

## Synthesis, structure of iron(III)-containing imidazolium salts and their catalytic activity in the alkylation of aryl Grignard reagents

XIA Ying, YAN ChunHui, LI Zhuang, GAO HuanHuan, SUN HongMei\*, SHEN Qi & ZHANG Yong

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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A series of iron(III)-containing imidazolium salts of the general formula [DRim][FeX<sub>4</sub>] (R = 2,6-diisopropylphenyl, IPr, X = Cl, **1**; R = IPr, X = Br, **2**; R = tertbutyl, <sup>t</sup>Bu, X = Cl, **3**; R = isopropyl, <sup>i</sup>Pr, X = Cl, **4**; R = benzyl, Bn, X = Cl, **5**; R = Bn, X = Br, **6**) have been prepared in high yields via reactions of anhydrous ferric halides with equivalent of the corresponding *N,N*-dihydrocarbylimidazolium halides, where **2–6** are novel ones. All of the complexes were characterized by elemental analysis, Raman spectroscopy, electrospray ionization mass spectroscopy, and X-ray crystallography for **1** and **2**. All of them were non-hygroscopic and air-stable, with four of them existing as solids (**1–4**) and two as liquids (**5** and **6**) at room temperature. A preliminary catalytic study on the coupling of 4-tolylmagnesium bromide with cyclohexyl bromide revealed that **1** and **3** possessed the highest activity. In comparison, **2**, **4** and **5** exhibited moderate activity and the least active complex was **6**.

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

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During recent decade the development of iron-based catalysts has received increasing attention with renewed enthusiasm for a variety of cross-coupling reactions since iron is more cost-effective and environmental benign than palladium or nickel [1].

Well-defined iron complexes, developed for the cross-coupling reaction of aryl Grignard reagents with primary or secondary alkyl halides bearing  $\beta$ -hydrogens, represent one of the most successful examples of iron-based catalytic systems in this area, which is mostly owing to their ability to efficiently suppress  $\beta$ -H elimination and their potentiality from a mechanistic perspective [2]. Related iron-based complexes, which including organoiron(-II) complexes [2,3], iron(III) salen-type complexes [4], iron(III) imine complexes [5] and iron(III) complexes of different amine-bridged bis(phenolate) ligands [6–9], have been

shown to be capability in this regard. Fe(acac)<sub>3</sub> (acac = acetylacetonate) are also active [10], although the addition of an amine additive was required to achieve a higher yield of the cross-coupled product [11]. Notably, an easily prepared iron(III)-containing imidazolium salt [bmim][FeCl<sub>4</sub>] (bmim = 1-butyl-3-methylimidazolium cation) can be used as a recyclable catalyst for the aryl Grignard cross-coupling of alkyl halides [12]. The use of imidazolium chloride can modify the highly hygroscopic FeCl<sub>3</sub> into a non-hygroscopic and air-stable complex, which provides a practical strategy for the design of iron(III)-based catalyst with potential large-scale applications [11]. [bmim][FeCl<sub>4</sub>] has already been successfully used as a catalyst in other organic transformations, including the Friedel-Crafts sulfonylation of aromatics [13], a Biginelli condensation for the synthesis of dihydropyrimidinones [14], 2,5-norbornadiene dimerization [15], oxidative desulfurization of fuels [16], the glycolysis of poly(ethylene terephthalate) [17], and the regioselective benzylation of arenes and heteroarenes [18].

\*Corresponding author (email: sunhm@suda.edu.cn)

However, the liquid state of this ionic iron(III) complex may lead to some problems with structural definition and handling. In this context, the careful design and optimization of catalyst structure to provide an alternative easy-to-use iron(III)-based analogue is of great interest.

In recent years there is an increasing interest in the application of ionic liquids (ILs) to modify transition metal-based homogeneous catalysts in terms of stability, activity, low toxicity and reusability of the catalysts [19]. Of various types of ILs available, imidazolium salts are the most popular one employed. In general, they are capable of being tuned with relative ease by the selection of the appropriate cation and anion combination. However, as far as we know, there are few works about the structural character and reactivity of the iron(III)-based catalysts modified by imidazolium cations [20], even if the study of metal complexation in ionic liquids (ILs) is of highly desirable to support the extensive applications of MetILs (so called transition metal containing ILs) that are currently under development [21]. In fact, structural data for ionic iron(III)-containing complexes of the type [imidazolium cation][FeX<sub>4</sub>] have been only scarcely reported, and the first structural data for an oily iron(III) complex, [C<sub>2</sub>mim][FeCl<sub>4</sub>] (C<sub>2</sub>mim = 1-ethyl-3-methylimidazolium cation), was recently determined by Mudring and co-workers [22] via the method of the *in situ* crystal growth. Another structural data for a 1,3-dibutylbenzimidazolium-based ionic iron(III) complex, [(C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>bim][FeCl<sub>4</sub>] [(C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>bim = 1,3-dibutylbenzimidazolium cation], were published soon after [23].

Very recently, we developed a 1,3-bis(2,6-diisopropylphenyl)imidazolium-modified iron(III)-containing complex [DIPrim][FeCl<sub>4</sub>] (IPr = 2,6-diisopropylphenyl), which was obtained as yellow-green crystals and could be used as an efficient and recyclable catalyst for cross-coupling of aryl Grignard reagents with alkyl halides [24]. As a continuation of our work on the development of iron-based catalysts for carbon-carbon bond formation [24,25], herein we reported the synthesis and structural characterization of a series of iron(III)-containing imidazolium salts (**1–6**) and their use in the catalytic cross-coupling of aryl Grignard reagents with alkyl halides bearing  $\beta$ -hydrogens.

## 1 Experimental

Since anhydrous FeCl<sub>3</sub>, FeBr<sub>3</sub>, 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride ([DIPrim]Cl), 1,3-bis(2,6-diisopropylphenyl)imidazolium bromide ([DIPrim]Br), 1,3-ditertbutylimidazolium chloride ([D<sup>t</sup>Buim]Cl), 1,3-diisopropylimidazolium chloride ([D<sup>i</sup>Prim]Cl), 1,3-dibenzylimidazolium chloride (DBnim]Cl) and 1,3-dibenzylimidazolium bromide ([DBnim]Br) are hydrophilic, all manipulations were carried out under an atmosphere of dry argon with rigorous exclusion of air and moisture using standard Schlenk techniques.

### 1.1 Materials

All organic solvents were freshly distilled from Na/benzophenone ketyl under pure argon prior to use. Anhydrous FeCl<sub>3</sub>, FeBr<sub>3</sub> and organic reagents used for cross-coupling reactions were bought from Acros Organics, Aldrich, and Alfa Aesar. 4-Methylphenylmagnesium bromide was diluted prior to use. ([DIPrim]Cl) [26], ([DIPrim]Br) [26], ([D<sup>t</sup>Buim]Cl) [27], ([D<sup>i</sup>Prim]Cl) [28], (DBnim]Cl) [28], ([DBnim]Br) [28] and [DIPrim][FeCl<sub>4</sub>] (**1**) [24] was prepared by established methods.

### 1.2 Synthesis

(i) Synthesis of [DIPrim][FeBr<sub>4</sub>] (**2**). A Schlenk flask was charged with [DIPrim]Br (1.50 g, 3.20 mmol), THF (20 mL) and a stirring bar. To this suspension, FeBr<sub>3</sub> (0.95 g, 3.20 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 orange-red crystals (2.28 g, 93%), mp: 139.50°C. Anal. calcd. for C<sub>27</sub>H<sub>37</sub>N<sub>2</sub>FeBr<sub>4</sub>: C, 42.39; H, 4.87; N, 3.66. Found: C, 42.26; H, 4.54; N, 3.68. MS (ESI+): *m/z* 389.2944 [C<sub>27</sub>H<sub>37</sub>N<sub>2</sub>]<sup>+</sup> (100%). Raman: 203.463 cm<sup>-1</sup> ([FeBr<sub>4</sub>]<sup>-</sup>).

(ii) Synthesis of [D<sup>t</sup>Buim][FeCl<sub>4</sub>] (**3**). By the procedure analogous to that described for **2**, the product [D<sup>t</sup>Buim][FeCl<sub>4</sub>] was precipitated as yellow solids in 95% yield (1.63 g). mp: 82.07°C. Anal. calcd. for C<sub>11</sub>H<sub>21</sub>N<sub>2</sub>FeCl<sub>4</sub>: C, 34.86; H, 5.59; N, 7.39. Found: C, 34.72; H, 5.98; N, 7.30. MS (ESI+): *m/z* 181.1704 [C<sub>11</sub>H<sub>21</sub>N<sub>2</sub>]<sup>+</sup> (100%). Raman: 335.956 cm<sup>-1</sup> ([FeCl<sub>4</sub>]<sup>-</sup>).

(iii) Synthesis of [D<sup>i</sup>Prim][FeCl<sub>4</sub>] (**4**). By the procedure analogous to that described for **2**, the product [D<sup>i</sup>Prim][FeCl<sub>4</sub>] was precipitated as yellow-brown solids in 91% yield (0.85 g), mp: 74.10°C. Anal. calcd. for C<sub>9</sub>H<sub>17</sub>Cl<sub>4</sub>N<sub>2</sub>Fe: C, 30.81; H, 4.88; N, 7.98. Found: C, 30.42; H, 4.78; N, 7.74. MS (ESI+): *m/z* 153.1389 [C<sub>9</sub>H<sub>17</sub>N<sub>2</sub>]<sup>+</sup> (100%). Raman: 335.956 cm<sup>-1</sup> ([FeCl<sub>4</sub>]<sup>-</sup>).

(iv) Synthesis of [DBnim][FeCl<sub>4</sub>] (**5**). By the procedure analogous to that described for **2**, the product [DBnim][FeCl<sub>4</sub>] was precipitated as yellow-brown oil in 83% yield (1.07 g). Anal. Calcd. for C<sub>17</sub>H<sub>17</sub>Cl<sub>4</sub>N<sub>2</sub>Fe: C, 45.68; H, 3.83; N, 6.27. Found: C, 44.28; H, 4.00; N, 6.20. MS (ESI+): *m/z* 249.1386 [C<sub>17</sub>H<sub>17</sub>N<sub>2</sub>]<sup>+</sup> (100%). Raman: 333.096 cm<sup>-1</sup> ([FeCl<sub>4</sub>]<sup>-</sup>).

(v) Synthesis of [DBnim][FeBr<sub>4</sub>] (**6**). By the procedure analogous to that described for **2**, the product [DBnim][FeBr<sub>4</sub>] was precipitated as black-red oil in 88% yield (1.91 g). Anal. calcd. for C<sub>17</sub>H<sub>17</sub>Br<sub>4</sub>N<sub>2</sub>Fe: C, 32.68; H, 2.74; N, 4.48. Found: C, 32.49; H, 2.62; N, 4.31. MS (ESI+): *m/z* 249.1390 [C<sub>17</sub>H<sub>17</sub>N<sub>2</sub>]<sup>+</sup> (100%). Raman: 203.463 cm<sup>-1</sup> ([FeBr<sub>4</sub>]<sup>-</sup>).

(vi) Typical cross-coupling procedure. A Schlenk tube was charged with iron(III)-based catalyst (0.01 mmol), alkyl

bromide (1.00 mmol), *n*-hexadecane (0.10 mmol) as internal standard, 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 changed color to black and was then stirred for 20 min at 30°C. After the reaction was quenched by adding dilute hydrochloric acid (1.0 mol/L, 0.5 mL), the mixture was extracted with diethyl ether (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 instrument. The Raman spectra were recorded on a LabRAM HR800 spectrometer. Electrospray Ionization-Mass spectrum (ESI-MS) data were recorded on a 6220 Accurate-Mass TOF LC/MS instrument. Gas chromatographic (GC) analysis was performed on a Varian CP-3800 instrument equipped with a flame ionization detector and a OV-101 capillary column (30 m × 0.32 mm i.d., 0.10 μm film). The oven temperature was held at 80°C for 2 min, increased to 280°C at 10°C/min, and held for 2 min. The melt points were determined on a Diamond DSC (Perkin Elmer) using powder samples under N<sub>2</sub> atmosphere (50 mL/min). The system was heated from 50 to 250°C at 20°C/min.

### 1.4 X-ray structural determination

Suitable crystals of complexes **1** and **2** were each sealed in a thin-walled glass capillary for single-crystal X-ray structural analysis. Diffraction data were collected on a Rigaku Mercury CCD area detector at 223(2) K. The structure was solved by direct methods and refined by full-matrix least-squares procedures based on *F*<sup>2</sup>. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions. The structures were solved and refined using SHELXL-97 and SHELXL-97 programs, respectively. Crystal data and collection and main refinement parameters are given in Table 1.

## 2 Results and discussion

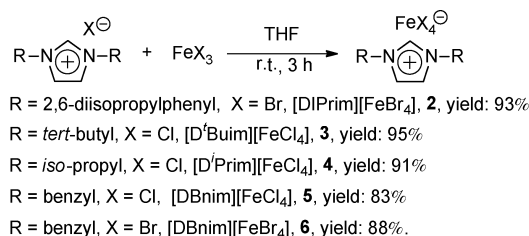
### 2.1 Synthesis and characterization of 2–6

The target imidazolium salt of iron(III) [DIPrim][FeCl<sub>4</sub>] (**1**) was easily synthesized according to a published procedure [24]. As shown in Scheme 1, similar reactions with other imidazolium halides provide the corresponding iron(III)-containing imidazolium salts **2–6** in nearly quantitative yields.

Although anhydrous FeCl<sub>3</sub>, FeBr<sub>3</sub> and the imidazolium halides are hydrophilic, the target iron(III)-containing

**Table 1** X-ray crystallographic data for **1** and **2**

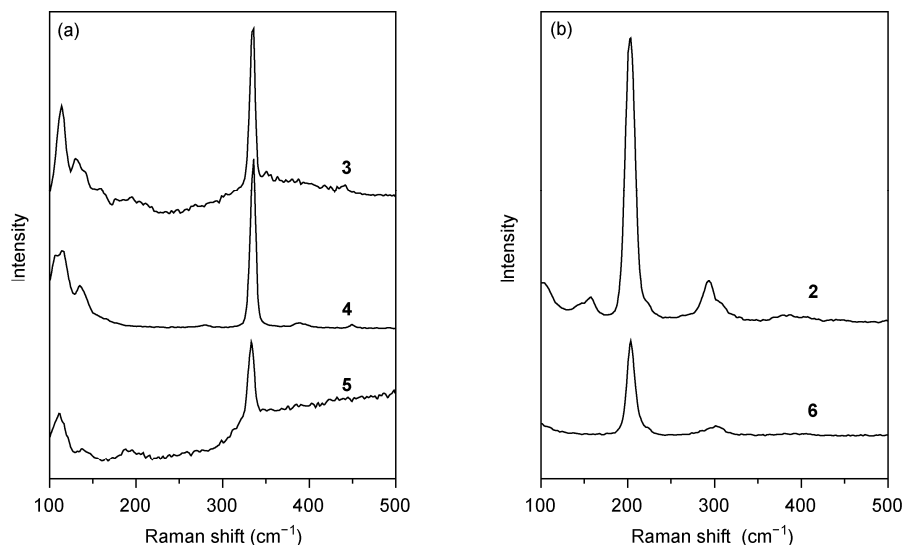
	<b>1</b> · C <sub>4</sub> H <sub>8</sub> O	<b>2</b> · C <sub>4</sub> H <sub>8</sub> O
Empirical formula	C <sub>31</sub> H <sub>45</sub> Cl <sub>4</sub> FeN <sub>2</sub> O	C <sub>31</sub> H <sub>45</sub> Br <sub>4</sub> FeN <sub>2</sub> O
Formula weight	659.34	837.18
Temperature (K)	223(2)	223(2)
λ(Mo Kα) (Å)	0.71075	0.71075
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
<i>a</i> (Å)	10.010(2)	10.084(1)
<i>b</i> (Å)	12.716(3)	12.782(2)
<i>c</i> (Å)	14.348(3)	14.770(2)
α (°)	82.947(7)	81.951(9)
β (°)	82.249(8)	81.120(9)
γ (°)	78.986(8)	77.836(8)
<i>V</i> (Å <sup>3</sup> )	1767.5(7)	1827.3(4)
<i>Z</i>	2	2
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.239	1.522
Absorption coefficient (mm <sup>-1</sup> )	0.753	4.810
<i>F</i> (000)	694	838
Crystal size	0.40 mm × 0.20 mm × 0.20 mm	0.50 mm × 0.40 mm × 0.10 mm
θ range (°)	3.17–25.50	3.09–27.50
No. of reflns collected	12741	17717
No. of reflns unique, <i>R</i> <sub>int</sub>	6449, 0.0518	8223, 0.0589
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.069	0.936
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0698, 0.1495	0.0567, 0.1265
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.1101, 0.1718	0.1335, 0.1562



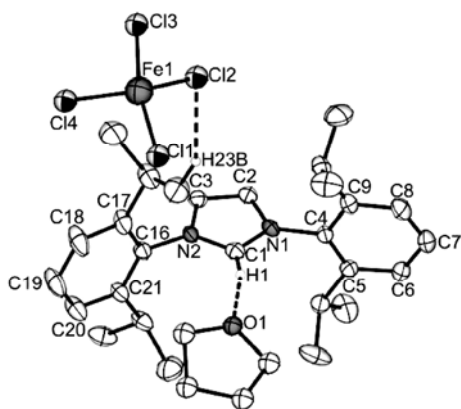
**Scheme 1** Synthesis of iron(III)-containing imidazolium salts **2–6**.

imidazolium salts **1–6** are non-hygroscopic and air-stable, and four of them (**1–4**) existed as solids at room temperature, making them easier to handle. Better solubility profiles were observed for **1–6** than in the corresponding imidazolium salts, and all of them dissolved easily in THF. The difference in solubility between the imidazolium halide and the corresponding iron(III)-containing imidazolium salt facilitated the effective purification of the target product.

The formation of ionic iron(III) complexes **1–6** was supported by elemental analysis, Raman spectroscopy, electrospray ionization mass spectroscopy (ESI-MS) and X-ray crystallography for complexes **1** and **2**. The Raman spectra of **1–6** confirmed the existence of [FeX<sub>4</sub>]<sup>−</sup> anions in them. As seen from Figures 1 and 2, a predominant feature of the spectra of **3–5** was one strong peak at the range of 333–336 cm<sup>−1</sup>, whereas the spectra of **2** and **6** showed only one



**Figure 1** Raman spectra of 3–5 (a) and 2 and 6 (b).



**Figure 2** Molecular structure of 1·C<sub>4</sub>H<sub>8</sub>O showing hydrogen bonds with thermal ellipsoids at the 30% probability level. Hydrogen atoms (except the hydrogen bonded hydrogen atoms) have been omitted for clarity.

strong peak at *ca.* 203 cm<sup>-1</sup>. These data coincided very closely to the literature values for the [FeCl<sub>4</sub>]<sup>-</sup> [29] and [FeBr<sub>4</sub>]<sup>-</sup> [30] species, respectively. The positive ion ESI-MS spectra of 2–6 were used to establish the presence of the imidazolium cations, and in all cases a peak with an intensity of almost 100% indicative of the parent cations was observed. Thus, these characteristic results confirmed that complexes 2–6 consisted of [DRim][FeX<sub>4</sub>] (X = Cl and Br). The <sup>1</sup>H NMR spectra of them, however, were less informative because they exhibit broad, shifted peaks with paramagnetism.

## 2.2 Crystal structures of 1 and 2

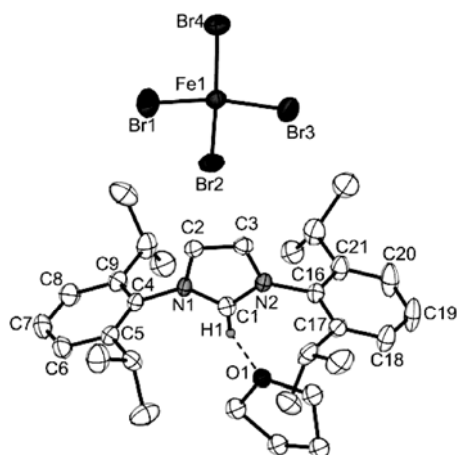
Single crystals of 1 and 2 suitable for an X-ray crystal structure determination were obtained from THF at -10°C. The selected bond lengths and angles are listed in Table 2. Their molecular structures are depicted in Figures 2 and 3,

**Table 2** Selected bond lengths (Å) and angles (°) for 1 and 2

	1·C <sub>4</sub> H <sub>8</sub> O	2·C <sub>4</sub> H <sub>8</sub> O	
Fe(1)–Cl(1)	2.186(2)	Fe(1)–Br(1)	2.331(1)
Fe(1)–Cl(2)	2.193(2)	Fe(1)–Br(2)	2.329(1)
Fe(1)–Cl(3)	2.185(2)	Fe(1)–Br(3)	2.335(1)
Fe(1)–Cl(4)	2.184(2)	Fe(1)–Br(4)	2.326(1)
Cl(4)–Fe(1)–Cl(3)	109.11(6)	Br(4)–Fe(1)–Br(3)	111.01(4)
Cl(4)–Fe(1)–Cl(1)	110.16(7)	Br(4)–Fe(1)–Br(1)	110.48(5)
Cl(3)–Fe(1)–Cl(1)	108.58(6)	Br(3)–Fe(1)–Br(1)	109.44(4)
Cl(4)–Fe(1)–Cl(2)	109.98(7)	Br(4)–Fe(1)–Br(2)	108.09(4)
Cl(3)–Fe(1)–Cl(2)	108.06(6)	Br(3)–Fe(1)–Br(2)	108.30(4)
Cl(1)–Fe(1)–Cl(2)	110.90(6)	Br(1)–Fe(1)–Br(2)	109.48(4)
Dihedral angle between benzene ring and the imidazolium ring			
Plane			
N1C1N2/IPr(1)	86.6(1)	C1N1C2/IPr(1)	87.7(2)
N1C1N2/IPr(2)	87.7(2)	C1N2C3/IPr(2)	87.4(2)
IPr(1)/IPr(2)	37.4(1)	IPr(1)/IPr(2)	37.9(2)
Hydrogen bonds			
C(1)–H(1)···O(1)	2.13	C(1)–H(1)···O(1)	2.16
C(3)–H(3)···Cl(2)	2.90		
C(1)–H(1)–O(1)	164.9(3)	C(1)–H(1)–O(1)	158.7(4)
C(3)–H(3)–Cl(2)	145.0(4)		

respectively.

As shown in Figures 2 and 3, each of the two molecular structures contains one imidazolium [DIPrim]<sup>+</sup> cation, one [FeX<sub>4</sub>]<sup>-</sup> anion, and one additional THF molecule. In 1 and 2, the bond distances and angles within the imidazolium ring and side chain were almost same in values, accompanied by the similar orientation of the IPr chain. Each plane of the phenyl ring in 1 and 2 was oriented nearly perpendicular to the plane of imidazolium ring with the dihedral angles equal to 86.6(1)° and 87.7(2)° for 1, and 87.7(2)° and



**Figure 3** Molecular structure of  $2 \cdot C_4H_8O$  showing hydrogen bonds with thermal ellipsoids at the 30% probability level. Hydrogen atoms (except the hydrogen bonded hydrogen atoms) have been omitted for clarity.

$87.4(2)^\circ$  for **2**, meanwhile they arranged themselves with a dihedral angle of  $37.4(1)^\circ$  in **1** and of  $37.9(2)^\circ$  in **2**.

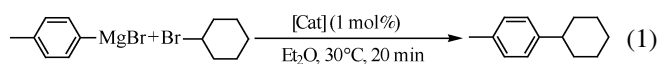
The  $[FeCl_4]^-$  anion in **1** formed a slightly distorted tetrahedron geometry around the iron center with the four Fe–Cl bond distances lying in a range of 2.184(2)–2.193(2) Å, which were in agreement with values found in other iron(III)-containing imidazolium salts [22,23]. The Cl–Fe–Cl angles of  $[FeCl_4]^-$  were between  $108.06(6)^\circ$  and  $110.90(6)^\circ$  with a mean value of  $109.47^\circ$ , which was close to the ideal tetrahedral angle at  $-50^\circ C$  [22]. Similarly, the  $[FeBr_4]^-$  anion in **2** also had a slightly distorted tetrahedral geometry, because the six Br–Fe–Br angles ranging from  $108.09(4)^\circ$  to  $111.01(4)^\circ$  were slightly different from each other, although each of the four Fe–Br bond lengths was almost the same (2.326(1)–2.335(1) Å). These values were in the expected range as found for other complexes containing  $[FeBr_4]^-$  anions [31].

Hydrogen bonding is very important for MetILs, especially the hydrogen bonding interaction between the imidazolium cation and halide anion is well established [21–23]. However, in **1** only one typical hydrogen bond of 2.90 Å are

formed between the chlorine atom of  $[FeCl_4]^-$  anion and the hydrogen atom of the isopropyl group in the imidazolium cation, whereas none of the cation-anion interatomic distances found in **2** fell within the generally accepted range for typical hydrogen bonding interactions [32]. Of note, the more acidic hydrogen atom at the 2-position of the imidazolium ring was not involved in the hydrogen bonding network between the imidazolium cation and  $[FeX_4]^-$  anion. Thus, both **1** and **2** can be described as a simple collection of ion pairs, which is somewhat different from those found either in  $[C_2mim][FeCl_4]$  [22] or in  $[(C_4H_9)_2bim][FeCl_4]$  [23]. The unique patterns in them, especially in **2**, are mostly attributed to the steric bulkiness of the aryl-substituted imidazolium cation [25].

### 2.3 Catalysis of 1–6

The reactivity of **1–6** was tested in the Kumada-Corriu reaction to disclose any effect due to the structural variation of an iron(III)-containing imidazolium salt on catalysis. The reaction outlined in Equation 1 was chosen as a model system, as it represents a prototype cross-coupling of aryl Grignard reagents with alkyl halides bearing  $\beta$ -hydrogens [4,6,7,24]. The results obtained are summarized in Table 3.



It is clear that all of iron(III)-containing imidazolium salts **1–6** provided good to excellent yields of the desired coupling product using cyclohexyl bromide as a starting reagent, whereas  $FeCl_3$  alone afforded the product in a significantly low yield (Table 3, entry 2). The mixture of  $FeCl_3$  and [DIPrim]Cl in a 1:1 molar ratio exhibited moderate activity and provided the coupling product in 62% yield (Table 3, entry 3). As can be seen from Table 3, **1** and **3** exhibit the highest catalytic activity for the cross-coupling of 4-tolylmagnesiumbromide with cyclohexyl bromide, providing almost quantitative yields of the desired coupling products (Table 3, entries 4 and 7). Under the same conditions, a considerably lower activity was seen when **4** or **5** was

**Table 3** Activities of catalytic systems based on iron(III) complexes<sup>a)</sup>

Entry	Catalyst	Yield <sup>b)</sup>	Entry	Catalyst	Yield <sup>b)</sup>
1	[DIPrim]Cl	3	7	[D <sup>1</sup> Buim][FeCl <sub>4</sub> ] ( <b>3</b> )	98
2	$FeCl_3$	14	8	[D <sup>1</sup> Prim][FeCl <sub>4</sub> ] ( <b>4</b> )	76
3	$FeCl_3$ + [DIPrim]Cl	62	9	[DBnim][FeCl <sub>4</sub> ] ( <b>5</b> )	75
4	[DIPrim][FeCl <sub>4</sub> ] ( <b>1</b> )	97	10	[DBnim][FeBr <sub>4</sub> ] ( <b>6</b> )	67
5	[DIPrim][FeBr <sub>4</sub> ] ( <b>2</b> )	88	11 <sup>d)</sup>	[bmim][FeCl <sub>4</sub> ]	89
6 <sup>c)</sup>	[DIPrim][FeBr <sub>3</sub> ]·C <sub>4</sub> H <sub>8</sub> O	74	12 <sup>e)</sup>	[Fe(IPr)Br <sub>3</sub> ](HIPr) <sub>3</sub> ·C <sub>7</sub> H <sub>8</sub>	96

a) Iron(III)-containing catalyst (1.0 mol%), cyclohexyl bromide (1.0 mmol), 4-MeC<sub>6</sub>H<sub>4</sub>MgBr (1.5 mmol), 4-MeC<sub>6</sub>H<sub>4</sub>MgBr was added in one portion at 30°C, 20 min, Et<sub>2</sub>O, total volume (2.5 mL), Ar. b) GC yield using *n*-hexadecane. c) [DIPrim][FeBr<sub>3</sub>]·C<sub>4</sub>H<sub>8</sub>O (3.0 mol %), 4-MeC<sub>6</sub>H<sub>4</sub>MgBr was added in one portion at 0°C, the reaction solution was stirred for 2 min and then refluxed for 30 min, ref [25]. d) [bmim][FeCl<sub>4</sub>] (5 mol %), 10 min, 0°C, ref [12]. e) [Fe(IPr)Br<sub>3</sub>](HIPr)<sub>3</sub>·C<sub>7</sub>H<sub>8</sub> (1.0 mol%), 4-MeC<sub>6</sub>H<sub>4</sub>MgBr was added in one portion at 0°C, the reaction solution was stirred for 2 min and then refluxed for 30 min, ref [25].

employed (Table 3, entries 8 and 9). The differences in activity among **1**, **3–5** and [bmim][FeCl<sub>4</sub>] (Table 3, entry 11) [12] suggest that a more steric bulkiness provided by the *N*-substituents should be of benefit to their higher catalytic activity, which can facilitate the reductive elimination to form the desired cross-coupling product together with impose a positive effect to suppress  $\beta$ -H elimination [33]. Replacement of the anion from [FeCl<sub>4</sub>]<sup>-</sup> to [FeBr<sub>4</sub>]<sup>-</sup> was also detrimental to performance, with **2** and **6** providing lower yields than those obtained with **1** and **5** (Table 3, entries 6 and 10), respectively. Notably, the present Fe(III)-based complex, i.e. **2**, showed better performance than the Fe(II) counterpart [DIPrim][FeBr<sub>3</sub>]·C<sub>4</sub>H<sub>8</sub>O reported previously (Table 3, entries 5 and 6) [25]. This is the same pattern as that previously reported with FeCl<sub>3</sub>/phosphine and FeCl<sub>2</sub>/phosphine systems [33]. However, the catalytic activity of **2** is somewhat lower than the Fe(II) counterpart containing a *N*-heterocyclic carbene ligand (Table 3, entries 5 and 12) [25].

It is worthy of note that the present cross-coupling reaction could be performed successfully at the mild temperature of 30°C, and that the Grignard reagent could be added in a single portion at room temperature without the requirement for slow addition via a syringe pump. Furthermore, the catalytic activity of **1** or **3** was compared with other related iron(III)-based catalysts reported in the literature. Normally, 2 mol%–5 mol% or higher loadings of the iron complexes were usually required to achieve satisfactory yields for reactions similar to those shown in Equation 1 [2–12,33]. Therefore, the present results suggest that **1** and **3** might be among the most efficient precatalysts for the cross-coupling reaction of aryl Grignard reagents with alkyl halides bearing  $\beta$ -hydrogens.

### 3 Conclusions

A family of easily synthesized and easy-to-handle iron(III)-containing imidazolium salts [DRim][FeX]<sub>4</sub> have been developed as excellent catalysts for the cross-coupling of aryl Grignard reagents with alkyl halides bearing  $\beta$ -hydrogens under mild conditions. Our studies demonstrate that the modification of imidazole ring with different *N*-substituents represents a promising pathway to improve the catalytic activity of iron(III)-containing imidazolium salts. The detailed structure-reactivity relationship study of iron(III)-containing imidazolium salts as well as the scope of these iron(III)-based catalysts in other reactions are currently under investigation in our laboratory.

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