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Iron-containing bis(phenol)-functionalized imidazolium salts as efficient precatalysts

for the coupling of aryl Grignard reagents with alkyl halides

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Ionic iron(III) complexes of bis(phenol)-functionalized imidazolium cations: synthesis, structures and catalysis for aryl Grignard cross-coupling of alkyl halides

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Abstract: series of bis(phenol)-functionalized imidazolium salts, А 1.3-bis(4.6-di- R^1 -2-hvdroxybenzyl)-2- R^2 -4.5-di- R^2 -imidazolium chlorides H₃LⁿCl (R^1 $= {}^{t}Bu, R^{2} = R^{3} = H, H_{3}L^{1}Cl, 1; R^{1} = CH_{3}, R^{2} = R^{3} = H, H_{3}L^{2}Cl, 2; R^{1} = {}^{t}Bu, R^{2} = H, H_{3}L^{2}Cl, 2; R^{3} = {}^{t}Bu, R^{2} = H, H_{3}L^{2}Cl, 2; R^{3} = {}^{t}Bu, R^{3} = {}^{t}Bu$ $R^3 = Cl$, H_3L^3Cl , **3**; $R^1 = {}^tBu$, $R^2 = CH_3$, $R^3 = H$, H_3L^4Cl , **4**), were used to produce a novel series of ionic iron(III) complexes $[H_3L^n]$ [FeX₄] (n = 1, X = Cl, 5; n = 2, X = Cl, **6**; n = 3, X = Cl, **7**; n = 4, X = Cl, **8**; n = 1, X = Br, **9**; n = 3, X = Br, **10**). All of the complexes were characterized by Raman spectroscopy and electrospray ionization mass spectrometry. Elemental analysis and X-ray crystallography were also used. All of the complexes were non-hygroscopic and air-stable, with five of them existing as solids (5, 7-10) and one as an oil (6) at room temperature. A preliminary catalytic study on the cross-coupling reactions of aryl Grignard reagents with primary and secondary alkyl halides bearing β -hydrogens, revealed that all of the ionic iron(III) complexes exhibited good to excellent catalytic activity. Complexes 5, 6 and 8 exhibited optimal activity, whereas 7, 9 and 10 showed only moderate activity. Furthermore, by simply decanting the cross-coupling product in the ether layer, complexes 5 and 6 could be reused in at least seven successive runs without significant loss in catalytic activity.

Introduction

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During the past decade there has been an explosion of interest in ionic liquids (ILs) with a wide range of applications because of their potential advantages over conventional organic solvent, such as wide liquid range, negligible vapor pressure, high thermal stability and good solubility.¹ Furthermore, given that ILs are salts generally composed of distinct organic cations with inorganic or organic anions, they are capable of being tuned with relative ease by the selection of the appropriate cation and anion combination,² and thereby can be designed for task-specific purposes.³

While a great deal of interest in ILs has centered on their use as environmentally friendly alternatives to volatile organic solvents,⁴ ILs are now being considered and even employed as attractive alternatives to traditional ligands and/or ionic tags of traditional ligands in the development of transition metal-based catalysts.⁵⁻⁶ In comparison with traditional ligand supported systems, such modified ionic transition metal complexes (*so called* transition metal containing ILs, MetILs⁷) can invariably offer their own distinct advantages in terms of stability, activity, low toxicity and reusability, which can lead to improved catalytic performance and provide green-chemistry strategies for chemical synthesis.⁶ Of various types of ILs available, imidazolium salts are the most popular one employed, mainly because their steric and electronic properties can be well-tailored to meet specific requirements by altering either the *N*-substituents or the ring-backbone. Furthermore, functionalized imidazolium cations have received considerable attention based on the notion that the presence of an appropriate coordinating group on the five-membered ring could

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immobilize metal catalysts effectively and thereby increase catalyst activity and improve catalyst recycling.^{6a} In this context, a range of different functional groups, including phosphines,⁸ nitriles,⁹ pyridines,¹⁰ pyrazoles,¹¹ amines,¹² ethers,¹³ alcohols,¹⁴ esters,¹⁵ alkoxysilanes,¹⁶ acids,¹⁷ salens,^{12b, 14b, 18} salicylaldoximes,^{18b} BINOLs,¹⁹ bis(oxazoline),²⁰ thioethers^{18a, 21} and sulfonamides,²² have been designed into the imidazolium cations. The resulting cations have exhibited great potential in several catalytic systems, including ruthenium-based systems for olefin metathesis reactions^{13a-b} and palladium-based systems for cross-coupling reactions.¹⁰ In this respect, it is of substantial interest to develop ionic transition metal complexes containing functionalized imidazolium cations since it can offer new opportunities in catalysis.

The development of iron-based catalysts has received increasing attention with renewed enthusiasm for a variety of cross-coupling reactions in recent years, because iron is more cost-effective and environmentally benign than palladium or nickel.²³ Well-defined iron complexes, developed for the cross-coupling reaction of aryl Grignard reagents with primary or secondary alky halides bearing β -hydrogens, represent one of the most successful examples of an iron-based catalytic system in this area, which is mostly owing to their ability to efficiently suppress β -H elimination and their potentiality from a mechanistic perspective.²⁴ For example, well-defined iron complexes, such as the low-valent iron(-II) complex,²⁴ iron(III) salen complexes,²⁵ iron(II) or iron(III) imine complexes,²⁶ and iron(III) amine-bis(phenolate) complexes,²⁷ have been used to good effect in this regard. A recent report on the

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utility of an easily prepared ionic iron(III) complex of imidazolium cation $[\text{bmim}][\text{FeCl}_4]$ (bmim = 1-butyl-3-methylimidazolium cation)²⁸ as a recyclable catalyst for the aryl Grignard cross-coupling of alkyl halides with superior activity is worthy of particular note.^{28b} The use of imidazolium chloride can modify the highly hygroscopic FeCl₃²⁹ into a non-hygroscopic and air-stable IL, which provides a practical strategy for the design of iron-based catalyst with potential large-scale applications. The liquid state of this ionic iron(III) complex may, however, lead to some problems with structural definition and handling. Moreover, although various functionalized imidazolium cations have been widely used to construct transition metal catalysts, as mentioned above, they have been hardly explored to any significant extent as immobilizing reagents for generating iron-based catalysts,³⁰ even though the presence of a functional group might facilitate their formation and improve their reactivity.

In a continuation of our work focused on the development of functionalized imidazolium salts³¹ and ionic iron complexes for application in carbon-carbon bond formation,³² we herein report the synthesis and corresponding structures of a series of bis(phenol)-functionalized imidazolium-based ionic iron(III) complexes and their application as catalysts in the aryl Grignard cross-coupling reaction of alky halides bearing β -hydrogens. Although bis(phenol)-functionalized imidazolium salts have been known for some time,³³ the use of this class of imidazolium salts as immobilizing reagents in the generation of metal-based catalysts has, to the best of our knowledge, not been reported in the literature.

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Results and Discussion

Synthesis and characterization of ionic iron(III) complexes

Three new imidazolium chlorides, H_3L^2Cl (2), H_3L^3Cl (3), and H_3L^3Cl (4), were readily synthesized according to a published procedure that used for 1^{31f} (Scheme 1), and characterized by elemental analysis and NMR spectroscopy. The most significant features of the ¹H NMR spectra of 2-3 were the signals assigned to the imidazolium protons (C2-H), appearing at 9.30 and 9.54 ppm, respectively.^{42f} The ¹H NMR spectrum of 4 showed characteristic resonances similar to those of 1,^{31f} except for the disappearance of a C2-H signal at 9-11 ppm and the presence of a singlet at 3.03 ppm, caused by replacement of the C2-H position with a methyl group.



Scheme 1 Synthesis of the bis(phenol)-functionalized imidazolium chlorides

All of the bis(phenol)-functionalized imidazolium chlorides (1-4) were obtained as air-stable non-hygroscopic white powders. All of the imidazolium chloride dissolved readily in chlorinated solvents, and compound **3**, which contained a 4,5-dichloroimidazole unit, was the most soluble of the four and also exhibited good solubility in THF. In contrast, the remaining three compounds (1, 2 and 4) were almost insoluble in THF. It is worthy of note that the melting point of **3** was much lower than that of **1**, indicating that the incorporation of chlorine groups at the C4 and

OH ΟH FeCl₄ yield: 90% ^tBu ^tBu \oplus $H_3L^1CI +$ r.t., 3 h yield: 87% FeCl₃ 6H₂O ^tBu ^tBu $[H_3L^1][FeCl_4]$ (5) $\operatorname{\mathsf{R}^2}_{\operatorname{\mathsf{I}}}\operatorname{\mathsf{FeCl}_4^{\operatorname{\mathsf{-}}}}$ OH OH R^1 \oplus FeCl₃ r.t., 3 h R^1 n = 2, [H₃L²][FeCl₄] (6): R¹ = CH₃, R² = H, R³ = H yield: 91% n = 3, [H₃L³][FeCl₄] (7): R¹ = ^tBu, R² = H, R³ = Cl yield: 80% n = 4, $[H_3L^4][FeCl_4]$ (8): $R^1 = {}^tBu, R^2 = CH_3, R^3 = H$ vield: 83%

C5 positions of the imidazolium ring tended to lead to a decrease in the melting point of the salt.³⁴

Scheme 2 Synthesis of ionic iron(III) complexes 5-8

The target ionic iron(III) complexes **5-8** were readily prepared by the reaction of anhydrous FeCl₃ with one equivalent of H_3L^nCl in THF at room temperature (Scheme 2). In an alternative procedure, for instance, complex **5** can be conveniently synthesized by a similar reaction using the inexpensive FeCl₃·6H₂O as a starting material.²⁸ After workup, $[H_3L^1][FeCl_4]$ (**5**), $[H_3L^2][FeCl_4]$ (**6**), $[H_3L^3][FeCl_4]$ (**7**), and $[H_3L^4][FeCl_4]$ (**8**) were isolated as yellow-green crystals (**5**, **7-8**) or a yellow-green oil (**6**) in high yields, respectively.

 $\begin{array}{rl} H_{3}L^{n}Cl + FeBr_{3} + 3 \text{ NaBr} & \frac{THF}{60 \ ^{o}C, \ 12 \ h} & [H_{3}L^{n}][FeBr_{4}] \\ n = 1, \ [H_{3}L^{1}][FeBr_{4}] \ (\textbf{9}) & \text{yield: } 85\% \\ n = 3, \ [H_{3}L^{3}][FeBr_{4}] \ (\textbf{10}) & \text{yield: } 80\% \end{array}$

Scheme 3 Synthesis of ionic iron(III) complexes 9-
--

It is worthy of note that the sodium bromide mediated exchange of the anion from $FeCl_4$ to $FeBr_4$ proceeded smoothly (Scheme 3). For example, the treatment of $FeBr_3$ with one equivalent of **1** and **3** in the presence of excess NaBr afforded the analogous

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complexes **9** and **10**, respectively, as brown-red crystals in high yields. These reactions, however, proceeded at slower rate than those presented in Scheme 2 because NaBr is poorly solvated in THF, and extend reaction times (12 h) and elevated temperatures were required to push the reaction to completion.

Although the ferric chlorides were highly hygroscopic, complexes **5-10** were non-hygroscopic and air-stable, and five of them (**5**, **7-10**) existed as solids at room temperature, making them easier to handle. Better solubility profiles were observed for the imidazolium-based ionic iron(III) complexes than in the corresponding imidazolium salts, and all of complexes dissolved easily in THF. In addition, complexes **7** and **10**, which contained the 4,5-dichloroimidazole unit, dissolved well in toluene. The difference in solubility between the bis(phenol)-functionalized imidazolium salt and the corresponding iron(III) complex facilitated the effective purification of the target product.

(Figures 1 and 2)

The formation of ionic iron(III) complexes **5-10** was supported by Raman spectroscopy and electrospray ionization mass spectroscopy (ESI-MS). Elemental analysis was also used for complexes **5**, **7-10** and X-ray crystallography for complexes **5** and **9**. The metal halide anions existed as discrete $[FeX_4]^-$ anions, which were easily identified by Raman spectroscopy. It is clear in Figure 1 that the spectrum of **5** shows one strong peak at 334 cm⁻¹, whereas the spectrum of **9** shows only one strong peak at 204 cm⁻¹. These data coincided very closely to the literature values for the $[FeCl_4]^-$ and $[FeBr_4]^-$ species, respectively.³⁵ For comparison, the observed bands

between 500 and 1700 cm⁻¹ were very similar to those of **1**, indicating the presence of the $[H_3L^1]^+$ cation in **5** and **9**. The Raman spectra for the synthesized ionic iron(III) complexes are shown totally in Figure 2. A predominant feature of the spectra was the clean $[FeCl_4]^-$ peak at the range of 333-337 cm⁻¹ for the ionic iron(III) chlorides and the clean $[FeBr_4]^-$ peak at the range of 202-204 cm⁻¹ for the bromide analogues. The positive ion ESI-MS spectra of **5-10** were used to establish the presence of the bis(phenol)-functionalized imidazolium cations, and in all cases a peak of high relative intensity indicative of the parent cations was observed. Thus, these characteristic results confirmed that complexes **5-10** consisted of $[H_3L^n][FeX_4]$. The ¹H NMR spectra of the complexes, however, were less informative because they exhibit broad, shifted peaks with paramagnetism.

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Single crystals of **5** and **9** were obtained from cold THF/hexane solutions, and their molecular structures were determined by X-ray crystallography. The crystallographic and measurement data are listed in Table 1. Their molecular structures are depicted in Figures 3 and 4, with key bond parameters provided in the captions. Half of the structure of **5** was C_2 -symmetrically generated, as depicted (Figure 3).

To date, structural data for imidazolium-based ionic iron(III) complexes of the type [imidazolium cation][FeX₄] have been only scarcely reported, even though the study of metal complexation in ILs is of great interest to support the extensive applications of MetILs that are currently under development.² Mudring and co-workers recently reported the first example of a crystal structure determined following the in situ crystal growth of an oily iron(III) complex, $[C_2mim][FeCl_4]$ ($C_2mim =$

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1-ethyl-3-methylimidazolium).^{36a} Structural data for а 1,3-dibutylbenzimidazolium-based ionic iron(III) complex, $[(C_4H_9)_2bim][FeCl_4]$ $[(C_4H_9)_2bim = 1,3-dibutylbenzimidazolium], were published soon after.^{36b}$ An additional example also from crystal structure of came the [BDMim]₄[Fe^{II}Cl₄][Fe^{III}Cl₄]₂, which was published by Kölle and Dronskowski in 2004.^{36c}

(Table 1)

(Figures 3 and 4)

As shown in Figures 1 and 2, each of the two molecular structures contains one bis(phenol)-functionalized imidazolium $[H_3L^1]^+$ cation and one $[FeX_4]^-$ anion, and two additional THF molecules in **9**. In **5** and **9**, the bond distances and angles within the imidazolium ring and side chain differed only slightly, corresponding well with the related imidazolium salt $[H_3L^1]Br$ reported by Kawaguchi.^{33b} A difference was observed, however, with respect to the orientation of the phenolic chain. In **5**, each plane of the phenolic ring was oriented almost perpendicular to the plane of the plane of the other phenolic ring in the system. In **9**, two phenolic rings were arranged in an almost parallel fashion, and oriented nearly perpendicular to the plane of the imidazolium ring with smaller dihedral angles in the range of 77.8 to 72.1°. Of note, for **5**, a hydrogen bond formed between the phenolic hydrogen atom and one of the carbon atoms of the *tert*-butyl group in the imidazolium cation, with a bond distance in the range of 2.64(5) to 2.82(5) Å. In contrast, the more acidic hydrogen atom at the

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2-H position of the imidazolium ring was not involved in the hydrogen bonding network. In **9**, two THF molecules were incorporated into the crystal structure during the crystallization process and were hydrogen bonded to the two phenolic hydrogen atoms through their own oxygen atoms.

The [FeCl₄]⁻ anion in **5** formed a slightly distorted tetrahedral geometry around the iron center with Fe-Cl(1) and Fe-Cl(2) bond distances of 2.186(2) and 2.200(2) Å, respectively, which were in agreement with values found in other imidazolium-based ionic iron(III) complexes.³⁶ The Cl-Fe-Cl angles of [FeCl₄]⁻ were between 105.91(9)° and 110.37(6)° with a mean value of 109. 45°, which was close to the ideal tetrahedral angle at -50°C.^{36a} Similarly, the [FeBr₄]⁻ anion in **9** also had a slightly distorted tetrahedral geometry, because the six Br-Fe-Br angles (107.05(7)°, 107.12(7)°, 107.62(7)°, 109.61(7)°, 110.54(8)°, 110.95(7)°) for [FeBr₄]⁻ were obviously different from each other, although each of four Fe-Br bond distances was almost the same (2.307(2)-2.325(2) Å). These values were in the expected range as found for other complexes containing [FeBr₄]⁻ anions.³⁷

Although the hydrogen bonding interaction between the imidazolium cation and halide anion is well established,^{7, 36} none of the cation-anion interatomic distances found in **5** and **6** fell within the generally accepted range for typical hydrogen bonding interactions.³⁸ Thus, both of **5** and **9** could be described as a simple collection of ion pairs. The unique pattern in **5** or **9** was most likely a consequence of the steric bulkiness of the bis(phenol)-functionalized imidazolium cation.^{32a}

Catalysis of ionic iron(III) complexes

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For the initial screening of catalyst performance, the reaction outlined in eq. 1 was chosen as a model system, as it is a prototypical cross-coupling reaction of an aryl Grignard reagents with alkyl halides bearing β -hydrogens.^{25, 29} This series of experiments was performed using both cyclohexyl bromide and chloride as starting reagents to highlight any differences in activity. The results obtained are summarized in Table 2.



(Table 2)

It is clear that all of the ionic iron(III) complexes provided good to excellent yields of the desired coupling product using cyclohexyl bromide as a starting reagent, whereas modest to good yields were obtained in the presence of cyclohexyl chloride with prolonged reaction times. Interestingly, the reaction proceeded smoothly without the requirement of an inert atmosphere, and there was no obvious difference between the use of an air atmosphere or pure argon (entry 4). Complexes, **5** and **8** showed the highest activity of all of the iron(III) complexes, providing almost quantitative yields of the desired coupling products when cyclohexyl bromide was used as the starting reagent (entries 4 and 15). Furthermore, the yields still reached 77 and 76% for **5** and **8**, respectively, even when cyclohexyl bromide was replaced with the chloride analogue (entries 6 and 17). The near equality in the activity of **5** and **8** indicated that the imidazolium tag present in **5** was catalytically silent and inert under the reaction conditions,^{6a} otherwise a significant effect would be observed on the coupling

reaction on changing the imidazolium cation at its C2 position. Under the same conditions, a slightly lower activity was seen when the bulky *tert*-butyl substituent on the phenolic motif was replaced by a methyl substituent (entries 10-12), implying that aryl substituent imposed a negligible effect. Iron(III) salen complexes displayed similar performances, where *para-* and *ortho-tert*-butyl modified analogues showed essentially the same activity as systems containing only hydrogen atoms at the same positions.²⁵ In contrast, replacing the hydrogen atoms at the 4- and 5-positions of the imidazole ring with chlorine atoms proved to be clearly unfavorable, with 7 showing lower activity than 8 (entries 13 and 14). Replacement of the anion from $[FeCl_4]^-$ to $[FeBr_4]^-$ was also detrimental to performance, with 9 and 10 providing lower yields than those obtained with 5 and 7 (entries 18-21), respectively.

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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 **5** was compared with other related iron(III)-based catalysts reported in the literature. Normally, 2-5 mol% or higher loadings of the iron complexes and 1.5-2 equiv of Grignard reagent were usually required to achieve satisfactory yields for reactions similar to those shown in eq. 1.²⁴⁻²⁹ Therefore, the present results suggest that **5** and **8** might be among the most efficient precatalysts for the cross-coupling reaction of aryl Grignard reagents with alkyl halides bearing β -hydrogens, which is mostly due to enhanced stabilization of catalytically active iron species via the aryloxo-functionalized

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imidazolium cations generated in situ during the catalytic procedures.

(Table 3)

Substrate screening was subsequently carried out, and the results obtained are summarized in Table 3. A comparison of the range of the Grignard reagents used in the reaction with cyclohexyl bromide (entries 1-6) indicated that electron-rich or electron-neutral aryl Grignard reagent reacted rapidly to give the desired coupling products (entries 1-3), whereas reagents with electron-withdrawing groups reacted sluggishly (entry 5). It is worthy of note that an excellent isolated yield was also obtained with 2-methylphenylmagnesium bromide (entry 2), although the introduction of two ortho-substituents led to a complete loss in activity (entry 4), which is consistent with observations from other iron(III)-based catalysts reported in the literature.^{25, 29b-c} To the best of our knowledge, there have been no other reports in the literature describing the cross-coupling of such sterically hindered aryl Grignard reagent, *i.e.* 2,6-dimethylphenylmagnesium bromide, with secondary alkyl halides.^{29c} Upon changing the Grignard reagent to phenylmagnesium chloride, the reaction proceeded smoothly, although with a lower isolated yield of 72% (entry 6). A higher isolated yield of the desired coupling product was typically obtained when cyclohexyl bromide was employed rather than the corresponding chloride or iodide. This general trend in the reactivity of cyclohexyl halides appeared to Br > I > Cl. This was the same pattern as that previously reported for iron(III) salen complexes.²⁵ [bmim][FeCl4],^{28b} and FeCl3/phosphine systems.^{29c} The current iron(III)-catalyzed cross-coupling was applicable to cycloheptyl bromide and cyclopentyl bromide under the same conditions described for cyclohexyl bromide, although the yields were lower than those recorded for cyclohexyl bromide (entries 8 and 9). Acyclic secondary alkyl bromides provided similar results to those of cyclohexyl bromide (entries 12 and 13), whereas the corresponding primary bromides were usually less reactive (entries 11 and 14). Unfortunately, tertiary alkyl bromide gave none of the desired coupling product (entry 15).

Recyclability of ionic iron(III) complexes

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(Table 4)

Recent research has revealed that some types of imidazolium-based ionic metal complexes can be reused several times without any significant loss in catalytic activity.^{6a} For example, 5 mol % of [bmim][FeCl₄] was reused in the cross-coupling of 4-fluorophenylmagnesium bromide and dodecyl bromide, with the isolated yield of the desired coupling product decreasing only slightly from 86% in the first run to 76% after the fifth run.^{28b} In our work, having established that complexes **5**, **6** and **8** showed optimal activity, we proceeded to study their recycling ability in the cross-coupling reaction of 4-methylphenylmagnesium bromide and cyclohexyl bromide. Starting with 5 mol % of **5**, the upper ether layer containing the desired coupling product was decanted after the reaction was complete, whereas the catalyst was left in the black sediment, which was washed twice with 0.5 mL of diethyl ether and evaporated to dryness. Fresh cyclohexyl bromide and *n*-hexadecane (as an internal standard) were mixed in a diethyl ether solvent and added to the remaining catalyst. The Grignard reagent was then added and the reaction was found to proceed

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smoothly under same conditions. The data listed in Table 4 indicated that complex 5 could be reused in at least seven successive runs of the model reaction, with cyclohexyl bromide being almost completed consumed. The isolated yield of desired coupling product, however, gradually dropped from 89% in the first run to 72% after the seventh run (entries 1-7). This may be attributed to catalyst leaching during the decanting and extraction steps.^{28b} Complex 6 showed similar recycling ability during the same recycling process. The recycling experiments with 8, however, led to a considerable decrease in the isolated yield from 89% in the first run to 40% after the fourth run, indicating that the introduction of a non-coordinating group (*i.e.* methyl group) at the C2 position of imidazolium cation facilitated catalyst leaching. Welton also observed a similar phenomenon, when a Pd(II)-based catalyst could not be efficiently trapped into 2-methylimidazolium salts, even in the presence of other ligands.³⁹ Nevertheless, nonfunctionalized supporting comparisons to [bmim][FeCl₄]^{28b} demonstrate the superiority of the present systems with respect to recyclability, which is mostly due to the weak interaction derived from the phenolic group.

Conclusions

A family of easily synthesized and easy-to-handle ionic iron(III) complexes of bis(phenol)-functionalized imidazolium cations (5-10) have been developed as excellent catalysts for the cross-coupling of aryl Grignard reagents with primary and secondary alkyl halides bearing β -hydrogens under mild conditions. Moreover, complexes 5 and 6 could be reused seven times without any significant loss in

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catalytic activity. This work has therefore demonstrated that the modification of imidazole ring with phenolic groups represents a promising pathway towards the design and synthesis of highly active and recyclable catalytic systems. The facile synthesis of the ionic iron(III) complexes, their readily tailored properties and their ease of handling makes them highly attractive for use in a wide range of catalytic reactions. Further studies evaluating the full scope of this new type of catalysts are currently being pursued.

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, FeCl₃·6H₂O 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. N-(4,6-Di-*tert*-butyl-2-hydroxybenzyl)-4,5-dichloroimidazole,^{33b} N-(4,6-di-*tert*-butyl-2-hydroxybenzyl)-2-methylimidazole,^{33b}

N-(4,6-dimethyl-2-hydroxybenzyl)imidazole,^{33b} and

1,3-bis(4,6-di-*tert*-butyl-2-hydroxybenzyl)imidazolium chloride $(H_3L^1Cl, 1)^{31f}$ were prepared by the published methods. Elemental analyses were performed by direct combustion on a Carlo-Erba EA-1110 instrument. NMR spectra were measured on a Varian Unity INOVA 400 or VNMRS 300 MHz spectrometer at 25 °C. The Raman

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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 FID detector and a capillary column AT.OV-101 (30 m \times 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.

Synthesis

 H_3L^2Cl (2). A flask was charged with N-(4,6-di-methyl-2-hydroxybenzyl)imidazole (4.06)20 mmol) and THF (20)mL), and then solution g, а of 2-chloromethyl-4,6-methylphenol (4.25 g, 25 mmol) in THF (25 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 white solid of H₃L²Cl (3.37 g, 45%). M.p. 176-178 °C. Anal. Calcd for C₂₁H₂₅N₂O₂Cl: C, 67.64; H, 6.76; N, 7.51. Found: C, 67.19; H, 6.89; N, 7.38. ¹H NMR (CDCl₃): δ 9.30 (s, 1H, NCHN), 8.57 (s, 2H, OH), 7.02 (d, J = 1.2 Hz, 2H, NCHC), 6.95 (s, 2H, Ph-H), 6.84 (s, 2H, Ph-H), 5.25 (s, 4H, PhCH₂N), 2.37 (s, 6H, CH₃), 2.21 (s, 6H, CH₃). ¹³C NMR (CDCl₃): δ 11.22 (CH₃), 15.22 (CH₃), 41.92 (CH₂), 118.70 (C), 120.59 (C), 122.57 (C), 122.96 (C), 124.34 (C), 126.73 (C), 132.28 (C), 145.82 (C).

 H_3L^3Cl (3). Following a procedure similar to the synthetic procedure of 2, a flask was charged with *N*-(4,6-di-*tert*-butyl-2-hydroxybenzyl)-4,5-dichloroimidazole (10.62)

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30.00 mmol) and THF (20)mL), and then solution of а g, 2-chloromethyl-4,6-di-tert-butylphenol (8.85 g, 35.00 mmol) in THF (25 mL) was slowly added at reflux temperature. After workup, the product was precipitated as white solid in 70% yield (12.40 g). M.p. 164-167 °C. Anal. Calcd for C₃₃H₄₇N₂O₂Cl₃: C, 64.96; H, 7.77; N, 4.59. Found: C, 64.87; H, 7.69; N, 4.58. ¹H NMR (CDCl₃): δ 9.54 (s, 1H, NCHN), 7.88 (s, 2H, OH), 7.42 (s, 1 H, Ph-H), 7.36 (s, 1H, Ph-H), 7.09 (s, 1 H, Ph-H), 7.07 (s, 1 H, Ph-H), 5.49 (s, 2H, PhCH₂N), 5.06 (s, 2H, PhCH₂N), 1.44 (s, 9H, $C(CH_3)_3$, 1.40 (s, 9H, $C(CH_3)_3$), 1.27 (s, 9H, $C(CH_3)_3$), 1.25 (s, 9H, $C(CH_3)_3$). ¹³C NMR (CDCl₃): δ 30.19 (CCH₃), 31.43 (CCH₃), 34.26 (CCH₃), 35.04 (CCH₃), 50.55 (CH₂), 119.06 (C), 120.42 (C), 125.87 (C), 126.21 (C), 137.06 (C), 140.27 (C), 143.41 (C), 152.32 (C).

 H_3L^4Cl (4). Following a procedure similar to the synthetic procedure of 2, a flask was charged with N-(4,6-di-tert-butyl-2-hydroxybenzyl)-2-methylimidazole (1.51 g, 5.00 THF (30)of mmol) and mL). and then а solution 2-chloromethyl-4,6-di-tert-butylphenol (1.78 g, 7.00 mmol) in THF (10 mL) was slowly added at reflux temperature. After workup, the product was precipitated as white solid in 86% yield (2.28 g). M.p. 252-254 °C. Anal. Calcd for $C_{34}H_{51}N_2O_2Cl: C$, 73.55; H, 9.26; N, 5.05. Found: C, 73.45; H, 9.25; N, 4.98. ¹H NMR (CDCl₃): δ 7.75 (s, 2H, OH), 7.39 (s, 2H, Ph-H), 7.07 (s, 2H, Ph-H), 6.74 (d, J = 1.6 Hz, 2 H, NCHC),5.23 (s, 4H, PhC H_2 N), 3.03 (s, 3H, C H_3), 1.39 (s, 18H, C(C H_3), 1.28 (s, 18H, C(CH₃)₂). ¹³C NMR (DMSO-*d*): δ 10.32 (CH₃), 30.23 (CCH₃), 31.73 (CCH₃), 34.36 (CCH₃), 35.19 (CCH₃), 48.28 (CH₂), 121.62 (C), 123.51 (C), 124.25 (C), 124.63 (C),

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139.19 (C), 142.76 (C), 144.59 (C), 151.57 (C).

[H₃L¹][FeCl₄] (5), procedure A. A Schlenk flask was charged with H₃L¹Cl (1.08 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 (1.26 g, 90%). M.p. 212–215 °C (dec). Anal. Calcd for C₃₃H₄₉N₂O₂FeCl₄: C, 56.35; H, 7.02; N, 3.98. Found: C, 56.48; H, 7.08; N, 3.95. MS (ESI+): m/z 505.3788 [C₃₃H₄₉N₂O₂]⁺ (100%). Raman spectrum: 334 cm⁻¹ ([FeCl₄]⁻).

[H₃L¹][FeCl₄] (5), procedure B. A Schlenk flask was charged with H₃L¹Cl (1.08 g, 2.00 mmol), THF (10 mL) and a stirring bar. To this suspension, FeCl₃·6H₂O (0.54 g, 2.00 mmol) in 10 mL of THF was added. The following preparation is similar to procedure **A**. After workup, the product was precipitated as yellow-green crystals in 87% yield (1.22 g). Anal. Calcd for $C_{33}H_{49}N_2O_2FeCl_4$: C, 56.35; H, 7.02; N, 3.98. Found: C, 56.43; H, 7.10; N, 3.97.

 $[H_3L^2][FeCl_4]$ (6). Following a procedure similar to the synthetic procedure A of 5, a Schlenk flask was charged with H_3L^2Cl (0.38 g, 1.00 mmol), THF (10 mL) and a stirring bar. To this suspension, FeCl₃ (0.16 g, 1.00 mmol) in 10 mL of THF was added. After workup, the product was precipitated as yellow-green oil in 91% yield (0.49 g). M.p.117–119 °C (dec). MS (ESI+): m/z 337.1927 $[C_{21}H_{25}N_2O_2]^+$ (100%). Raman spectrum: 335 cm⁻¹ ([FeCl₄]⁻).

 $[H_3L^3]$ [FeCl₄] (7). Following a procedure similar to the synthetic procedure A of 5,

a Schlenk flask was charged with H₃L³Cl (1.22 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. After workup, the product was precipitated as yellow-green crystals in 80% yield (1.23 g). M.p. 171–173 °C (dec). Anal. Calcd for $C_{33}H_{47}N_2O_2FeCl_6$: C, 51.32; H, 6.13; N, 3.63. Found: C, 50.89; H, 5.91; N, 3.88. MS (ESI+): *m/z* 573.3036 $[C_{33}H_{47}N_2O_2Cl_2]^+$ (100%). Raman spectrum: 337 cm⁻¹ ([FeCl₄]⁻).

[H₃L⁴][FeCl₄] (8). Following a procedure similar to the synthetic procedure A of 5, a Schlenk flask was charged with H₃L⁴Cl (1.11 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. After workup, the product was precipitated as yellow-green crystals in 83% yield (1.18 g). M.p. 143–146 °C (dec). Anal. Calcd for C₃₄H₅₁N₂O₂FeCl₄: C, 56.92; H, 7.17; N, 3.90. Found: C, 56.84; H, 7.06; N, 3.57. MS (ESI+): m/z 519.3963 [C₃₄H₅₁N₂O₂]⁺ (100%). Raman spectrum: 333 cm⁻¹ ([FeCl₄]⁻).

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[H₃L¹][FeBr₄] (9). A Schlenk flask was charged with H₃L¹Cl (1.08 g, 2.00 mmol), NaBr (0.31 g, 3.00 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 (1.50 g, 85%). M.p. 218–220 °C (dec). Anal. Calcd for $C_{33}H_{49}N_2O_2FeBr_4(C_4H_8O)$: C, 46.62; H, 6.03; N, 2.94. Found: C, 46.30; H, 5.90; N, 2.80. MS (ESI+): *m/z* 505.3806 [C₃₃H₄₉N₂O₂]⁺ (100%). Raman spectrum: 204 cm⁻¹ ([FeBr₄]⁻).

[H₃L³][FeBr₄] (10). Following a procedure similar to the synthetic procedure of 9,

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a Schlenk flask was charged with H_3L^3Cl (1.22 g, 2.00 mmol), NaBr (0.31 g, 3.00 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. After workup, the product was precipitated as brown-red crystals in 80% yield (1.52 g). M.p. 185–187 °C (dec). Anal. Calcd for $C_{33}H_{47}N_2O_2FeCl_2Br_4$: C, 41.72; H, 4.99; N, 2.95. Found: C, 41.96; H, 4.95; N, 3.12. MS (ESI+): m/z 573.3017 $[C_{33}H_{47}N_2O_2Cl_2]^+$ (100%). Raman spectrum: 202 cm⁻¹ ([FeBr₄]⁻).

X-ray structural determination

Suitable single crystals of **5** and **9** were sealed in a thin-walled glass capillary for X-ray structural analysis. Diffraction data were collected on a Rigaku Mercury CCD area detector at 223(2) K. 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 (deg) of these complexes are given in Figures 3 and 4, respectively.

General procedure for the cross-coupling reactions

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

(1.15 mL) and a stirring bar. The mixture was stirred at 0 °C for 2 min. 4-Methylphenylmagnesium bromide (1.35 mL, 1.20 mmol) was added to this solution at 0 °C. The resulting solution turned black immediately and was then stirred for 30 min in an oil bath at 30 °C. After the reaction was quenched by 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 eluent gave the isolated yield of desired coupling product. The identity of the product was confirmed by ¹H NMR spectroscopy and TLC.

Procedure for the recycling of iron(III) complexes catalyzed cross-coupling of Grignard reagents with alkyl halides

A Schlenk tube was charged with an iron(III)-based catalyst (0.05 mmol), cyclohexyl bromide (1.00 mmol), *n*-hexadecane (0.10 mmol) as internal standard, diethyl ether (1.15 mL) and a stirring bar. The mixture was stirred at 0 °C for 2 min. 4-Methylphenylmagnesium bromide (1.35 mL, 1.20 mmol) was added to this solution at 0 °C. The resulting solution turned black immediately. Stirring was continued for 30 min in an oil bath at 30 °C and the reaction 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

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were subjected directly to GC analysis, and then were concentrated to flash column chromatography as shown above.

The remaining catalyst layer was evaporated to dryness, then fresh cyclohexyl bromide (1.00 mmol), *n*-hexadecane (0.10 mmol) and diethyl ether (1.15 mL) were added again to the catalyst. Subsequent addition of 4-methylphenylmagnesium bromide (1.35 mL, 1.20 mmol) at 0 °C started the reaction and the reaction procedure was repeated like described above.

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	5	9·2THF
Formula	$C_{33}H_{49}Cl_4FeN_2O_2$	C41H65Br4FeN2O4
Formula weight	703.39	1025.44
Temperature / K	223(2)	223(2)
Radiation used	Μο-Κα	Μο-Κα
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	P 21/c
Unit cell dimensions		
<i>a</i> / Å	18.221(10)	21.235(2)
<i>b</i> / Å	22.283(10)	11.9530(11)
<i>c</i> / Å	9.501(5)	18.3053(17)
eta / °	110.727(13)	92.370(3)
$V/\text{\AA}^3$	3608(3)	4642.4(7)
Ζ	4	4
$Dc / g cm^{-3}$	1.295	1.467
μ / mm ⁻¹	0.745	3.806
<i>F</i> (000)	1484	2092
heta range / °	3.01-27.49	3.00 - 25.50
Reflection collected	9524	22721
Independent reflections, R _{int}	4087, 0.0504	8620, 0.0513
Goodness-of-fit on F^2	1.079	1.127
$R_1, wR_2 [I > 2\sigma(I)]$	0.0741, 0.1826	0.0969, 0.2412
R_1 , wR_2 (all data)	0.1255, 0.2181	0.1351, 0.2661

Entry	Catalyst	[ArMgBr]/[R-X] (molar ratio)	Time (min)	Х	Yield (%)
1	H_3L^1Cl	1.2	30	Br	5
2	FeCl ₃	1.2	30	Br	30
3	$FeCl_3 + H_3L^1Cl$	1.2	30	Br	63
4	5	1.2	30	Br	99(89 ^b 84 ^c)
5	5	1.2	60	Cl	68
6	5	1.2	120	Cl	77
7	5	1.5	30	Br	97
8	5	1.0	30	Br	89
9^d	5	1.2	30	Br	68
10	6	1.2	30	Br	96
11	6	1.2	60	Cl	62
12	6	1.2	120	Cl	70
13	7	1.2	30	Br	94
14	7	1.2	60	Cl	51
15	8	1.2	30	Br	99
16	8	1.2	60	Cl	68
17	8	1.2	120	Cl	76
18	9	1.2	30	Br	84
19	9	1.2	60	Cl	50
20	10	1.2	30	Br	82
21	10	1.2	60	Cl	46

Table 2 Cross-coupling of 4-MeC₆H₄MgBr with cyclohexyl halides catalyzed by ionic iron(III) complexes^{*a*}

^{*a*} Reaction conditions: Fe(III) complex (1.0 mol %), 4-MeC₆H₄MgBr (1.2 mmol) was added in one

portion, cyclohexyl halide (1.0 mmol), Et₂O, total volume (2.5 mL), GC yield using *n*-hexadecane as internal standard, average of 2 trials. ^{*b*} Isolated yield. ^{*c*} In air, isolated yield. ^{*d*} External temperature 45 °C, reaction temperature 36–38 °C.

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Entry	ArMgX	Alkyl halide	Product	Isolated yield (%)
1		Br		89
2	MgBr			90
3	MgBr			81
4	MgBr			0
5	F		F	60
6	MgCl			72
7	MgBr			85
8		Br		45
9		Br		65
10		n-C ₈ H ₁₇ -Br		85
11		Br		64
12		Br		83
13		Br		73
14		Br		65

Table 3 Cross-coupling of aryl Grignard reagents with alkyl halides by 5^a

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15 <i>t</i> -C ₄ H ₉ Br —	
15 $t-C_4H_9Br$ —	

^{*a*} Reaction conditions: catalyst **5** (1.0 mol %), ArMgX (1.2 mmol) was added in one portion, alkyl halide (1.0 mmol), Et₂O (2.5 mL), 30 °C, 30 min.

Entry	Run	Conv. ^{b, c} (%)	Isolated yield ^c (%)	Conv. ^{b, d} (%)	Isolated yield ^d (%)	Conv. ^{b, e} (%)	Isolated yield ^e (%)
1	1	>99	89	>99	89	>99	89
2	2	>99	89	>99	87	>99	84
3	3	>99	84	>99	86	96	79
4	4	>99	82	98	81	60	40
5	5	96	80	98	81	/	/
6	6	95	79	94	76	/	/
7	7	90	72	82	68	/	/

Table 4 Recycling of **5**, **6** and **8** in the cross-coupling of 4-MeC₆H₄MgBr with cyclohexyl bromide^{*a*}

^{*a*} Reaction conditions: 4-MeC₆H₄MgBr (1.2 mmol) was added in one portion, cyclohexyl bromide (1.0 mmol), Et₂O (2.5 mL), 30 °C, 30 min. ^{*b*} The conversion of cyclohexyl bromide determined by GC using *n*-hexadecane as internal standard. ^{*c*} catalyst **5** (5.0 mol %). ^{*d*} catalyst **6** (5.0 mol %). ^{*e*} **8** (5.0 mol %).

Figure captions

Fig. 1 Raman spectra of 1, 5 and 9.

Fig. 2 Raman spectra of 5-8 (left) and 9-10 (right).

Molecular structure of **5** with thermal ellipsoids at the 30% probability level. Fig. 3 Hydrogen atoms (except the hydrogen bonded hydrogen atoms) have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe(1)-Cl(1) 2.1863(2), Fe(1)-Cl(1)' 2.1863(2), Fe(1)-Cl(2) 2.2002(2), Fe(1)-Cl(2)' 2.2002(2), H(1A)-C(11) 2.64(5), H(1A)'-C(11)' 2.64(5), H(1A)-C(13) 2.82(5), H(1A)'-C(13)' 2.82(5), Cl(1)-Fe(1)-Cl(2)109.90(6), Cl(1)-Fe(1)-Cl(1)' 110.31(8), Cl(1)-Fe(1)-Cl(2)' 110.37(6), 110.37(6), 105.91(9), Cl(2)-Fe(1)-Cl(1)' Cl(2)-Fe(1)-Cl(2)' Cl(1)'-Fe(1)-Cl(2)' 109.90(6).

Fig. 4 Molecular structure of **9-2THF** 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 (deg): Fe(1)-Br(1) 2.3087(2), Fe(1)-Br(2) 2.3073(2), Fe(1)-Br(3) 2.3251(2), Fe(1)-Br(4) 2.3176(2), H(1)-O(3) 1.97, H(2)-O(4) 2.01, Br(1)-Fe(1)-Br(2) 111.18(7), Br(2)-Fe(1)-Br(4) 107.12(7), Br(1)-Fe(1)-Br(4) 109.69(7), Br(2)-Fe(1)-Br(3) 110.84(6), Br(1)-Fe(1)-Br(3) 107.71(6), Br(4)-Fe(1)-Br(3) 110.33(7).



Fig. 2



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Fig. 3







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TOC

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Ionic iron(III) complexes of bis(phenol)-functionalized imidazolium cations: synthesis, structures and catalysis for aryl Grignard cross-coupling of alkyl halides

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А bis(phenol)-functionalized imidazolium series of salts. 1,3-bis(4,6-di-R¹-2-hydroxybenzyl)-2-R²-4,5-di-R²-imidazolium chlorides H₃LⁿCl (R¹ $= {}^{t}Bu, R^{2} = R^{3} = H, H_{3}L^{1}Cl, 1; R^{1} = CH_{3}, R^{2} = R^{3} = H, H_{3}L^{2}Cl, 2; R^{1} = {}^{t}Bu, R^{2} = H, H_{3}L^{2}Cl, 2; R^{3} = {}^{t}Bu, R^{2} = H, H_{3}L^{2}Cl, 2; R^{3} = {}^{t}Bu, R^{3} = {}^{t}Bu$ $R^3 = Cl_1 H_3 L^3 Cl_1 3$; $R^1 = {}^tBu_1 R^2 = CH_3 R^3 = H_1 H_3 L^4 Cl_1 4$), were used to produce a novel series of ionic iron(III) complexes $[H_3L^n][FeX_4]$ (n = 1, X = Cl, 5; n = 2, X = Cl, **6**; n = 3, X = Cl, **7**; n = 4, X = Cl, **8**; n = 1, X = Br, **9**; n = 3, X = Br, **10**). A preliminary catalytic study on the cross-coupling reactions of aryl Grignard reagents with primary and secondary alkyl halides bearing β -hydrogens, revealed that all of the ionic iron(III) complexes exhibited good to excellent catalytic activity. Complexes 5, 6 and 8 exhibited optimal activity, whereas 7, 9 and 10 showed only moderate activity. Furthermore, by simply decanting the cross-coupling product in the ether layer, complexes 5 and 6 could be reused in at least seven successive runs without significant loss in catalytic activity.