenyl Grignard Reagents with Aryl- and Heteroaryl Nitriles: Activation of the C–CN Bond. *Tetrahedron Lett.* **2003**, *44*, 1907–1910.

(12) Norinder, J.; Matsumoto, A.; Yoshikai, N.; Nakamura, E. Iron-Catalyzed Direct Arylation through Directed C–H Bond Activation. *J. Am. Chem. Soc.* **2008**, *130*, 5858–5859.

(13) Yoshikai, N.; Matsumoto, A.; Norinder, J.; Nakamura, E. Iron-Catalyzed Chemoselective ortho-Arylation of Aryl Imines by Directed C–H Bond Activation. *Angew. Chem., Int. Ed.* **2009**, *48*, 2925–2928.

(14) Ilies, L.; Asako, S.; Nakamura, E. Iron-Catalyzed Stereospecific Activation of Olefinic C–H Bonds with Grignard Reagent for Synthesis of Substituted Olefins. *J. Am. Chem. Soc.* **2011**, *133*, 7672–7675.

(15) Asako, S.; Ilies, L.; Nakamura, E. Iron-Catalyzed Ortho-Allylation of Aromatic Carboxamides with Allyl Ethers. *J. Am. Chem. Soc.* **2013**, *135*, 17755–17757.

(16) Matsubara, T.; Asako, S.; Ilies, L.; Nakamura, E. Synthesis of Anthranilic Acid Derivatives through Iron-Catalyzed Ortho Amination of Aromatic Carboxamides with N-Chloroamines. *J. Am. Chem. Soc.* **2013**, *136*, 646–649.

(17) Shang, R.; Ilies, L.; Matsumoto, A.; Nakamura, E. β -Arylation of Carboxamides via Iron-Catalyzed C(sp^3)–H Bond Activation. *J. Am. Chem. Soc.* **2013**, *135*, 6030–6032.

(18) Shang, R.; Ilies, L.; Asako, S.; Nakamura, E. Iron-Catalyzed C(sp^2)–H Bond Functionalization with Organoboron Compounds. *J. Am. Chem. Soc.* **2014**, *136*, 14349–14352.

(19) Li, Z.; Cao, L.; Li, C.-J. FeCl₂-Catalyzed Selective C–C Bond Formation by Oxidative Activation of a Benzylic C–H Bond. *Angew. Chem., Int. Ed.* **2007**, *46*, 6505–6507.

(20) Li, Y. Z.; Li, B. J.; Lu, X. Y.; Lin, S.; Shi, Z. J. Cross Dehydrogenative Arylation (CDA) of a Benzylic C–H Bond with Arenes by Iron Catalysis. *Angew. Chem., Int. Ed.* **2009**, *48*, 3817–3820.

(21) Song, C.-X.; Cai, G.-X.; Farrell, T. R.; Jiang, Z.-P.; Li, H.; Gan, L.-B.; Shi, Z.-J. Direct Functionalization of Benzylic C–Hs with Vinyl Acetates via Fe-Catalysis. *Chem. Commun.* **2009**, 6002–6004.

(22) Scott, W. J.; Crisp, G. T.; Stille, J. K. Palladium-Catalyzed Coupling of Vinyl Triflates with Organostannanes. A Short Synthesis of Pleraplysin-1. *J. Am. Chem. Soc.* **1984**, *106*, 4630–4632.

(23) Sherry, B. D.; Fürstner, A. The Promise and Challenge of Iron-Catalyzed Cross Coupling. *Acc. Chem. Res.* **2008**, *41*, 1500–1511.

(24) Fürstner, A.; Leitner, A.; Mendez, M.; Krause, H. Iron-Catalyzed Cross-Coupling Reactions. *J. Am. Chem. Soc.* **2002**, *124*, 13856–13863.

(25) Silberstein, A. L.; Ramgren, S. D.; Garg, N. K. Iron-Catalyzed Alkylations of Aryl Sulfamates and Carbamates. *Org. Lett.* **2012**, *14*, 3796–3799.

(26) Ogiwara, Y.; Kochi, T.; Kakiuchi, F. Ruthenium-Catalyzed Conversion of sp^3 C–O Bonds in Ethers to C–C Bonds Using Triarylboroxines. *Org. Lett.* **2011**, *13*, 3254–3257.

(27) Luo, S.; Yu, D. G.; Zhu, R. Y.; Wang, X.; Wang, L.; Shi, Z. J. Fe-Promoted Cross Coupling of Homobenzylic Methyl Ethers with Grignard Reagents via sp^3 C–O Bond Cleavage. *Chem. Commun.* **2013**, *49*, 7794–7796.

(28) Nakamura, M.; Hirai, A.; Nakamura, E. Iron-Catalyzed Olefin Carbometalation. *J. Am. Chem. Soc.* **2000**, *122*, 978–979.

(29) Yasuda, M.; Onishi, Y.; Ueba, M.; Miyai, T.; Baba, A. Direct Reduction of Alcohols: Highly Chemoselective Reducing System for Secondary or Tertiary Alcohols Using Chlorodiphenylsilane with a Catalytic Amount of Indium Trichloride. *J. Org. Chem.* **2001**, *66*, 7741–7744.

(30) Ranade, V. S.; Prins, R. Hydrogenolysis of Benzylic Alcohols on Rhodium Catalysts. *Chem.—Eur. J.* **2000**, *6*, 313–320.

(31) Nishibayashi, Y.; Shinoda, A.; Miyake, Y.; Matsuzawa, H.; Sato, M. Ruthenium-Catalyzed Propargylic Reduction of Propargylic Alcohols with Silanes. *Angew. Chem., Int. Ed.* **2006**, *45*, 4835–4839.

(32) Shinokubo, H.; Oshima, K. Transition Metal-catalyzed Carbon–Carbon Bond Formation with Grignard Reagents—Novel Reactions with a Classic Reagent. *Eur. J. Org. Chem.* **2004**, 2081–2091.

(33) Nakamura, E.; Yoshikai, N. Low-Valent Iron-Catalyzed C–C Bond Formation—Addition, Substitution, and C–H Bond Activation. *J. Org. Chem.* **2010**, *75*, 6061–6067.

(34) Hata, T.; Sujaku, S.; Hirone, N.; Nakano, K.; Imoto, J.; Imade, H.; Urabe, H. Iron-Mediated and -Catalyzed Metalative Cyclization of Electron-Withdrawing-Group-Substituted Alkynes and Alkenes with Grignard Reagents. *Chem.—Eur. J.* **2011**, *17*, 14593–14602.

(35) Shirakawa, E.; Ikeda, D.; Masui, S.; Yoshida, M.; Hayashi, T. Iron-Copper Cooperative Catalysis in the Reactions of Alkyl Grignard Reagents: Exchange Reaction with Alkenes and Carbometalation of Alkynes. *J. Am. Chem. Soc.* **2012**, *134*, 272–279.

(36) Gosmini, C.; Begouin, J. M.; Moncomble, A. Cobalt-Catalyzed Cross-Coupling Reactions. *Chem. Commun.* **2008**, 3221–3233.

(37) Cahiez, G.; Moyeux, A. Cobalt-Catalyzed Cross-Coupling Reactions. *Chem. Rev.* **2010**, *110*, 1435–1462.

(38) Gao, K.; Yoshikai, N. Low-Valent Cobalt Catalysis: New Opportunities for C–H Functionalization. *Acc. Chem. Res.* **2014**, *47*, 1208–1219.

(39) Gao, K.; Lee, P. S.; Fujita, T.; Yoshikai, N. Cobalt-Catalyzed Hydroarylation of Alkynes through Chelation-Assisted C–H Bond Activation. *J. Am. Chem. Soc.* **2010**, *132*, 12249–12251.

(40) Li, B.; Wu, Z. H.; Gu, Y. F.; Sun, C. L.; Wang, B. Q.; Shi, Z. J. Direct Cross-Coupling of C–H Bonds with Grignard Reagents through Cobalt Catalysis. *Angew. Chem., Int. Ed.* **2011**, *50*, 1109–1113.

(41) Chen, Q.; Ilies, L.; Nakamura, E. Cobalt-Catalyzed ortho-Alkylation of Secondary Benzamide with Alkyl Chloride through Directed C–H Bond Activation. *J. Am. Chem. Soc.* **2010**, *133*, 428–429.

(42) Tan, B. H.; Dong, J. H.; Yoshikai, N. Cobalt-Catalyzed Addition of Arylzinc Reagents to Alkynes to Form ortho-Alkenylarylzinc Species through 1,4-Cobalt Migration. *Angew. Chem., Int. Ed.* **2012**, *51*, 9610–9614.

(43) Ilies, L.; Chen, Q.; Zeng, X.; Nakamura, E. Cobalt-Catalyzed Chemoselective Insertion of Alkene into the Ortho C–H Bond of Benzamide. *J. Am. Chem. Soc.* **2011**, *133*, 5221–5223.

(44) Gao, K.; Yoshikai, N. Cobalt-Catalyzed Ortho Alkylation of Aromatic Imines with Primary and Secondary Alkyl Halides. *J. Am. Chem. Soc.* **2013**, *135*, 9279–9282.

(45) Andou, T.; Saga, Y.; Komai, H.; Matsunaga, S.; Kanai, M. Cobalt-Catalyzed C4-Selective Direct Alkylation of Pyridines. *Angew. Chem., Int. Ed.* **2013**, *52*, 3213–3216.

(46) Chalk, A. J. Group IV-Cobalt Complexes as Catalysts for Silylation and Cyclic Ether Polymerization. *J. Chem. Soc. D* **1970**, 847–848.

(47) Seki, Y.; Murai, S.; Yamamoto, I.; Sonoda, N. Co₂(CO)₈ Catalyzed Reactions of Cyclic Ethers with Hydrosilanes and Carbon Monoxide. *Angew. Chem., Int. Ed.* **1977**, *16*, 789–789.

(48) Amatore, M.; Gosmini, C.; Périchon, J. Cobalt-Catalyzed Vinylation of Functionalized Aryl Halides with Vinyl Acetates. *Eur. J. Org. Chem.* **2005**, *2005*, 989–992.

(49) Wenkert, E.; Michelotti, E. L.; Swindell, C. S. Nickel-Induced Conversion of Carbon–Oxygen into Carbon–Carbon Bonds. One-Step Transformations of Enol Ethers into Olefins and Aryl Ethers into Biaryls. *J. Am. Chem. Soc.* **1979**, *101*, 2246–2247.

- (50) Dankwardt, J. W. Nickel-Catalyzed Cross-Coupling of Aryl Grignard Reagents with Aromatic Alkyl Ethers: An Efficient Synthesis of Unsymmetrical Biaryls. *Angew. Chem., Int. Ed.* **2004**, *43*, 2428–2432.
- (51) Tobisu, M.; Shimasaki, T.; Chatani, N. Nickel-Catalyzed Cross-Coupling of Aryl Methyl Ethers with Aryl Boronic Esters. *Angew. Chem., Int. Ed.* **2008**, *47*, 4866–4869.
- (52) Guan, B. T.; Xiang, S. K.; Wu, T.; Sun, Z. P.; Wang, B. Q.; Zhao, K. Q.; Shi, Z. J. Methylation of Arenes via Ni-Catalyzed Aryl C–O/F Activation. *Chem. Commun.* **2008**, 1437–1439.
- (53) Guan, B. T.; Xiang, S. K.; Wang, B. Q.; Sun, Z. P.; Wang, Y.; Zhao, K. Q.; Shi, Z. J. Direct Benzylic Alkylation via Ni-Catalyzed Selective Benzylic sp^3 C–O Activation. *J. Am. Chem. Soc.* **2008**, *130*, 3268–3268.
- (54) Taylor, B. L. H.; Swift, E. C.; Waetzig, J. D.; Jarvo, E. R. Stereospecific Nickel-Catalyzed Cross-Coupling Reactions of Alkyl Ethers: Enantioselective Synthesis of Diarylethanes. *J. Am. Chem. Soc.* **2010**, *133*, 389–391.
- (55) Wisniewska, H. M.; Swift, E. C.; Jarvo, E. R. Functional-Group-Tolerant, Nickel-Catalyzed Cross-Coupling Reaction for Enantioselective Construction of Tertiary Methyl-Bearing Stereocenters. *J. Am. Chem. Soc.* **2013**, *135*, 9083–9090.
- (56) Zhou, Q.; Srinivas, H. D.; Dasgupta, S.; Watson, M. P. Nickel-Catalyzed Cross-Couplings of Benzylic Pivalates with Arylboroxines: Stereospecific Formation of Diarylalkanes and Triarylmethanes. *J. Am. Chem. Soc.* **2013**, *135*, 3307–3310.
- (57) Kakiuchi, F.; Usui, M.; Ueno, S.; Chatani, N.; Murai, S. Ruthenium-Catalyzed Functionalization of Aryl Carbon–Oxygen Bonds in Aromatic Ethers with Organoboron Compounds. *J. Am. Chem. Soc.* **2004**, *126*, 2706–2707.
- (58) Guan, B. T.; Wang, Y.; Li, B. J.; Yu, D. G.; Shi, Z. J. Biaryl Construction via Ni-Catalyzed C–O Activation of Phenolic Carboxylates. *J. Am. Chem. Soc.* **2008**, *130*, 14468–14470.
- (59) Ishizu, J.; Yamamoto, T.; Yamamoto, A. Selective Cleavage of C–O Bonds in Esters through Oxidative Addition to Nickel(0) Complexes. *Chem. Lett.* **1976**, 1091–1094.
- (60) Li, Z.; Zhang, S.-L.; Fu, Y.; Guo, Q.-X.; Liu, L. Mechanism of Ni-Catalyzed Selective C–O Bond Activation in Cross-Coupling of Aryl Esters. *J. Am. Chem. Soc.* **2009**, *131*, 8815–8823.
- (61) Sun, C. L.; Wang, Y.; Zhou, X. A.; Wu, Z. H.; Li, B. J.; Guan, B. T.; Shi, Z. J. Construction of Polysubstituted Olefins through Ni-Catalyzed Direct Activation of Alkenyl C–O of Substituted Alkenyl Acetates. *Chem.—Eur. J.* **2010**, *16*, 5844–5847.
- (62) Li, B. J.; Li, Y. Z.; Lu, X. Y.; Liu, J.; Guan, B. T.; Shi, Z. J. Cross-Coupling of Aryl/Alkenyl Pivalates with Organozinc Reagents through Nickel-Catalyzed C–O Bond Activation under Mild Reaction Conditions. *Angew. Chem., Int. Ed.* **2008**, *47*, 10124–10127.
- (63) Huang, K.; Li, G.; Huang, W. P.; Yu, D. G.; Shi, Z. J. Arylation of Alpha-pivaloxyl Ketones with Arylboronic Reagents via Ni-Catalyzed sp^3 C–O Activation. *Chem. Commun.* **2011**, *47*, 7224–7226.
- (64) Antoft-Finch, A.; Blackburn, T.; Snieckus, V. *N,N*-Diethyl O-Carbamate: Directed Metalation Group and Orthogonal Suzuki–Miyaura Cross-Coupling Partner. *J. Am. Chem. Soc.* **2009**, *131*, 17750–17752.
- (65) Xu, L.; Li, B. J.; Wu, Z. H.; Lu, X. Y.; Guan, B. T.; Wang, B. Q.; Zhao, K. Q.; Shi, Z. J. Nickel-Catalyzed Efficient and Practical Suzuki–Miyaura Coupling of Alkenyl and Aryl Carbamates with Aryl Boroxines. *Org. Lett.* **2010**, *12*, 884–887.
- (66) Wenkert, E.; Michelotti, E. L.; Swindell, C. S.; Tingoli, M. Transformation of Carbon–Oxygen into Carbon–Carbon Bonds Mediated by Low-Valent Nickel Species. *J. Org. Chem.* **1984**, *49*, 4894–4899.
- (67) Yu, D. G.; Li, B. J.; Zheng, S. F.; Guan, B. T.; Wang, B. Q.; Shi, Z. J. Direct Application of Phenolic Salts to Nickel-Catalyzed Cross-Coupling Reactions with Aryl Grignard Reagents. *Angew. Chem., Int. Ed.* **2010**, *49*, 4566–4570.
- (68) Yu, D. G.; Shi, Z. J. Mutual Activation: Suzuki–Miyaura Coupling through Direct Cleavage of the sp^2 C–O Bond of Naphtholate. *Angew. Chem., Int. Ed.* **2011**, *50*, 7097–7100.
- (69) Nakao, Y.; Hirata, Y.; Hiyama, T. Cyanoesterification of 1,2-Dienes: Synthesis and Transformations of Highly Functionalized α -Cyanomethylacrylate Esters. *J. Am. Chem. Soc.* **2006**, *128*, 7420–7421.
- (70) Yu, D.-G.; Yu, M.; Guan, B.-T.; Li, B.-J.; Zheng, Y.; Wu, Z.-H.; Shi, Z.-J. Carbon–Carbon Formation via Ni-Catalyzed Suzuki–Miyaura Coupling through C–CN Bond Cleavage of Aryl Nitrile. *Org. Lett.* **2009**, *11*, 3374–3377.