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Fe-Catalyzed Cross-Coupling Reaction of Vinylic Ethers with Aryl Grignard Reagents

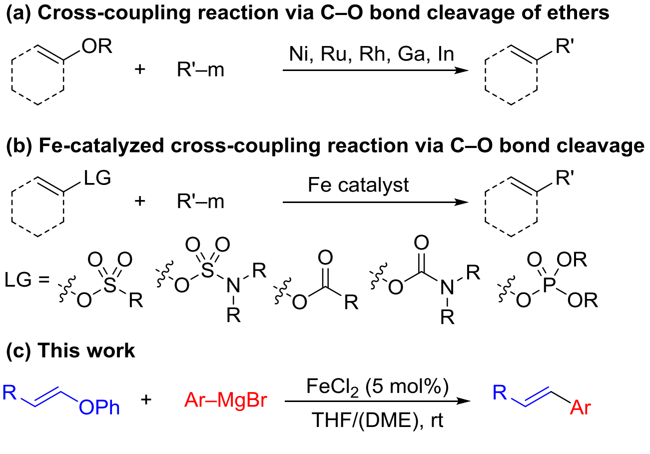
Takanori Iwasaki*, Ryo Akimoto, Hitoshi Kuniyasu, and Nobuaki Kambe*

Abstract: Iron-catalyzed cross-coupling reaction of vinylic ethers with aryl Grignard reagents is described. The reaction proceeded at rt with a catalytic amount of a Fe salt without the aid of costly ligands and additives. In this catalytic system, vinylic C–O bonds were preferentially cleaved over aromatic C–O bonds of aryl ethers or aryl sulfonates.

The development of transition metal-catalyzed cross-coupling reactions using stable unactivated carbon-based reagents provides synthetically useful routes for constructing C–C bonds.[1] In this context, the use of ethers instead of esters or organohalides as a coupling partner has attracted considerable attention in view of establishing economically and environmentally more ideal C–C bond forming reactions.[2] Pioneering studies on the cross-coupling reaction of ethers with organometallic reagents via C(sp^2)–O bond cleavage were published by Wenkert in 1979.[3] This chemistry attracted much attention and has been extensively studied since the beginning of this century.[4-7] As the result, various efficient catalytic transformations have been achieved by the aid of Ni,[3,4] Ru,[5] Rh,[6] and group 13 elements, Ga and In,[7] as the catalysts (Scheme 1a). Our efforts on such transformation led to the development of Rh-catalyzed cross-coupling reaction of vinyl ethers with aryl Grignard reagents, where a unique anionic diarylrhodium complex plays important roles as an active catalytic intermediate.[6a]

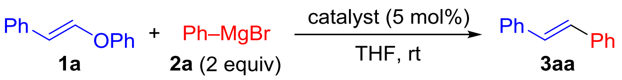
Not only due to the big advantage of iron as an abundant and economical resource, Fe has attractive features as catalysts[8] and has been employed for cross-coupling reaction of oxygen containing substrates including sulfonates,[9] sulfamates,[9d,g,h,10] esters,[11] carbamates,[10b,12] and phosphates.[13] However, Fe-catalyzed cross-coupling reaction of ethers, a simplest unactivated oxygen containing family, has not yet been accomplished to date (Scheme 1b). Herein, we report the first example of Fe-catalyzed cross-coupling reaction of vinylic ethers with aryl Grignard reagents (Scheme 1c).

Firstly, the reaction of phenyl styryl ether (**1a**) with PhMgBr (**2a**) in THF was examined at rt using various transition metal salts. As shown in Table 1, the desired cross-coupling product **3aa** was formed in 92% yield by use of 5 mol% of $FeCl_2$ without any ligands (entry 1), indicating that iron catalysts have similar catalytic activities for this transformation as the Rh catalysts reported by us previously (entry 12).[6a] Under the same conditions, $FeCl_3$ and $Fe(acac)_2$ afforded **3aa** in moderate yields and FeF_2 did not promote the cross-coupling reaction (entries 2-4). This difference between $FeCl_2$ and FeF_2 might be due in part



Scheme 1. Cross-coupling reaction through C–O bond cleavage.

Table 1. Coupling Reaction of Phenyl Styryl Ether (**1a**) with PhMgBr (**2a**)[a]



Entry	Catalyst	Time [h]	Conv. of **1a** [%]	Yield of **3aa** [%]
1	$FeCl_2$	7	100	92
2	$FeCl_3$	7	83	62
3	$Fe(acac)_2$	7	69	54
4	FeF_2	24	28	n.d.
5	$CpFe(CO)_2I$	7	32	22
6	$[CpFe(CO)_2]_2$	7	34	22
7	$CoCl_2$	24	57	36
8	$NiCl_2$	24	94	79
9	$CuCl_2$	24	5	trace
10	none	24	2	trace
11[b]	$FeCl_2$	48	100	97
12	$[RhCl(cod)]_2$	8	–	90

[a] Reaction conditions: A mixture of **1a** (0.5 mmol), PhMgBr (**2a**) (1.0 mmol), and catalyst (5 mol% on metal) in THF was stirred at rt. Yield and conversion were determined by GC. [b] Reaction was conducted in THF/DME = 1.0/0.4 mL.

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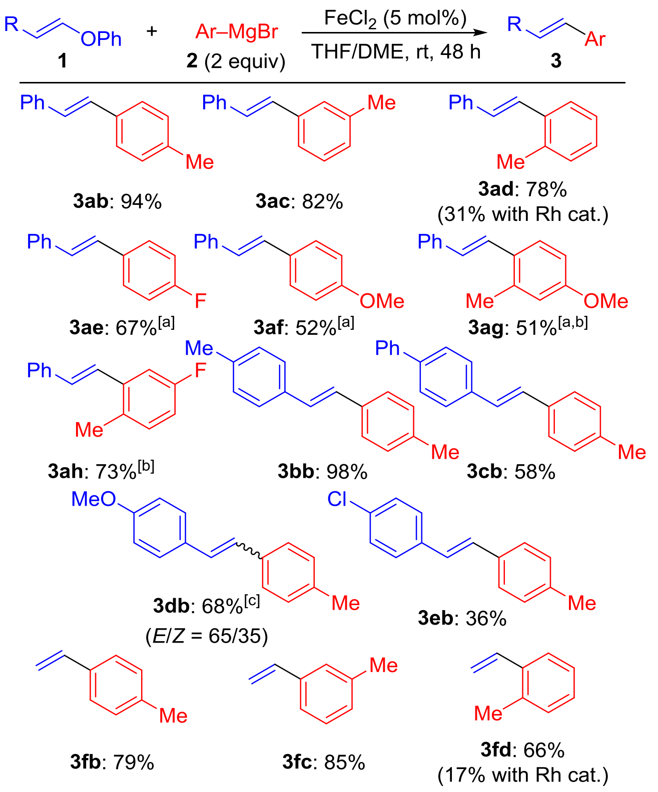
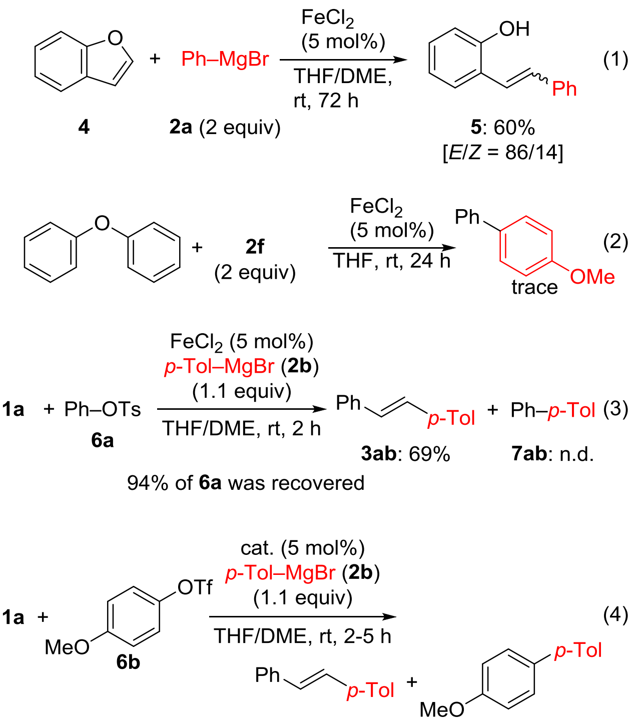
to the slow transmetalation of FeF_2 with Grignard reagents.[14] Iron complexes having a Cp ligand were less effective (entries 5-6) and ferrocene showed no catalytic activity. Although $CoCl_2$ and $NiCl_2$ gave **3aa** in 36% and 79% yields, respectively, $CuCl_2$ was ineffective resulting in the recovery of **1a** (entries 7-9). The coupling reaction did not proceed without catalyst (entry 10). Addition of 1,2-dimethoxyethane (DME) increased the product selectivity giving **3aa** in 97% yield after 48 h (entries 1 and 11), although the reaction rate was somewhat decreased (11% yield in 4 h and 88% yield in 24 h).[15]

Scheme 2 summarizes the results of the cross-coupling of various vinylic ethers with aryl Grignard reagents under the optimized conditions shown in entry 11 of Table 1. Aryl Grignard reagents carrying a methyl substituent at their *para*-, *meta*-, or *ortho*-position coupled with **1a** in good to excellent yields, indicating that the present Fe catalyst is not sensitive to the steric hindrance and applicable to a wide scope of Grignard reagents. This is in large contrast to the Rh catalytic system, which gave poor yields when *ortho*-substituted aryl Grignard reagents was employed.[6a] Both electron-withdrawing (**2e** and **2h**) and donating (**2f** and **2g**) substituents slightly affected the reaction. The evidence that biaryls arising from the cross-coupling via aromatic C–O bond cleavage was not formed suggests that the present catalytic system prefers the vinylic C–O bond over the aromatic C–O bond.[16] Aryl styryl ethers **1b-e** having *para*-substituent gave the corresponding coupling products in good yields, although the chlorinated substrate **1e** resulted in 36% yield due to the competing hydrodehalogenation. When an *E*/*Z* mixture of **1d** (*E*/*Z* = 55/45) was used, an *E*/*Z* mixture of coupling product **3db** was yielded in 68% combined yield with *E*/*Z* = 65/35. Simple phenyl vinyl ether (**1f**) also coupled with tolyl Grignard reagents **2b-d** affording the corresponding methylstyrenes **3fb**, **3fc**, and **3fd** in good yields. Unfortunately, the coupling reaction of phenyl vinyl ether (**1f**) with electron deficient aryl Grignard reagents resulted in somewhat lower yields due to the polymerization of the formed styrene derivatives under the reaction conditions.[17]

When benzofuran (**4**) was employed as an cyclic ether in the reaction with PhMgBr, the expected phenol derivative **5** was yielded as a mixture of *E*/*Z* isomers with a 86/14 ratio, indicating that an *E*/*Z* isomerization process is involved [Eq. (1)].[3,18] When diphenyl ether was employed, the coupling reaction did not take place at all and Ph_2O was recovered unchanged [Eq. (2)]. Furthermore, a competitive reaction using a 1:1 mixture of vinylic ether **1a** and PhOTs (**6a**) with *p*-TolMgBr (**2b**) gave **3ab** exclusively and no biaryl **7ab** arising from the coupling reaction of PhOTs (**6a**) with **2b** was observed [Eq. (3)].[9] Another competitive reaction using a more reactive aryl triflate **6b** led to the same result [Eq. (4)]. In any reactions of Eqs. 1-4, cross-coupling products via Ar–O bond cleavage were not found. This distinctive preference for vinyl ethers against aryl ethers may imply that the present reaction proceeds through addition of aryliron species toward vinylic ether and subsequent β-oxygen elimination. Similar chemoselectivities were also observed in a Rh-catalyzed cross-coupling reaction of vinyl ethers.[6a]



Scheme 2. Fe-catalyzed cross-coupling reaction of vinylic ethers with aryl Grignard reagents. [a] Without DME. [b] Reaction time was 96 h. [c] **1d** (*E*/*Z* = 55/45) was used.

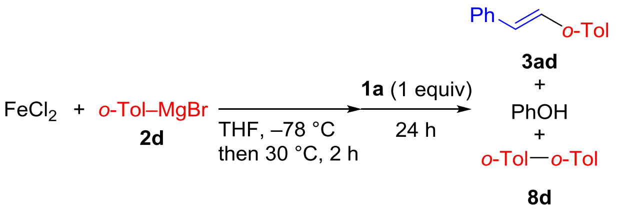


cat.	3ab	7bb
$FeCl_2$	45%	trace
$NiCl_2$(dppp)	25%	38%

Since $NiCl_2$ also represented a high catalytic activity for this transformation as shown in Table 1,[3,4] we run the same competitive reaction using $NiCl_2$(dppp) as the catalyst and found that this Ni catalyst[3c] is non-selective giving rise to a nearly 4:6 mixture of the coupling products [Eq. (4)].[19]

To gain insight into the reaction pathways, we conducted stoichiometric reactions using different amounts of Grignard reagents and the results are summarized in Table 2. When $FeCl_2$ was treated with 1 or 2 equiv of *o*-TolMgBr (**2d**) and then **1a** was added to the resulting mixture, the coupling product **3ad** was not formed at all and almost all of **1a** was recovered (entries 1 and 2). The evidence that a biaryl **8d**, arising probably from transmetalation of $FeCl_2$ with *o*-Tol-MgBr followed by reductive elimination, was generated in substantial amounts in these reactions suggests that neither $Ar_2Fe(II)$ nor ArFe(I) species[20] being expected to be formed in situ is the active catalytic species toward vinylic ethers. On the other hand, a similar reaction using 3 equiv of the Grignard reagent **2d** afforded the corresponding coupling product in 49% yield accompanied by the comparable amount of phenol (41%) (Entry 3). These yields were improved to 71% and 62%, respectively, when 4 equiv of **2d** was employed (Entry 4). In entries 3 and 4, **8d** was formed in 62% and 70% yields based on $FeCl_2$. These results imply that the reduction of $FeCl_2$ by two equiv of Grignard reagents takes place prior to the coupling reaction to generate Fe(0) and/or Fe(I), which do not react alone with vinyl ethers but do react in the presence of a Grignard reagent giving rise to the cross-coupling product.

Table 2. Stoichiometric Reaction of Phenyl Styryl Ether (**1a**) with *o*-TolMgBr (**2d**)[a]

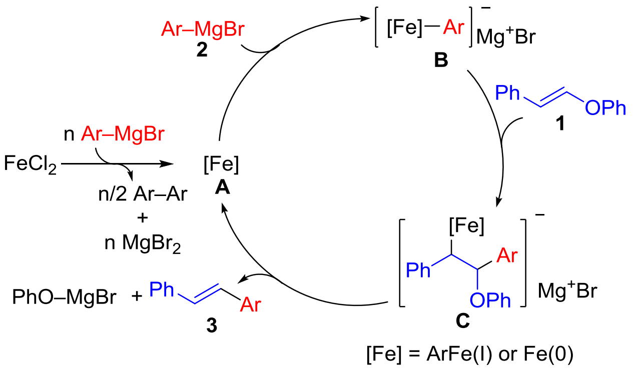


Entry	2d	Conv. of 1a [%]	3ad [%]	PhOH [%]	8d [%][b]
1	1 equiv	17	n.d.	n.d.	35
2	2 equiv	17	n.d.	n.d.	59
3	3 equiv	49	49	41	62
4	4 equiv	71	71	62	70

[a] Yields and conversion were determined by GC.

[b] Based on $FeCl_2$ as a two electron oxidizing agent.

Based on these results along with previously proposed mechanisms regarding Fe-catalyzed cross-coupling reactions,[20-24] a possible catalytic cycle is depicted in Scheme 3. Although the actual structure of the catalytic intermediates is not clear yet, $FeCl_2$ may undergo reduction by ArMgBr to form Fe(I)[22] or Fe(0)[23] accompanied by the formation of biaryls.[15] Thus formed low valent Fe species **A** react with aryl Grignard reagents to form anionic aryliron species **B**.[24,25] The addition of thus formed Fe complex **B** toward C–C double bonds of vinyl ethers to afford **C** and subsequent *anti*-β-oxygen elimination assisted by Mg cation gives the coupling products. The observed unique chemoselectivity in favor of vinylic C–O bond cleavage over aromatic C–O bond cleavage of ethers and even sulfonates could be explained by this addition-elimination mechanism.



Scheme 3. A possible catalytic cycle.

In conclusion, we found that Fe catalyzes the cross-coupling reaction of aryl vinyl ethers with aryl Grignard reagents via selective cleavage of the vinylic C–O bond. In addition, vinylic ethers underwent cross-coupling reaction even in the presence of aryl esters such as tosylates and triflates of phenols. The current Fe catalysis does not require costly ligands and is applicable to sterically hindered *ortho*-substituted aryl Grignard reagents. Preliminary mechanistic studies imply the intermediacy of low valent anionic Fe species in the C–O bond cleavage process.

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Keywords: arylation • chemoselectivity • C–O bond cleavage • cross-coupling reaction • iron

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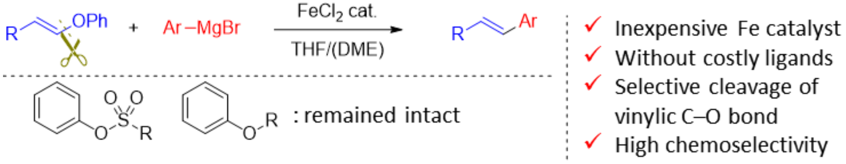
COMMUNICATION



Robust Fe catalysis: vinylic carbon-oxygen bonds were selectively cleaved by Fe catalyst to couple with aryl Grignard reagents without costly ligands and additives. Under the Fe catalysis, much more reactive oxygen containing functional groups such as aryl tosylates and triflates as well as aromatic C–O bond of ethers remained unchanged, implying a unique chemoselectivity of the Fe catalyst.

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Fe-Catalyzed Cross-Coupling Reaction of Vinylic Ethers with Aryl Grignard Reagents