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Introduction

Over the past decade, significant efforts have been made to develop iron-based catalysts as an alternative or complementary catalyst to traditional palladium- or nickel-based catalysts that can be used in various cross-coupling reactions. In comparison with established palladium- or nickel-based systems, iron-based catalysts offer distinct advantages of being low cost, environmentally benign, with a lack of toxicity and having unique reactivity, which provides a "greener" strategy for organic synthesis.¹

Following the original work of Kochi *et al.*,^{2*a*} recent reports on the alkylation of aryl Grignard reagents using unactivated primary or secondary alkyl halides show the potential of ironbased catalysts, whereas palladium- or nickel-based catalysts do not perform as well because of competing β -hydride elimination reactions.^{2*b*-*e*} To date, a variety of iron-based catalysts have been designed and proven active for such cross-coupling. For example, while simple iron salts such as FeCl₃,^{2*b*,3,4*a*}

Efficient cross-coupling of aryl Grignard reagents with alkyl halides by recyclable ionic iron(III) complexes bearing a bis(phenol)-functionalized benzimidazolium cation†

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A novel bis(phenol)-functionalized benzimidazolium salt, 1,3-bis(3,5-di-*tert*-butyl-2-hydroxybenzyl)benzimidazolium chloride (H₃LCl, **1**), was designed and used to prepare ionic iron(III) complexes of the type [H₃L][FeX₄] (X = Cl, **2**; X = Br, **3**). Both **2** and **3** were characterized by elemental analysis, Raman spectroscopy, electrospray ionization mass spectrometry and X-ray crystallography. The catalytic performances of **2** and **3** in cross-coupling reactions using aryl Grignard reagents with primary and secondary alkyl halides bearing β -hydrogens were studied. This analysis shows that complex **2** has good potential for alkyl chloride-mediated coupling. In comparison, complex **3** showed slightly lower catalytic activity. After decanting the product contained in the ethereal layer, complex **2** could be recycled at least eight times without significant loss of catalytic activity.

> $FeCl_2 \cdot 2LiCl^5$ and $Fe(acac)_3$ (acac = acetylacetonate)^{2d,4} can be used effectively in the presence of appropriate additives, structurally well-defined low-valency $iron(\pi)$ complexes^{2c,6} and $\operatorname{iron}(II)^{7-11}$ or $\operatorname{iron}(III)^{2e,4a,12-15}$ complexes have also been successfully developed as single component catalysts. From most reports, alkyl bromides and iodides are the intensively used electrophilic coupling partners. However, less reactive, yet less expensive and readily available alkyl chlorides, particularly unactivated alkyl chlorides, remain challenging substrates. Only a few examples of alkyl chloride-mediated coupling are known so far. FeCl₃/stoichiometric TMEDA (TMEDA = N, N, N', N'-tetramethylethylenediamine)^{2b} and FeCl₃/[DIPrim]Cl-([DIPrim]Cl = 1,3-bis(2,6-diisopropylphenyl)imidazolium chlor- $(de)^{3e}$ have been used for coupling of alkyl chlorides, with FeCl₂ alone or with iron(II) bisphosphine complexes¹¹ and iron(III) amine-bis(phenolate) complexes^{12b,e,f} either for benzylic chlorides^{11,12b,f} or for the double C-Cl activation in CH₂Cl₂ with aryl Grignard reagents.^{12e} The latter cross-coupling reaction can also be catalyzed by iron(III) pyridine-bis(carboxamide) complexes.¹⁴ To achieve a high yield of the desired cross-coupling product, the aryl Grignard reagent is usually added slowly via a syringe pump^{2b,3e,11,12e} or added dropwise,^{12b,f} with 5 mol% or higher loadings of iron-based catalysts that is necessary for the above reactions. Moreover, the direct use of FeCl₃ is inconvenient for large-scale applications as it is highly hygroscopic and the yields of targeted products vary according to the purity and commercial source of FeCl₃.¹⁶ Therefore, an alternative easy-to-

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use, highly efficient and well-defined iron-based catalyst is desirable to address this challenge.

The imidazolium cations and their derivatives have received increasing attention as alternatives to traditional ligands and/ or ionic tags of traditional ligands for the development of transition metal-based catalysts.¹⁷ Recent papers have documented such tailored ionic catalysts for providing many advantages such as low toxicity, good stability, high activity and reusability, which make them promising candidates for optimizing synthetic efficiency and ensuring green processes.^{17a} In this context, an easily prepared ionic iron(III) complex, [BMim]-[FeCl₄] (BMim = 1-butyl-3-methylimidazolium cation), was established by Gaertner to couple aryl Grignard reagents with alkyl halides.¹⁵ Imidazolium salt can modify the highly hygroscopic FeCl₃ into a non-hygroscopic and reusable catalyst. Recently, we reported the synthesis of several well-defined ionic iron(II) complexes, which contained either N-hydrocarbylsubstituted imidazolium cations^{18a-b,d} or bis(phenol)-functionalized imidazolium cations.^{18c} They can be used as highly active and/or recyclable catalysts for the alkylation of aryl Grignard reagents with unactivated alkyl bromides. Comparison of these ionic iron(III) complexes indicates that the bulky N-substituent has been incorporated, particularly the bulky phenolic groups on the imidazolium ring (i.e. H₃L'Cl, Scheme 1), which is beneficial to their catalytic activity and reusability.

Compared to imidazole framework, we envision that the ligand H_3LCl (Scheme 1) that contained a benzimidazole skeleton might be an alternative candidate to generate more reactive, robust and recyclable catalysts. In this paper, we describe the synthesis of novel bis(phenol)-functionalized benzimidazolium salt H_3LCl (1) and its derived ionic iron(m) complexes $[H_3L][FeX_4]$ (X = Cl, 2; X = Br, 3). We also report preliminary results of the catalysis of 2 and 3 in the cross-coupling of aryl Grignard reagents with alky halides, particularly with unactivated primary and secondary chlorides. The incorporation of the anionic aryoxide group on both nitrogen atoms is a novel modification of the benzimidazole framework.¹⁹ The

benzimidazole skeleton is found in a variety of palladium- and nickel-based catalytic systems developed for cross-coupling reactions. These allow for superior or at least match catalytic activities of these systems compared with imidazole framework derived systems.²⁰ However, its potential utility in iron-based catalytic systems remains poorly explored.^{1k,21}

Results and discussion

Synthesis and characterization of ionic iron(III) complexes

Inexpensive, readily available benzimidazole can be easily modified through its nitrogen atoms by stepwise alkylation with 2-chloromethyl-4,6-di-*tert*-butylphenol. This process is similar to the published procedure used for its imidazole-derived analogues.^{18c,22}

As shown in Scheme 2, the reaction of benzimidazole with a slightly excess of 2-chloromethylphenol in refluxing THF under basic conditions produces the intermediate, *N*-(3,5-di*tert*-butyl-2-hydroxybenzyl)benzimidazole, which was then treated with 1 equiv. of 2-chloromethylphenol in refluxing THF to produce new benzimidazolium chloride H₃LCl [H₃LCl = 1,3bis(3,5-di-*tert*-butyl-2-hydroxybenzyl)benzimidazolium chloride, 1] as a non-hygroscopic white power. The overall yield for this reaction sequence is 86%. The elemental analysis and NMR spectra of 1 are consistent with its formula. The ¹H NMR singlet signal for the benzimidazolium proton in 1 appeared at 9.34 ppm (DMSO-*d*₆), which agrees with the literature values for 1,3-disubstituted benzimidazolium salts.²³

Salt 1 reacted rapidly with 1 equiv. of anhydrous FeCl₃ in THF at room temperature (Scheme 3). Although salt 1 is insoluble in THF, the mixture quickly changed from a suspended state to a yellowish transparent liquid when FeCl₃ was added to a THF suspension of 1. After this workup, the target ionic iron(Π) complex $[H_3L]$ [FeCl₄] (2) was obtained as yellow-green crystals with an 82% yield. In addition, even when more or less than 1 equiv. of anhydrous FeCl₃ was added, only the desired complex 2 was obtained. Notably, the [FeCl₄]⁻ anion exchanged smoothly with the [FeBr₄]⁻ anion with the addition of sodium bromide (NaBr). As shown in Scheme 3, the reaction of 1 with FeBr3 and NaBr in a 1:1:3 molar ratio in THF afforded the analogous bromide 3 in the form of brown-red crystals with an 85% yield. However, extended reaction times and elevated temperatures were required to push the reaction to completion, mostly because of the poor solubility of NaBr in THF.



Scheme 2 Synthesis of bis(phenol)-functionalized benzimidazolium chloride 1.



Scheme 3 Synthesis of ionic iron(III) complexes 2 and 3.

Although FeCl₃ and FeBr₃ are highly hygroscopic, both 2 and 3 exist as non-hygroscopic and air-stable solids at room temperature, which makes them easier to handle. Better solubility profiles were observed for complexes 2 and 3 than in the corresponding benzimidazolium salts 1, and both 2 and 3 can readily dissolve in THF. In contrast, the salt 1 is insoluble in THF. The difference in solubility between the ionic iron(m) complex and the corresponding bis(phenol)-functionalized benzimidazolium salt allows for easy purification of the target product.

Initial characterizations of 2 and 3 are supported by elemental analysis, Raman spectroscopy and electrospray ionization mass spectroscopy (ESI-MS). The metal-containing anion exists as a discrete $[FeX_4]^-$ species, which is evident in the Raman spectrum. For example, the Raman spectrum of 2 shows a very strong peak at *ca.* 333 cm^{-1} , while a similar peak is present at $ca. 200 \text{ cm}^{-1}$ in the spectrum of 3. These data coincide closely with literature values for the $[FeCl_4]^-$ and [FeBr₄]⁻ species.²⁴ The presence of the bis(phenol)-functionalized benzimidazolium cation can be identified by the positive ion ESI-MS spectra of 2 and 3. In both cases, a peak with an intensity of almost 100% indicated that the parent cation is present. These characteristic results suggest that both 2 and 3 contain [FeX₄]⁻ anions and benzimidazolium cation. However, the ¹H NMR spectra of the complexes were less informative as they exhibited broad peaks shifted with paramagnetism.

The formations of complexes 2 and 3 were further confirmed by X-ray crystallography. Crystals suitable for X-ray diffraction studies were grown from cold THF-hexane solutions of 2 and 3. The crystallographic data are listed in Table 1. Their molecular structures are depicted in Fig. 1 and 2, with key bond parameters given in the captions.

During the past decade, the development of ionic iron(m) complexes based on the imidazolium moiety (including closely related other azolium) has received increasing attention with a wide range of applications, such as organic catalysis²⁵ and magnetic materials.²⁶ However, reports on their crystal structures are relatively rare,^{18d,27} and only one paper providing structural data for a 1,3-dibutylbenzimidazolium-based ionic iron(m) complex has been noted.^{27c}

As shown in Fig. 1 and 2, each of the molecular structure contains one bis(phenol)-functionalized benzimidazolium $[H_3L]^+$ cation and one $[FeX_4]^-$ anion. The bond lengths and angles within the benzimidazolium ring and the benzyl group in 2 are very close to the values found for 3. These parameters are comparable to those of other benzimidazolium salts.^{19,23} In both structures, the $[FeX_4]^-$ anion has a slightly distorted tetrahedral geometry with a mean X–Fe–X angle of 109.2° for 2

Table 1 X-ray crystallographic data for 2 and 3

	2	3
Formula	C ₃₇ H ₅₁ Cl ₄ FeN ₂ O ₂	C ₃₇ H ₅₁ Br ₄ FeN ₂ O ₂
Formula weight	753.45	931.29
Temperature/K	202(2)	223(2)
Radiation used	0.71073	0.71075
Crystal system	Monoclinic	Triclinic
Space group	P21/c	$P\bar{1}$
Unit cell dimensions		
a/Å	12.6980(6)	10.364(3)
b/Å	16.1029(9)	11.468(3)
c/Å	19.8555(9)	19.427(5)
$\alpha / ^{\circ}$	90	93.341(2)
$\beta/^{\circ}$	98.257(5)	99.459(6)
γ/°	90	115.939(6)
$V/Å^3$	4017.9(3)	2026.0(9)
Ζ	4	2
$D_{\rm c}/{\rm g}~{\rm cm}^{-3}$	1.246	1.527
μ/mm^{-1}	0.673	4.349
F(000)	1588	938
θ range/°	2.81-25.50	3.14 - 25.50
Reflection collected	24 045	16 475
Independent reflections, <i>R</i> _{int}	7454, 0.0396	7479, 0.0463
Goodness-of-fit on F^2	1.055	1.051
$R_1, WR_2 \left[I > 2\sigma(I) \right]$	0.0667, 0.1811	0.0743, 0.1964
R_1, WR_2 (all data)	0.0950, 0.1970	0.1221, 0.2254



Fig. 1 Molecular structure of **2** with thermal ellipsoids at the 30% probability level. Hydrogen atoms and *tert*-butyl groups have been omitted for clarity. Selected bond lengths (Å) and angles (°): Fe(1)–Cl(1) 2.246(13), Fe(1)–Cl(2) 2.330(12), Fe(1)–Cl(3) 2.225(15), Fe(1)–Cl(4) 2.179(1), Cl(1)–Fe(1)–Cl(2) 114.2(5), Cl(1)–Fe(1)–Cl(3) 108.1(7), Cl(1)–Fe(1)–Cl(4) 106.2(6), Cl(2)–Fe(1)–Cl(3) 120.7(8), Cl(2)–Fe(1)–Cl(4) 102.7(5), Cl(3)–Fe(1)–Cl(4) 103.2(9).

and 109.5° for 3, which is close to the ideal tetrahedral angle at -50 °C.^{27b} The bond lengths of the four Fe–Cl bonds or the four Fe–Br bonds agree with the values found in previously published papers on [FeX₄]⁻ anions.^{18c,d,27}

The hydrogen bonding interactions between the imidazolium cation and halide anion have been well established,²⁷ however, none of the hydrogens observed in **2** are in contact



Fig. 2 Molecular structure of **3** with thermal ellipsoids at the 30% probability level. Hydrogen atoms (except the hydrogen bonded hydrogen atoms) and *tert*-butyl groups have been omitted for clarity. Selected bond lengths (Å) and angles (°): Fe(1)–Br(1) 2.323(2), Fe(1)–Br(2) 2.327(2), Fe(1)–Br(3) 2.328(1), Fe(1)–Br(4) 2.351(2), Br(1)–Fe(1)–Br(2) 110.08(6), Br(1)–Fe(1)–Br(3) 111.24(5), Br(1)–Fe(1)–Br(4) 108.51(6), Br(2)–Fe(1)–Br(3) 110.14(6), Br(2)–Fe(1)–Br(4) 108.85(6), Br(3)–Fe(1)–Br(4) 107.95(6).

below 3 Å, which is the generally accepted range for typical hydrogen bonding interactions. Similar observations have been made for its imidazolium-based analogues.^{18c} The $[FeBr_4]^-$ anion of 3 is close to the three hydrogen atoms of hydroxyl groups belonging to the two different cations with distances between 2.59 and 2.91 Å. However, most acidic hydrogen atoms in the C2 position of the benzimidazolium ring are not involved in the typical hydrogen-bonding network.

Catalysis of ionic iron(m) complexes

Based on our previous work with related ionic iron(m) complexes of bis(phenol)-functionalized imidazolium cations,^{18c} we chose the reaction outlined in eqn (1) as a typical example of aryl Grignard cross-coupling of unactivated alkyl halides bearing β -hydrogen for initial catalytic investigations. Similar reaction conditions, *i.e.* using diethyl ether as a solvent, with one-portion addition of the Grignard reagent, 1 mol% loading of an iron(m) complex and 30 °C as reaction temperature, are employed to demonstrate any structural variation effects on catalysis. The results are summarized in Table 2.



Using cyclohexyl bromide as a starting reagent, the reaction catalyzed by 2 proceeded rapidly within 15 min, providing almost quantitative yield of the desired coupling product (Table 2, entry 3). The yield still reached 93% even for 2 when its loading was reduced to 0.5 mol%, however, an extended

Table 2 Cross-coupling of 4-MeC_6H_4MgBr with C_6H_1X catalyzed by iron(iii)-based catalysts $^{\rm a}$

					Product yield (%)			
Entry	Catalyst	$T(^{\circ}C)$	t (min)	Х	A	В	С	D
1	FeCl ₃	30	15	Br	42	19	12	8
2	$FeCl_3 + 1$	30	15	Br	2	78	12	8
3	2	30	15	Br	0	$99(92^{b})$	1	0
4	2^c	30	45	Br	0	93	5	2
5	3	30	15	Br	0	85	10	5
6	$[H_3L'][FeCl_4]^d$	30	30	Br	0	$99(89^{b})$	1	0
7	$FeCl_3 + 1$	30	120	Cl	11	55	18	15
8	2	30	15	Cl	68	46	6	4
9	2	30	120	Cl	2	92	3	2
10	[H ₃ L'][FeCl ₄]	30	120	Cl	2	77^d	12	9
11^e	2	30	120	Cl	0	97	1	1
12^e	[H ₃ L'][FeCl ₄]	30	120	Cl	1	75	14	9
13^e	3	30	120	Cl	0	86	10	5
$14^{e,f}$	2	30	120	Cl	2	92	3	1
15^g	2	30	120	Cl	0	96	2	1
16^e	2	45^h	120	Cl	0	89	8	4
17^e	2	0	120	Cl	45	34	5	4

^{*a*} Conditions: iron(m) complex (1.0 mol%), cyclohexyl halide (1.0 mmol), 4-MeC₆H₄MgBr (1.2 mmol) was added in one portion, Et₂O (total volume: 2.5 mL), GC yield using *n*-hexadecane as an internal standard, average of 2 trials. ^{*b*} Isolated yield. ^{*c*} Iron(m) complex (0.5 mol%). ^{*d*} Ref. 18*c*. ^{*e*} 4-MeC₆H₄MgBr (1.5 mmol) was added in one portion. ^{*f*} In air. ^{*g*} 4-MeC₆H₄MgBr (1.5 mmol) was added dropwise. ^{*h*} External temperature 45 °C, reaction temperature 36–38 °C.

reaction time (45 min) was required to push the reaction to completion (Table 2, entry 4). The desired coupling product produced was compared with the analogous 3-catalyzed reaction, which afforded the same product with a lower yield of 85% along with cyclohexene and cyclohexane byproducts in yields of 10% and 5%, respectively (Table 2, entry 5). Under the same conditions, a mixture of FeCl₃ and salt 1 in a 1:1 molar ratio exhibited moderate activity, and the coupling product was produced with a 78% yield (Table 2, entry 2). In comparison, FeCl₃ alone afforded the product at a very low yield of 19% (Table 2, entry 1).

Interestingly, the catalytic activity of 2 was obviously higher than that reported for [H₃L'][FeCl₄] [H₃L' = 1,3-bis(3,5-di-tertbutyl-2-hydroxybenzyl)imidazolium cation].18c The latter complex provided the same yield of the desired product within 30 min (Table 2, entry 6). Using less reactive cyclohexyl chloride as the starting reagent, the same catalytic activity trends were observed. For example, the cross-coupling reaction of cyclohexyl chloride with 4-methylphenylmagnesium bromide gave a 92% yield of 4-methylbiphenyl with 1.0 mol% loading of 2 in 120 min (Table 2, entry 9). For [H₃L'][FeCl₄] the yield was reduced to 77% along with significant amounts of byproducts, i.e. 12% yield of cyclohexene and 9% yield of cyclohexane (Table 2, entry 10). Moreover, complex 2 could provide an almost quantitative yield of the cross-coupled product (*i.e.* 97%) when the molar ratio of 4-methylphenylmagnesium bromide with cyclohexyl chloride was increased from 1.2 to 1.5 (Table 2, entry 11), which is very close to the result obtained by FeCl₃/[DIPrim]Cl ([DIPrim]Cl = 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride).3e Nevertheless, this was in stark

contrast to the result obtained by $[H_3L']$ [FeCl₄], where still a 75% yield of the desired product was obtained (Table 2, entry 12). The difference in catalytic performance between 2 and $[H_3L']$ [FeCl₄] suggests that replacing imidazole framework with the benzimidazole skeleton is beneficial to the catalytic activity of the iron(III) complex, especially impose a positive effect to suppress β -H elimination, which might be related to the benzannulation effect of the benzimidazole skeleton.^{20a,28}

Notably, the present cross-coupling reaction could be performed smoothly without an inert atmosphere (Table 2, entry 14), and that the Grignard reagent could be added in one portion without the requirement for its slow addition because there was no difference between the addition of the Grignard reagent at one portion and the use of dropwise addition (Table 2, entry 15). By the way, the present cross-coupling reaction could be carried successfully at a mild temperature, *i.e.* 30 °C, further increasing the reaction temperature led to a slightly lower yield of 89% for the desired product accompanied by small amounts of byproducts, *i.e.* 8% yield of cyclohexene and 4% yield of cyclohexane (Table 2, entry 16). Meanwhile, decreasing the temperature to 0 °C significantly reduced the reaction rate but also reduced the side effects (Table 2, entry 17).

Catalyst recycling is important for industrial applications and environmentally friendly processing. Incorporating the imidazolium moiety into the catalyst structure is probably the most straightforward strategy to achieve recycling.^{17a} We previously found that the bis(phenol)-functionalized imidazolium-based ionic iron(III) complex, [H₃L'][FeCl₄], could be reused in seven successive runs of the model reaction (eqn (1), X = Br) without significant loss of catalytic activity.^{18c} To evaluate the influence of the cationic component of the ionic iron(III) in detail, the recyclability of 2 was examined in the same cross-coupling reaction with 5% loading of 2. Using the same protocol,^{15,18b-c} the upper ether layer containing the product was decanted after the reaction was complete, whereas the catalytic system was left as a black sediment, which was washed, dried and reused. The data listed in Table 3 indicate that the coupling reaction of 4-methylphenylmagnesium bromide and cyclohexyl bromide with 2 could be successfully performed at least eight times with almost complete conversion of cyclohexyl bromide. However, the GC yield of the desired product dropped slowly from 99% in the first run to 86% after the eighth run. This may be due to catalyst leaching during the decanting and extraction steps.^{15,18b-c,29} Comparisons with imidazolium-based complex [H3L'][FeCl4] suggest that replacing imidazole framework with the benzimidazole skeleton can also improve the reusability of the catalyst.

Encouraged by the results mentioned above, the scope of the cross-coupling reaction using a variety of unactivated alkyl chlorides was subsequently carried out with 1–2 mol% loading of **2** at 30 °C. As seen from Table 4, cyclohexyl chloride, a typical unactivated second alkyl chloride, was coupled with phenyl and *para*-substituted aryl Grignard reagents to give the desired products in 80–97% yield (Table 4, entries 1–5). Using the moderately sterically demanding 2-tolylmagnesium

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Table 3 Recycling of 2 in the cross-coupling of 4-MeC₆H₄MgBr with C₆H₁₁Br^a

Entry	Run	Conversion ^{b} (%)	Yield (%)
1	1	100	99
2	2	100	99
3	3	100	98
4	4	100	98
5	5	100	97
6	6	97	95
7	7	95	90
8 ^c	7	90	78
9	8	93	86
10 ^c	8	60	45
11	9	75	60

^{*a*} Reaction conditions: 2 (5.0 mol%), cyclohexyl bromide (1.0 mmol), 4-MeC₆H₄MgBr (1.2 mmol) was added in one portion, Et₂O (2.5 mL), 30 °C, 15 min, GC yield using *n*-hexadecane as an internal standard, average of 2 trials. ^{*b*} GC conversion of cyclohexyl bromide using *n*-hexadecane as an internal standard. ^{*c*} [H₃L'][FeCl₄] (5.0 mol%).

bromide as the starting reagent, the yield can be increased from 60% to 80% when the catalyst loading was increased from 1 mol% to 2 mol%. However, the bulky mesitylmagnesium bromide failed to give a product even with 2 mol% loading of 2. To the best of our knowledge, there have been no other reports describing the cross-coupling of such sterically hindered aryl Grignard reagents.³

Changing the cyclic chloride to cyclopentyl chloride as well as to cycloheptyl chloride the reaction proceeded also smoothly, although with lower yields of 78% and 82%, respectively. Fortunately, improved yields of 90% and 93% were obtained with both cyclopentyl chloride and cycloheptyl chloride when the catalyst loading was increased from 1 mol% to 2 mol%, respectively (Table 4, entries 8 and 9). 2 mol% of complex 2 was also an effective catalyst for the cross-coupling of typically acyclic primary and secondary chlorides, resulting in desired products with yields in the range of 40% to 85% (Table 4, entries 10-14). Interestingly, a competitive crosscoupling of 1-bromo-3-chloropropane lead to a selective attack at the bromide site, affording 1-(3-chloropropyl)-2-methylbenzene in 45% yield (Table 4, entry 15), similar to the result obtained by an iron(III) amine-bis(phenolate) complex.^{12b} However, benzyl chloride showed very poor cross-coupling activity, and provided significant amounts of homo-coupling products and dehalogenated products (Table 4, entries 16 and 17). Tertiary alkyl chloride was attempted, but no desired product was obtained, even if the chloride was consumed smoothly (Table 4, entry 18). These results were similar to the results obtained for other ionic iron(m) analogues based on azolium cations.^{15,18} Nevertheless, the last case was obviously different from the result obtained by a mixture of FeCl₃ and [DIPrim]Cl, where 12% yield of the desired product was obtained by using tert-butyl chloride as a substrate.^{3e} This difference suggests that the bulky N-substituent on the imidazole ring could play an important role on the iron-based catalytic system because the bulky N-substituents can impose a positive effect to suppress β -H elimination as well as facilitate

 Table 4
 Cross-coupling of aryl Grignard reagents with alkyl chlorides by 2^a

Entry	ArMgX	Alkyl halide	Product	Yield (%)
1		CI		97 (89 ^b /99 ^c)
2	MgBr			85 (80 ^{<i>b</i>} /85 ^{<i>c</i>})
3	MgCl			80 (85 ^c)
4	O			90 $(86^b/92^c)$
5	F		F	84 (78 ^b /87 ^c)
6	MgBr			$60 \left(80^{d}/74^{b,d}/78^{c}\right)$
7 ^c	MgBr			0
8	— MgBr	CI		$78 \left(90^d/82^{b,d}\right)$
9		CI		$82 (93^d/84^{b,d})$
10		CI		$40 \left(80^{d} / 72^{b,d} / 89^{c}\right)$
11	O			$38(70^d)$
12	MgBr	CI CI		73 (85 ^c /79 ^{b,c})
13		CI		$29 \left(40^{d}/30^{b,d}/68^{c}\right)$
14		<i>n</i> -C ₈ H ₁₇ -Cl		30 (45 ^{<i>d</i>} /39 ^{<i>b</i>,<i>d</i>} /65 ^{<i>c</i>})
15 ^{<i>c</i>}	MgBr	CI	CI	45
16	MgBr	CI		$18^{d} (23^{e})$

Table 4 (Contd.)



^{*a*} Reaction conditions: catalyst 2 (1.0 mol%), alkyl chloride (1.0 mmol), ArMgX (1.5 mmol) was added in one portion, Et₂O (2.5 mL), 30 °C, 120 min, GC yield using *n*-hexadecane as internal standard, average of 2 trials. ^{*b*} Isolated yield. ^{*c*} Using corresponding alkyl bromides (1.0 mmol) as a substrate, ArMgX (1.2 mmol), 15 min. ^{*d*} Catalyst 2 (2.0 mol%). ^{*e*} GC yield of homo-coupling of benzyl chloride, using *n*-hexadecane as an internal standard, average of 2 trials. ^{*f*} GC yield of toluene derived from benzyl chloride, using *n*-hexadecane as an internal standard, average of 2 trials.

the reductive elimination to form the desired cross-coupling product.

Finally, the catalytic activity of **2** was compared with other related iron(m)-based catalysts reported in the literature. In general, 5 mol% loadings of the iron complexes and the slow addition of aryl Grignard reagents *via* a syringe pump^{2b,3e,11,12e} or dropwise^{12b,f} are usually required to achieve satisfactory yields of alkyl chlorides mediated cross-coupling reactions. These results suggest that **2** might be among the most efficient and easy-to-use pre-catalysts for the cross-coupling reaction of aryl Grignard reagents with unactivated alkyl chlorides bearing β -hydrogens, accompanied by good recyclability.

Conclusions

Ionic iron(m) complexes based on a novel bis(phenol)-functionalized benzimidazolium cation have been easily synthesized and can be easily handled. Under mild conditions, the two complexes have great potential as efficient catalysts for the cross-coupling of aryl Grignard reagents with primary and secondary alkyl chlorides bearing β -hydrogens. Moreover, complex 2 could be reused eight times without any significant loss of catalytic activity. As various benzimidazolium cations bearing different functional groups are easily available; this work suggests that the introduction of a benzimidazole skeleton can be used as an alternative strategy for the design and synthesis of single-component, highly active and recyclable iron catalysts. Further work evaluating the full scope of this new type of iron(m)-based catalysts is currently underway in our laboratory.

Experimental section

General procedures

All manipulations were performed under pure argon with rigorous exclusion of air and moisture using standard Schlenk techniques. Solvents were distilled from Na/benzophenone ketyl under pure argon prior to use. Anhydrous FeCl₃, FeBr₃ and organic reagents used for the cross-coupling reactions were purchased from Acros Organics, Sigma-Aldrich and Alfa Aesar. ArMgX was diluted prior to use. 2-chloromethyl-4,6-ditert-butylphenol³⁰ and $[H_3L'][FeCl_4]$ $[H_3L' = 1,3-bis(3,5-di-tert$ butyl-2-hydroxybenzyl)imidazolium)]^{18d} were prepared by the published methods. Elemental analyses were performed by direct combustion using a Carlo-Erba EA-1110 instrument. The melting points were determined using an Electrothermal 1A 8103 Digital Melting point apparatus and were uncorrected. NMR spectra were measured using a Varian Unity INOVA 400 or VNMRS 300 MHz spectrometer at 25 °C. The Raman spectra were recorded using a LabRAM HR800 spectrometer. Electrospray ionization-mass spectrum (ESI-MS) data were recorded using a 6220 Accurate-Mass TOF LC/MS instrument. Gas chromatographic (GC) analysis was performed using a Varian CP-3800 instrument equipped with a FID detector and a capillary column AT.OV-101 (30 m \times 0.32 mm i.d., 0.10 μ m film). The oven temperature was held at 80 °C for 2 min, increased to 280 °C at 10 °C min⁻¹, and held for 2 min.

Synthesis

N-(3,5-di-tert-butyl-2-hydroxybenzyl)benzimidazole. A flask was charged with benzimidazole (11.81 g, 100 mmol), NaHCO₃ (9.24 g, 110 mmol) and THF (70 mL), and then a solution of 2-chloromethyl-4,6-di-tert-butylphenol (27.96 g, 110 mmol) in THF (100 mL) was slowly added to the mixture at reflux temperature. After stirring for 12 h, the mixture was poured into water, and the product was extracted with Et₂O. The combined organic layers were dried over anhydrous Na₂SO₄ and then the volatiles were removed in vacuo. Washing of the crude product by Et₂O gave a white solid in 91% yield (30.60 g). M.p. 211-213 °C. Anal. Calcd for C22H28N2O: C, 78.53; H, 8.39; N, 8.33. Found: C, 78.36; H, 8.41; N, 8.43. ¹H NMR (CDCl₃): δ 7.83 (s, 1H, NCHN), 7.60-7.57 (m, 1H, Ph-H), 7.43-7.41 (m, 1H, Ph-H), 7.31 (s, 1H, Ph-H), 7.23-7.21 (m, 1H, Ph-H), 7.18-7.15 (m, 1H, Ph-H), 7.08 (s, 1H, Ph-H), 6.09 (s, 1H, OH), 5.31 (s, 2H, ArC H_2 N), 1.44 (s, 9H, C(C H_3)₃), 1.26 (s, 9H, C(C H_3)₃). ¹³C NMR $(DMSO-d_6)$: 34.82, 36.32, 38.98, 39.78, 43.92, 44.13, 44.34, 44.55, 44.76, 44.96, 45.18, 126.95, 129.27, 130.30, 131.56, 136.34, 147.42, 156.57.

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H₃LCl (1). A flask was charged with N-(3,5-di-tert-butyl-2hydroxybenzyl)benzimidazole (10.09 g, 30 mmol) and THF (25 mL), and then a solution of 2-chloromethyl-4,6-di-tertbutylphenol (8.89 g, 35 mmol) in THF (30 mL) was slowly added at reflux temperature. After stirring for 12 h, the solution was evaporated to dryness to give the crude product. The product was washed with THF, and dried in vacuo, which yielded a white solid of H₃LCl in 95% (15.80 g). M.p. 238-239 °C. Anal. Calcd for C₃₇H₅₁N₂O₂Cl: C, 75.16; H, 8.69; N, 4.74. Found: C, 74.98; H, 8.71; N, 4.65. ¹H NMR (DMSO-*d*₆): δ 9.34 (s, 1H, NCHN), 8.93 (s, 2H, OH), 8.03-8.05 (m, 2H, Ph-H), 7.64-7.66 (m, 2H, Ph-H), 7.23-7.24 (m, 4H, Ph-H), 5.82 (s, 4H, PhCH₂N), 1.33 (s, 18H, C(CH₃)₃), 1.19 (s, 18H, C(CH₃)₃). ¹³C NMR (DMSO-*d*₆): 34.84, 36.34, 39.00, 39.80, 43.93, 44.14, 44.35, 44.56, 44.77, 44.97, 45.18, 52.23, 119.08, 127.12, 129.23, 130.31, 131.53, 136.35, 143.91, 146.23, 147.40, 156.63.

[H₃L][FeCl₄] (2). A Schlenk flask was charged with H₃LCl (1.18 g, 2.00 mmol), THF (10 mL) and a stirring bar. To this suspension, FeCl₃ (0.32 g, 2.00 mmol) in 10 mL of THF was added. The reaction mixture was stirred for 3 h at room temperature, filtered and evaporated to dryness. The residue was recrystallized from THF and hexane to yield yellow–green crystals (1.24 g, 82%). M.p. 102–103 °C (dec). Anal. Calcd for $C_{37}H_{51}N_2O_2FeCl_4$: C, 58.98; H, 6.82; N, 3.72. Found: C, 58.46; H, 6.94; N, 3.79. MS (ESI+): *m/z* 555.39 [$C_{37}H_{51}N_2O_2$]⁺ (100%). Raman spectrum: 333 cm⁻¹ ([FeCl₄]⁻).

[H₃L][FeBr₄] (3). A Schlenk flask was charged with H₃LCl (1.18 g, 2.00 mmol), NaBr (0.618 g, 6.0 mmol), THF (10 mL) and a stirring bar. To this suspension, FeBr₃ (0.59 g, 2.00 mmol) in 10 mL of THF was added. The reaction mixture was stirred for 12 h at 60 °C, filtered and evaporated to dryness. The residue was recrystallized from THF and hexane to yield brown-red crystals (1.58 g, 85%). M.p. 113–114 °C (dec). Anal. Calcd for $C_{37}H_{51}N_2O_2FeBr_4$: C, 47.71; H, 5.52; N, 3.01. Found: C, 47.89; H, 5.46; N, 2.97. MS (ESI+): *m/z* 555.39 $[C_{37}H_{51}N_2O_2]^+$ (100%). Raman spectrum: 200 cm⁻¹ ([FeBr₄]⁻).

X-ray structural determination

Suitable single crystals of 2 and 3 were sealed in a thin-walled glass capillary for X-ray structural analysis. Diffraction data were collected using a Rigaku Mercury CCD area detector at 202(2) K for 2 and 223(2) K for 3. The structures were solved by direct methods and refined by full-matrix least-squares procedures based on F^2 . All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions. The structures were solved and refined using SHELXS-97 and SHELXL-97 programs, respectively. Crystal data and collection and main refinement parameters are given in Table 1. Selected bond lengths (Å) and angles (°) of these complexes are given in Fig. 1 and 2, respectively.

General procedure for the cross-coupling reactions

A Schlenk tube was charged with an iron(m)-based catalyst (0.01 mmol), alkyl halides (1.00 mmol), *n*-hexadecane (0.10 mmol) as an internal standard, diethyl ether (1.10 mL)

and a stirring bar. The mixture was stirred at 0 °C for 2 min. 4-Methylphenylmagnesium bromide (1.40 mL, 1.20 mmol) was added to this solution at 0 °C. The resulting solution turned black immediately and was then stirred for 15 min in an oil bath at 30 °C. After the reaction was quenched by the addition of saturated ammonium chloride solution, the mixture was extracted with diethyl ether (3×2 mL) and dried over MgSO₄. The GC yield of the desired product is determined by GC analysis, using *n*-hexadecane as an internal standard. GC analysis was done directly from the reaction as well as from the crude product and proved to be identical.

Purification of the crude mixture by flash column chromatography using petroleum ether (60–90 °C) as an eluent gave the isolated yield of the desired coupling product. The identity of the product was confirmed by ¹H NMR spectroscopy and TLC.

Procedure for the recycling of 2-catalyzed cross-coupling of Grignard reagents with alkyl halides

A Schlenk tube was charged with 2 (0.05 mmol), cyclohexyl bromide (1.00 mmol), *n*-hexadecane (0.10 mmol) as an internal standard, diethyl ether (1.10 mL) and a stirring bar. The mixture was stirred at 0 °C for 2 min. 4-Methylphenylmagnesium bromide (1.40 mL, 1.20 mmol) was added to this solution at 0 °C. The resulting solution turned black immediately. Stirring was continued for 15 min in an oil bath at 30 °C and the reaction mixture was left to settle down. The upper ether layer containing the product was decanted carefully and the remaining catalyst layer was washed twice with 0.5 mL of diethyl ether each. The combined organic layers were subjected directly to GC analysis and flash column chromatography.

The remaining catalyst layer was evaporated to dryness, then fresh cyclohexyl bromide (1.00 mmol), *n*-hexadecane (0.10 mmol) and diethyl ether (1.10 mL) were added again to the catalyst. Subsequent addition of 4-methylphenylmagnesium bromide (1.40 mL, 1.20 mmol) at 0 $^{\circ}$ C started the reaction and the reaction procedure was repeated like described above.

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