An efficient and recyclable iron(III)-containing imidazolium salt catalyst for cross-coupling of aryl Grignard reagents with alkyl halides

YAN ChunHui, WANG LinLin, GAO HuanHuan, SUN HongMei* & SHEN Qi*

The Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China

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1,3-Bis(2,6-diisopropylphenyl)imidazolium chloride, [DIPrim]Cl, was used to produce a novel iron(III)-containing imidazolium salt [DIPrim][FeCl₄], which included a *N,N*-diarylimidazolium cation (R = 2,6-diisopropylphenyl), [DIPrim]⁺, and tetrachloroferrate(III) anion, [FeCl₄][−]. This compound was an effective and easy-to-use catalyst for the cross-coupling of aryl Grignard reagents with primary and secondary alkyl halides bearing β -hydrogens. After simply decanting the cross-coupling product in the ether layer, [DIPrim][FeCl₄] could be reused in at least four successive runs without significant loss of catalytic activity.

iron(III) complex, imidazolium salt, alkyl halide, cross-coupling, Grignard reagent

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The transition metal-catalyzed Grignard cross-coupling reaction is a powerful and widely used method for the construction of carbon-carbon bonds [1]. Although a variety of palladium or nickel-based catalysts are particularly effective for the cross-coupling of alkenyl or aryl halides, recent reports on the use of alkyl halides, especially those with β -hydrogen atoms, as substrates suggests iron catalysis has potential in this field [2,3]. In comparison with established palladium or nickel-based systems, iron-based catalysts offer a cost efficient, safe and more environmentally benign approach, and the capacity to suppress undesirable β -hydride eliminations.

To date, a variety of iron-based catalysts have been developed for the cross-coupling of an aryl Grignard reagent with primary or secondary alkyl halides bearing β -hydrogens. For example, well-defined iron complexes, such as the iron (II) tetrakisferrate complex [4], iron(III) salen complexes [5], iron(II) or iron(III) imine complexes [6] and iron(III) amine-bis(phenolate) complexes [7], have shown good cross-coupling activity. In addition, although Fe(acac)₃ (acac =

acetylacetonate) can catalyze this cross-coupling reaction [8], amine additives are necessary to achieve higher yields of the cross-coupled product [9]. Notably, FeCl₃ can be used effectively in the presence of appropriate additives, such as amines [9–11], phosphines, phosphites, arsines and carbene precursors [12]. Although the direct use of FeCl₃ generally suffers from limitations such as high hygroscopicity of FeCl₃ and the variable yield according to the purity and commercial source of FeCl₃ [13], this method appears particularly attractive because of the simplicity and low cost of the metal salt combined with the high efficiency of the catalytic system. Consequently, this method represents a very powerful approach, if these limitations can be overcome [9,11].

Two reports describing the use of FeCl₃ have appeared in the literature. Cahiez et al. [9] discovered that hygroscopic FeCl₃ could be easily modified into a hydrophobic and air-stable iron(III) complex [(FeCl₃)₂(tmeda)₃] (tmeda = *N,N,N',N'*-tetramethylethylenediamine) by direct reaction of FeCl₃ with tmeda in a 2:3 molar ratio. Moreover, this complex showed significantly better activity than a stoichiometric mixture of FeCl₃ and tmeda [10,11]. Of particular note is a

*Corresponding authors (email: sunhm@suda.edu.cn; qshen@suda.edu.cn)

recent report on the use of 1-butyl-3-methylimidazolium chloride, [BMim]Cl, instead of the amine ligand to modify FeCl_3 to a hydrophobic and air-stable imidazolium salt of iron(III), [BMim][FeCl_4] [14]. [BMim][FeCl_4] has high activity for the aryl Grignard cross-coupling of alkyl halides, and is a recyclable catalyst. It is also found to be a very efficient catalyst for other organic transformations, such as Friedel-Crafts sulfonylation of aromatics [15], dimerization of 2,5-norbornadiene [16], and glycolysis of poly(ethylene terephthalate) [17]. However, there may be issues with handling and structural definition of the liquid state of this ionic iron(III) complex. In view of this, an alternative easy-to-use, well-defined iron-based catalyst is highly desirable.

Modification of transition metal-based catalysts with imidazolium cations has attracted increasing attention [18]. The use of imidazolium salts as more environmentally benign alternatives to traditional ligands, such as amines and phosphines, provides many advantages over traditional systems in terms of stability, activity, reusability, and low toxicity of the modified catalysts. Thus, imidazolium salts are promising candidates for optimizing synthetic efficiency and addressing green sustainability issues [19].

As a continuation of our work on the development of iron-based catalysts for carbon-carbon bond formation [20], here we report the modification of anhydrous FeCl_3 or $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ with 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride, [DIPrim]Cl. This produced a very efficient and easy-to-use iron(III)-containing imidazolium salt [DIPrim][FeCl_4] for the cross-coupling of aryl Grignard reagents with primary or secondary alkyl halides bearing β -hydrogens.

1 Experimental

Since anhydrous FeCl_3 , $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride ([DIPrim]Cl) are hydrophilic, all manipulations were performed under pure argon with rigorous exclusion of air and moisture using standard Schlenk techniques.

1.1 Materials

Solvents were distilled from Na/benzophenone ketyl under pure argon prior to use. Anhydrous FeCl_3 , $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and organic reagents used for the cross-coupling reactions were purchased from Acros Organics (Geel, Belgium), Sigma-Aldrich (St. Louis, MO), and Alfa Aesar (Ward Hill, MA). Phenylmagnesium bromide was diluted prior to use. [DIPrim]Cl was prepared by an established method [21].

1.2 Synthesis

(i) Synthesis of [DIPrim][FeCl_4]. Procedure A: A Schlenk flask was charged with [DIPrim]Cl (2.40 g, 5.68 mmol), tetrahydrofuran (THF, 20 mL) and a stirring bar. To this

suspension, FeCl_3 (0.92 g, 5.68 mmol) in 20 mL of THF was added. The reaction mixture was stirred for 2 h at room temperature, filtered, and evaporated to dryness. The residue was recrystallized from THF and hexane to yield yellow-green crystals (3.15 g, 95%). Decomposition temperature: 254.1°C. Anal. Calcd for $\text{C}_{27}\text{H}_{37}\text{Cl}_4\text{N}_2\text{Fe}$: C, 55.22; H, 6.35; N, 4.77. Found: C, 54.53; H, 6.27; N, 4.78. MS (ESI⁻): m/z 197.8097 [FeCl_4]⁻ (100%). MS (ESI⁺): m/z 389.2954 [$\text{C}_{27}\text{H}_{37}\text{N}_2$]⁺ (100%). Raman: 335.956 cm^{-1} (FeCl_4).

Procedure B: Following a procedure similar to the synthetic procedure A, a Schlenk flask was charged with [DIPrim]Cl (2.12 g, 5 mmol), THF (20 mL), and a stirring bar. To this suspension, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1.35 g, 5 mmol) in 20 mL of THF was added. After workup, the product was precipitated as yellow-green crystals in 90% yield (2.63 g). Anal. Calcd for $\text{C}_{27}\text{H}_{37}\text{Cl}_4\text{N}_2\text{Fe}$: C, 55.22; H, 6.35; N, 4.77. Found: C, 54.44; H, 6.31; N, 4.78.

(ii) Typical cross-coupling procedure. A Schlenk tube was charged with the iron(III)-based catalyst (0.01 mmol), alkyl bromide (1.00 mmol), diethyl ether (0.8 mL) and a stirring bar. 4-Methylphenylmagnesium bromide (1.50 mmol, 1.07 mol/L solution in diethyl ether) was added to this solution at 30°C. The resulting solution turned black, and was then stirred for 20 min in an oil bath at 30°C. After the reaction was quenched by adding dilute hydrochloric acid (1 mol/L, 0.5 mL), the mixture was extracted with ethyl acetate (3 × 4 mL). The yield of the desired product is determined by GC analysis, using *n*-hexadecane as an internal standard.

1.3 Analyses

Carbon, hydrogen and nitrogen analyses were performed by direct combustion with a Carlo-Erba EA-1110 (Carlo-Erba Instruments, Milan, Italy). The Raman spectra were recorded on a LabRAM HR800 spectrometer (ESI-MS) data were recorded on a 6220 Accurate-Mass TOF LC/MS instrument (Agilent, Santa Clara, CA). Gas chromatographic (GC) analysis was performed on a Varian CP-3800 instrument (Varian, Palo Alto, CA) equipped with a flame ionization detector and a OV-101 capillary column (30 m × 0.32 mm I.D., 0.10 μm , Analytical Technology, Collegeville, PA). The oven temperature was held at 80°C for 2 min, increased to 280°C at 10°C/min, and held for 2 min.

2 Results and discussion

2.1 Synthesis and characterization of [DIPrim][FeCl_4]

As shown in Scheme 1, the target imidazolium salt of iron (III) [DIPrim][FeCl_4] was easily prepared by reacting anhydrous FeCl_3 with one equivalent of 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride [DIPrim]Cl in THF at room temperature [20]. Although [DIPrim]Cl is insoluble in THF, when a THF solution of FeCl_3 was added to a suspension of [DIPrim]Cl in THF, the mixed solution quickly changed

Scheme 1 Synthesis of $[\text{DIPrim}][\text{FeCl}_4]$.

from a suspended state to a transparent liquid. Following workup, $[\text{DIPrim}][\text{FeCl}_4]$ was obtained as yellow-green crystals in almost quantitative yields. Alternatively, $[\text{DIPrim}][\text{FeCl}_4]$ can be conveniently synthesized by a similar reaction using the inexpensive $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ as a starting material. However, the yield was only 90%.

Although both of the ferric chlorides and the imidazolium chloride are hydrophilic, $[\text{DIPrim}][\text{FeCl}_4]$ is hydrophobic and air-stable in the solid state, and is therefore easy to use. This complex is also thermally stable unless the temperature is increased above 254°C , which results in decomposition (not melting). The imidazolium chloride $[\text{DIPrim}]\text{Cl}$ decomposed at *ca.* 277°C . This complex was soluble in THF, Et_2O and CHCl_3 , sparingly soluble in toluene, and insoluble in hexane.

$[\text{DIPrim}][\text{FeCl}_4]$ was initially identified by elemental analysis and further characterized by Raman spectroscopy and ESI-MS. The metal-containing anion exists as a discrete FeCl_4^- species, which is evident in the Raman spectrum [22,23]. Figure 1 compares the Raman spectrum of $[\text{DIPrim}][\text{FeCl}_4]$ with that of $[\text{DIPrim}]\text{Cl}$. The spectrum of $[\text{DIPrim}][\text{FeCl}_4]$ shows a strong band at 335.956 cm^{-1} , which is very close to the literature value of about 330 cm^{-1} for $[\text{BMim}][\text{FeCl}_4]$ [17,22]. This band has been previously assigned to the tetrahedral $[\text{FeCl}_4]^-$ species, because of the totally symmetric Fe–Cl stretching vibration [17]. The bands observed between 900 and 1500 cm^{-1} are very similar to those of $[\text{DIPrim}]\text{Cl}$, which indicated the presence of the $[\text{DIPrim}]^+$ species in the obtained iron(III) complex [17]. The negative

Figure 1 Raman spectra of $[\text{DIPrim}][\text{FeCl}_4]$ and $[\text{DIPrim}]\text{Cl}$.

ion ESI-MS spectrum of $[\text{DIPrim}][\text{FeCl}_4]$ showed a peak at m/z 197.8 with an intensity of almost 100%, and a peak at m/z 335.956 with an intensity of almost 100% was observed in the positive ion ESI-MS spectrum of $[\text{DIPrim}][\text{FeCl}_4]$. The characteristic results clearly confirm that the obtained complex is the imidazolium salt of iron(III), $[\text{DIPrim}][\text{FeCl}_4]$.

2.2 Catalysis with $[\text{DIPrim}][\text{FeCl}_4]$

To assess the catalytic activity of $[\text{DIPrim}][\text{FeCl}_4]$ and related iron(III)-based salts, the reaction outlined in eq. (1) was selected, as it represents a prototype cross-coupling of aryl Grignard reagents with alkyl halides bearing β -hydrogens [20].

Based on the conditions developed by Gaertner for the $[\text{BMim}][\text{FeCl}_4]$ -catalyzed cross-coupling reaction between aromatic Grignard reagents and alkyl halides [14], a set of experiments were tested to optimize the reaction conditions. Some reported conditions were found to work effectively, including the use of Et_2O as solvent, the addition of the Grignard reagent in one portion, and a 1.5:1 molar ratio of the Grignard reagent and the alkyl halide. The present cross-coupling reaction can be performed successfully at elevated temperatures with reduced catalyst loading.

When the reaction was performed in the presence of $[\text{DIPrim}][\text{FeCl}_4]$ (amount-of-substance fraction 1 mol%) in Et_2O at 30°C for 20 min, the desired coupling product was obtained in almost quantitative yield (96%) (Table 1, entry 4). Under the same conditions, the mixture of FeCl_3 and $[\text{DIPrim}]\text{Cl}$ in a 1:1 molar ratio exhibited moderate activity and provided the coupling product in 62% yield (Table 1, entry 3). The least active was FeCl_3 alone which afforded the product in a low 12% yield (Table 1, entry 2). The use of $[\text{DIPrim}]\text{Cl}$ alone showed no activity (Table 1, entry 1). However, increasing the reaction temperature led to a lower yield (75%) even when the catalyst amount-of-substance fraction was increased to 2 mol% (Table 1, entry 6). Interestingly, the reaction proceeded smoothly without an inert atmosphere, and there was no obvious difference between an air atmosphere and the use of pure argon (Table 1, entry 5).

The current procedure is advantageous compared to the one catalyzed by $[\text{BMim}][\text{FeCl}_4]$ [14]. The coupling is performed at 30°C instead of 0°C , and the complex $[\text{DIPrim}][\text{FeCl}_4]$ is a solid, whereas $[\text{BMim}][\text{FeCl}_4]$ is an oil at

Table 1 Activities of catalytic systems based on iron(III) complexes ^{a)}

Entry	Catalyst	[Catalyst] (mol%)	[ArMgBr]/[R-Br] (molar ratio)	T (°C)	t (min)	Yield ^{b)}
1	[DIPrim]Cl	1	1.5	30	20	0
2	FeCl ₃	1	1.5	30	20	12
3	FeCl ₃ + [DIPrim]Cl	1	1.5	30	20	62
4	[DIPrim][FeCl ₄]	1	1.5	30	20	96
5 ^{c)}	[DIPrim][FeCl ₄]	1	1.5	30	20	92
6	[DIPrim][FeCl ₄]	2	1.5	Refluxing ^{d)}	30	75
7 [14]	[BMim][FeCl ₄]	5	1.5	0	10	89
8 [14]	[BMim][FeCl ₄]	1	1.5	0	10	80
9 [9]	[(FeCl ₃) ₂ (TMEDA) ₃]	1.5	1.3	rt	45	91
10 [8]	Fe(acac) ₃	5	2.0	Refluxing ^{d)}	30	69
11 [5]	[FeCl(salen)]	5	2.0	45	30	90

a) Cyclohexyl bromide (1.0 mmol), 4-MeC₆H₄MgBr (1.5 mmol), 4-MeC₆H₄MgBr was added in one portion at 30°C, Et₂O, total volume (2.5 mL), Ar.
b) GC yield using *n*-hexadecane as internal standard. c) In air. d) External temperature 45°C, reaction temperature 36–38°C.

room temperature. Finally, the catalytic activity of [DIPrim][FeCl₄] is somewhat higher than that of [BMim][FeCl₄] (Table 1, entries 7,8). This is in agreement with the general idea that a sterically bulky ligand can facilitate the reductive elimination to form the desired coupling products and regenerate the catalytic active species [21]. Furthermore, the catalytic performance of [DIPrim][FeCl₄] was compared

with other related iron(III)-based catalysts reported in the literature. As seen in Table 1, amount-of-substance fractions of 3 mol%–5 mol% for iron(III) are usually required to achieve satisfactory yields of the reaction in eq. (1) [5,8,9]. Therefore, the present results suggest that [DIPrim][FeCl₄] is a novel efficient catalyst for the cross-coupling reaction of aryl Grignard reagents with alkyl halides bearing β-hydrogens.

Table 2 Cross-coupling of ArMgBr with alkyl halides catalyzed by [DIPrim][FeCl₄] ^{a)}

Entry	ArMgX	Alkyl halide	Product	Yield (%) ^{b)}
1				90
2				84
3				76 ^{c)}
4				56 ^{d)}
5				64 ^{d)}
6				82
7				70
8		<i>n</i> -C ₈ H ₁₇ -Br		82
9		<i>n</i> -C ₈ H ₁₇ -Cl		32 ^{c)}
10				82
11				72
12				89
13				43 ^{d)}
14				91

a) Conditions: ArMgBr (1.5 mmol), alkyl halide (1.0 mmol), [DIPrim][FeCl₄] (amount-of-substance fraction 1.0%), Et₂O total volume (2.5 mL), 30°C, 20 min.
b) Isolated yield, average of two runs. c) 60 min. d) Catalyst (amount-of-substance fraction 2.0%). e) Catalyst (amount-of-substance fraction 2.0%), 45°C.

To study the generality of this process preliminary substrate screening was performed and the results are summarized in Table 2. Similar to cyclohexyl bromide, both cyclohexyl iodide and chloride were found to be suitable for the cross-coupling. However, the isolated yields of the desired products were slightly lower (Table 2, entries 2 and 3). The general trend for cyclohexyl halides reactivity appeared to be $\text{Br} > \text{I} > \text{Cl}$. This is the same pattern as that previously reported with the Fe-salen systems [5], FeCl_3 /phosphine systems [12] and $[\text{BMim}][\text{FeCl}_4]$ [14]. Noticeably lower activity was observed if cyclohexyl bromide was replaced by its seven-ring or five-ring analogs (Table 2, entries 4 and 5), and yields of only 56% and 64% for the desired product were obtained even when the catalyst amount-of-substance fraction was increased to 2%. Primary and open chain secondary alkyl bromides could be coupled effectively (Table 2, entries 6–8), whereas the corresponding chloride was less reactive and gave the desired product in 32% yield with a catalyst amount-of-substance fraction of 2% at an elevated temperature (Table 2, entry 9). Furthermore, the cross-coupling was also applicable to a range of Grignard reagents (Table 2, entries 1,10–14), and an electron-rich aryl Grignard reagent was found to react rapidly to give the desired product [12].

2.3 Recyclability of $[\text{DIPrim}][\text{FeCl}_4]$

Recyclability of $[\text{DIPrim}][\text{FeCl}_4]$ was examined by the optimized coupling of 4-methylphenylmagnesium bromide and cyclohexyl bromide with 3% (amount-of-substance fraction) of $[\text{DIPrim}][\text{FeCl}_4]$. After the reaction was complete, the upper ether layer containing the product was decanted and the catalyst was left in the black sediment, which was washed twice with 0.5 mL of diethyl ether. The sediment containing $[\text{DIPrim}][\text{FeCl}_4]$ could be reused in at least four successive runs for the model reaction.

As shown in Table 3, the conversion of cyclohexyl bromide went essentially to completion. However, the isolated yield of the desired coupling product gradually decreased from 90% in the initial run to 78% after the fifth run. This

Table 3 The recyclability of $[\text{DIPrim}][\text{FeCl}_4]$ in the cross-coupling of 4-tolylmagnesium bromide with cyclohexyl bromide ^{a)}

Entry	Run	Conversion of cyclohexyl bromide (%) ^{b)}	Yield (%) ^{c)}
1	1	>99	90
2	2	>99	89
3	3	>99	85
4	4	96	80
5	5	94	78

a) Cyclohexyl bromide (1.0 mmol), 4-tolylmagnesiumbromide (1.5 mmol), 4-MeC₆H₄MgBr was added in one portion at 30°C, $[\text{DIPrim}][\text{FeCl}_4]$ (0.03 mmol), Et₂O (0.8 mL), 20 min, 30°C, Ar. b) GC yield using *n*-hexadecane internal standard. c) Isolated yield.

may be attributed to the loss of the catalyst during the decanting and extraction steps.

3 Conclusions

In conclusion, an efficient, easy to synthesize and handle, recyclable iron(III)-based catalyst $[\text{DIPrim}][\text{FeCl}_4]$ was developed for the cross-coupling of aryl Grignard reagents with primary and secondary alkyl halides bearing β -hydrogens under mild conditions. Comparison between $[\text{DIPrim}][\text{FeCl}_4]$ and the previously reported $[\text{BMim}][\text{FeCl}_4]$ indicates that the *N*-substituent of the imidazolium ring exerts a significant effect on the performance of the corresponding imidazolium salt of iron(III). Modification of the *N*-substituent is readily accessible, and there is the potential to further fine-tune the catalytic activity of the iron(III)-containing imidazolium salt by evaluating other *N*-substituents. The detailed structure-reactivity relationship of iron(III)-containing imidazolium salts and the scope of this catalyst are currently under investigation in our laboratory.

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