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Cross-coupling Reaction of Alkyl Halides with Alkyl Grignard Reagents Catalyzed by Cp-Iron Complexes in the Presence of 1,3-Butadiene

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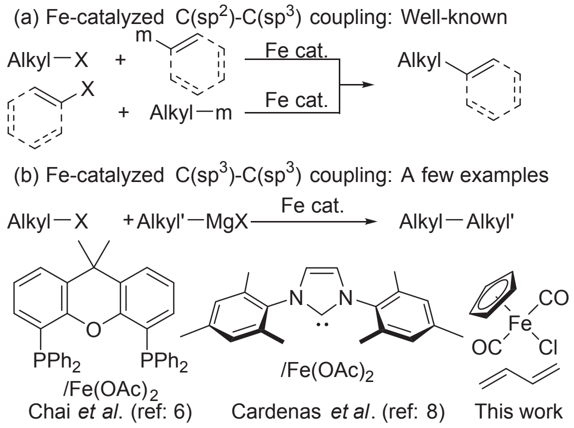
Iron-catalyzed cross-coupling reaction of alkyl halides with alkyl Grignard reagents by the combined use of cyclopentadienyl ligand and 1,3-butadiene additive is described. The reaction smoothly proceeds at room temperature using unactivated alkyl bromides and fluorides via non-radical mechanism, which is in sharp contrast with hitherto known Fe-catalyzed cross-coupling reactions of alkyl halides.

Keywords: Cross-coupling reaction | Fe complex catalyst | Alkyl Grignard reagent

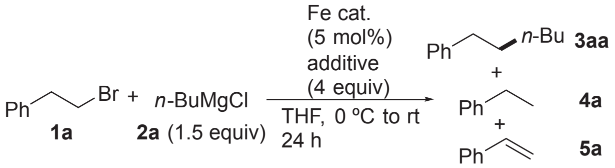
Iron-catalyzed cross-coupling reaction has attracted a great deal of attention in organic syntheses due to the economic advantage, ubiquity, and less toxic feature of iron.[1] Among Fe-catalyzed cross-coupling on sp^3-hybridized carbon centers, reaction of aryl or alkenyl halides with alkyl metal reagents[2,3] and that of alkyl halides with aryl or alkenyl metal reagents[3,4] have been well established (Scheme 1a). However, only a few reports are available for the cross-coupling of alkyl halides with alkyl metal reagents.[5–9] Chai and co-workers disclosed the cross-coupling of unactivated alkyl bromides with alkyl Grignard reagents using Fe(OAc)$_2$-xantphos catalytic system (Scheme 1b).[6] Nakamura *et al.* employed this catalytic system in the Suzuki-Miyaura alkyl-alkyl cross-coupling reaction.[7] Another example is Kumada-Tamao-Corriu coupling using an Fe-NHC complex reported by Cárdenas (Scheme 1b).[8] However, undesirable reduction, elimination, and homo-coupling reactions of the reagents used still remained as serious problems to be solved. During the course of our study on cross-coupling using Grignard reagents, we developed alkyl-alkyl cross-coupling reactions using first row transition metal catalysts and unsaturated hydrocarbon additives.[10–12] We recently reported iron-catalyzed cross-coupling reaction of vinyl ethers via C–O bond cleavage.[13] Here we disclose that the combined use of cyclopentadienyl (Cp) ligand and 1,3-butadiene additive is effective to achieve the coupling reaction between sp^3-carbon centers by Fe catalysts.



Scheme 1. Iron-catalyzed cross-coupling reaction of organo halides with organometallic reagents.

We initiated our study using phenethyl bromide (**1a**) and *n*-BuMgCl (**2a**) as the coupling partners. Various iron salts were tested in the presence of 1,3-butadiene as an additive, and the results are summarized in Table 1. Simple Fe(II) and Fe(III) salts afforded the coupling product, hexylbenzene (**3aa**), in poor yields (Entries 1 and 2).[14] Among iron complexes tested,[14] CpFe(CO)$_2$Cl (**6**) was found to be a suitable catalyst precursor and improved the yield of **3aa** to 51% (Entry 3). Methyl substituted dienes as well as tetraene[10c] and an internal alkyne[11a] were not effective (Entries 4–6).[14] PPh$_3$ facilitated the reduction to give ethylbenzene (**4a**) (Entry 7). The addition of TMEDA, which is frequently used as a ligand for Fe-catalyzed cross-coupling reactions,[4a,4c,4d,4g–4i,15] resulted in a poor yield of **3aa** (Entry 8). In the absence of additives, the reduction of **1a** predominated to afford **4a**, and no coupling product **3aa** was obtained (Entry 9). The cross-coupling reaction was sluggish in the absence of iron catalyst (Entry 10).

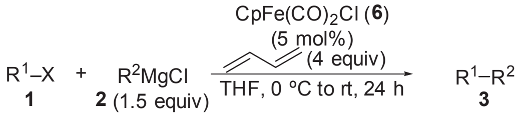
Table 1. Optimization of the reaction conditions[a]

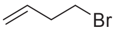
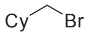
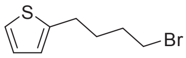
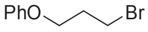
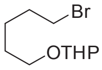
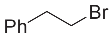
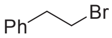


Entry	Catalyst	Additive	GC Yield/%[b]		
			3aa	**4a**	**5a**
1	FeCl$_2$	1,3-butadiene	7	6	7
2	FeCl$_3$	1,3-butadiene	n.d.	5	10
3	CpFe(CO)$_2$Cl (**6**)	1,3-butadiene	51	10	3
4	CpFe(CO)$_2$Cl (**6**)	1,3-pentadiene	n.d.	6	8
5	CpFe(CO)$_2$Cl (**6**)	isoprene	3	3	7
6	CpFe(CO)$_2$Cl (**6**)	2,3-dimethyl-1,3-butadiene	n.d.	6	7
7	CpFe(CO)$_2$Cl (**6**)	PPh$_3$	n.d.	59	7
8[c]	CpFe(CO)$_2$Cl (**6**)	TMEDA[d]	5	3	8
9	CpFe(CO)$_2$Cl (**6**)	none	n.d.	43	5
10	none	none	5	11	2

[a]Reaction conditions: **1a** (2.0 mmol), **2a** (3.0 mmol), catalyst (0.1 mmol), and additive (8.0 mmol) were stirred at 0 °C for 2 h and then at rt for 22 h. [b]Yields were determined by GC. [c]In the presence of 1,3-butadiene (4 mmol). [d]2 equiv.

Table 2. Fe-catalyzed cross-coupling reaction of alkyl halides with alkyl Grignard reagents[a]



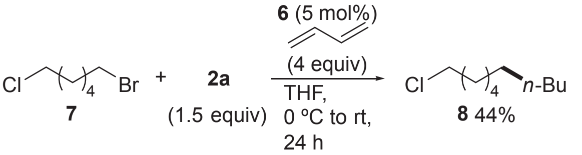
Entry	R^1–X	R^2–MgCl	Yield/%[b]
1	*n*-Non–F **1b**	*n*-BuMgCl **2a**	35
2	*n*-Non–Cl **1c**	*n*-BuMgCl **2a**	n.d.
3	*n*-Non–Br **1d**	*n*-BuMgCl **2a**	54
4	*n*-Non–I **1e**	*n*-BuMgCl **2a**	9
5	*n*-Non–OTs **1f**	*n*-BuMgCl **2a**	5
6	 **1g**	*n*-BuMgCl **2a**	62
7	 **1h**	*n*-BuMgCl **2a**	61
8	 **1i**	*n*-BuMgCl **2a**	47
9	 **1j**	*n*-BuMgCl **2a**	54(40)[c]
10	 **1k**	*n*-BuMgCl **2a**	42
11	 **1a**	*n*-OctMgCl **2b**	47
12	 **1a**	*s*-BuMgCl **2c**	56

[a]Reaction conditions: RX (1.0 mmol), *n*-BuMgCl (1.5 mmol, in THF), $CpFe(CO)_2Cl$ (0.05 mmol), 1,3-butadiene (4.0 mmol). [b]Yields were determined by GC. [c]Isolated yield. THP: tetrahydropyranyl.

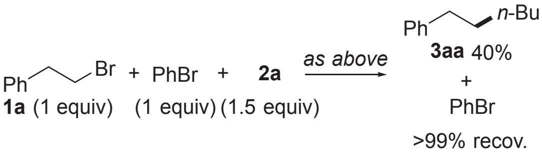
It has been reported that Cu impurity in Fe salts worked as the genuine catalytic active species in cross-coupling reactions.[16] We thus conducted ICP-AES analysis of the reaction mixture and observed the contamination of Cu and Pd only in 0.79 and 0.21 ppm (11 and 1.7 molppm), respectively. Ni could not be detected in the analysis.[17] In addition, when iron complex **6** synthesized from distilled $Fe(CO)_5$[18] was used as a catalyst, yield of **3aa** did not change. These results rule out the effect of trace amounts of metal impurities in the reaction.

Under the optimized reaction conditions,[14,19] we tested the reactivity of alkyl (pseudo)halides. Although *n*-Non-Cl (**1c**) did not react under the present conditions (Table 2, Entry 2), the reaction of *n*-Non-F (**1b**) and *n*-Non-Br (**1d**) afforded the coupling product in 35% and 54% yield, respectively (Entries 1 and 3). This is the first example of an alkyl-alkyl cross-coupling of alkyl fluorides[20] using iron catalyst albeit in a low yield.[4t] Reaction of iodide **1e** and tosylate **1f** resulted in a complex mixture including the cross-coupling product, tridecane, in a poor yield (Entries 4 and 5). In the former case, no *n*-Non-I remained, and the possible by-products formed by dehydrohalogenation, reduction, or dimerization of *n*-Non-I were observed only in 1% yield or less although other products could not be identified by GC analysis. The cross-coupling reaction of **1g** and sterically hindered **1h** smoothly proceeded to afford the corresponding coupling products (Entries 6 and 7). Alkyl bromides bearing thiophene **1i**, ether **1j**, and acetal **1k** also afforded the desired products in moderate yields (Entries 8–10). While no reaction took place when secondary and tertiary alkyl bromides were employed, secondary alkyl Grignard reagent **2c** afforded the desired coupling product **3ac** in 56% yield (Entry 12). Grignard reagents having no β-H such as methyl, phenyl, and benzyl Grignard reagents did not participate in the coupling reaction (*vide infra*).

When 1-bromo-6-chlorohexane (**7**) was employed, the cross-coupling reaction with *n*-BuMgCl (**2a**) took place site selectively at the C–Br carbon, providing decyl chloride (**8**) in 44% yield without formation of other possible coupling products, i.e. decyl bromide and tetradecane (eq 1). In addition, **1a** selectively coupled with *n*-BuMgCl (**2a**) even in the presence of PhBr,[4b] which was completely recovered after the reaction (eq 2).

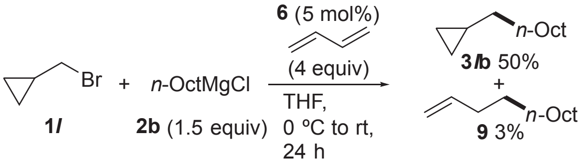


(1)



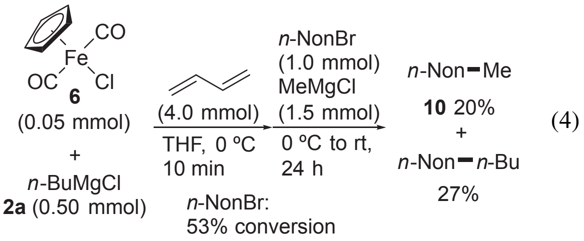
(2)

It was reported that Fe-catalyzed cross-coupling reaction of alkyl halides involved single electron transfer (SET) to generate alkyl radicals arising from alkyl halides due to the facile one electron redox behavior of iron.[4h,15] We thus examined the reaction of **1*l***.[21] It is noteworthy that the direct coupling product **3*l*b** was obtained in 50% yield accompanied by only 3% yield of a linear product **9**, indicating that radical intermediates are not produced from alkyl bromides in the present catalytic reaction. This is in sharp contrast to hitherto known Fe-catalyzed reactions (eq 3).[21]



(3)

Low valent Fe(–II) species, $\{Fe(MgX)_2\}_n$, formed by the treatment of $FeCl_2$ with 4 equiv of alkyl Grignard reagent bearing β-hydrogen, were proposed to act as catalytic active species for the cross-coupling reaction employing alkyl Grignard reagents as the coupling partner.[22,23] At the early stage of our catalytic system, similar transmetalation and β-H elimination might occur to form the iron hydride species, which might react with 1,3-butadiene to form CpFe(π-allyl) complexes. To confirm the β-H elimination process, we conducted reactions of *n*-Non-Br with Grignard reagents having no β-hydrogen such as methyl, benzyl, and phenyl Grignard reagents and revealed that no reaction took place. When reaction of *n*-Non-Br with MeMgCl was conducted similarly, but with preceded pretreatment of the iron complex **6** with *n*-BuMgCl (**2a**) to form iron hydride species, the cross-coupling did proceed to afford **10** in 20% yield along with tridecane in 27% yield (eq 4). These results strongly suggest that the formation of Fe-H species is essential to trigger this catalytic reaction.

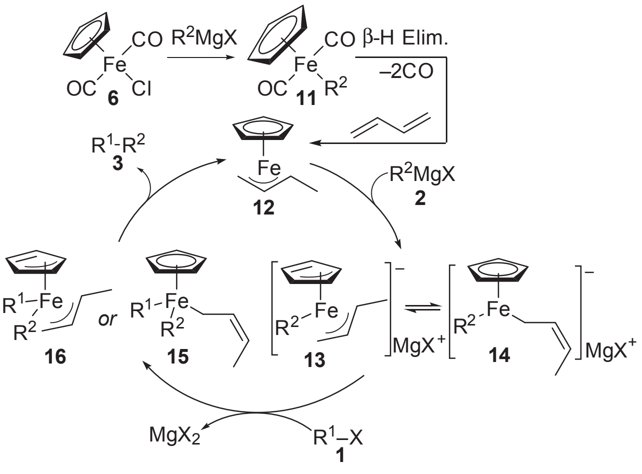


(4)

The IR spectrum of the complex **6** showed two signals assignable to CO ligands at 2049 and 1997 cm^{-1} in THF. Although these signals remained unchanged by the addition of 1,3-butadiene, the subsequent addition of *n*-BuMgCl shifted these peaks to 1999 and 1942 cm^{-1}.[24] This species remained unchanged after stirring for 6 h at room temperature even in the presence of an excess amount of Grignard reagents. When **1a** was added to this mixture, the signals disappeared, indicating no CO ligand coordinates to the active species.[14]

Although the detailed reaction mechanisms of the present catalytic system remain yet unclear, taking into account these results, a possible reaction pathway of this cross-coupling is shown in Scheme 2. At first, complex **6** undergoes transmetalation[25] to give **11** which undergoes elimination of CO ligand(s)[26] and β-H elimination[22,23] to form a hydride species. Subsequent insertion of 1,3-butadiene into the Fe–H bond[27b] provides d^{16} electron CpFe(π-allyl) complex **12**[27] possessing an isoelectric structure with respect to bis(π-allyl)Ni complexes[10] and (π-allyl)Co complexes[12] which were previously reported by us as catalytic active species for alkyl-alkyl cross-coupling reactions. The complex **12** reacts with alkyl Grignard reagents to form ate complexes **13** or **14**,[28] in which η^5-Cp and η^3-allyl ligands change their hapticity to η^3-Cp and σ-allyl, respectively, to keep the d^{16} electron state of Fe. The resulting ate complexes undergo nucleophilic attack toward alkyl halides to give coupling products and regenerate complex **12** directly or through an Fe(IV) complex **15** or **16** via an ionic mechanism.

In conclusion, the cross-coupling reaction of unactivated alkyl halides, including alkyl fluoride, with alkyl Grignard reagents was found to proceed with the combined use of CpFe(CO)$_2$Cl (**6**) and 1,3-butadiene, in which both unsaturated hydrocarbon ligands were essential to obtain the coupling products. The present catalytic system enabled selective cross-coupling of alkyl bromides with alkyl Grignard reagents in the presence of alkyl chlorides and aryl bromides. This reaction proceeds through a non-radical mechanism, which is in sharp contrast to previously reported Fe-catalyzed cross-coupling reaction of alkyl halides.



Scheme 2. A possible catalytic cycle.

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17 Control experiments with trace amount of Ni and Cu revealed that 25 molppm of Ni or 100 molppm of Cu was required to attain quantitative yield. The addition of 50 and 100 molppm of Cu to the reaction conditions indicated in Table 1, Entry 3 resulted in almost same yield (44 and 55%, respectively). In addition, at these concentration of Cu, 1,3-diene showed no significant additive effect on the catalytic activity of Cu (see ref 11c) in sharp contrast with the present result (Table 1, Entry 9). Concentration of Ni in the reaction mixture was very low and ICP analysis showed no significant peaks of Ni (<0.1 ppm). The evidence that tetraene and isoprene, which are good additives for Ni catalyst, showed almost no effect denies the contamination of Ni.

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19 **Typical Experimental Procedure for the Fe-Catalyzed Cross-Coupling:** *n*-BuMgCl (2 M in THF, 1.5 mL, 3.0 mmol), undecane (internal standard), 1,3-butadiene (180 mL as gas, 8.0 mmol), and phenethyl bromide (276 µL, 2.0 mmol) were added to a dry, nitrogen-flushed Schlenk tube containing CpFe(CO)$_2$Cl (**6**) (21.2 mg, 0.1 mmol) with dry ice/EtOH bath cooling. The cold bath was changed to ice bath and stirred for 2 h then at rt for 22 h. Reaction was quenched by the addition of sat. NH$_4$Cl aq., extracted with hexane, and analyzed by GC.

20 Our recent reports on alkylation reactions using alkyl fluorides: a) T. Iwasaki, R. Shimizu, R. Imanishi, H. Kuniyasu, N. Kambe, *Angew. Chem., Int. Ed.* **2015**, *54*, 9347. b) T. Iwasaki, X. Min, A. Fukuoka, H. Kuniyasu, N. Kambe, *Angew. Chem., Int. Ed.* **2016**, *55*, 5550. Also see ref 12c.

21 Radical ring-opening of cyclopropylmethyl halides was observed, see: refs 4d,f,j,l,n,p,t,y, 5, 8, and 15. Alkyl radicals were proved by other techniques, see: refs 4c,e,q–s,u,x. In sharp contrast to the Fe catalyses, Ni, Cu, and Co catalyses employing unsaturated hydrocarbon additives proceed through an ionic mechanism, and no evidence of alkyl radical intermediates was observed, see: refs 10a,b, 11a,b, and 12.

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28 Ate complexes of Ni were isolated and determined their structure, see: a) T. Iwasaki, A. Fukuoka, X. Min, W. Yokoyama, H. Kuniyasu, N. Kambe, *Org. Lett.* **2016**, *18*, 4868. b) T. Iwasaki, A. Fukuoka, W. Yokoyama, X. Min, I. Hisaki, T. Yang, M. Ehara, H. Kuniyasu, N. Kambe, *Chem. Sci.* **2018**, *9*, 2195.