Dalton Transactions

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ROYAL SOCIETY OF CHEMISTRY

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View Article Online
DOI: 10.1039/C6DT02995G

Dalton Transactions

ARTICLE

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Alkyl Grignard cross-coupling of aryl phosphates catalyzed by new, highly active ionic iron(II) complexes containing a phosphine ligand and an imidazolium cation

Zhuang Li,[a] Ling Liu,[a] Hong-mei Sun,*[a] Qi Shen[a] and Yong Zhang[a]

Abstract: A novel family of ionic iron(II) complexes of general formula [HL][Fe(PR'$_3$)X$_3$] (HL = 1,3-bis(2,6-diisopropylphenyl)imidazolium cation, HIPr, R' = Ph, X = Cl, **2**; HL = HIPr, R' = Cy, X = Cl, **3**; HL = HIPr, R' = Ph, X = Br, **4**; HL = HIPr, R' = Cy, X = Br, **5**; HL = 1,3-bis(2,4,6-trimethylphenyl)imidazolium cation, HIMes, R' = Cy, X = Br, **6**) were easily prepared *via* a stepwise approach in 88%–92% yields. In addition, an ionic iron(II) complex, [HIPr][Fe(C_4H_8O)Cl$_3$] (**1**), has been isolated from the reaction of FeCl$_2$(THF)$_{1.5}$ with one equiv of [HIPr]Cl in 90% yield and can further react with one equiv of PPh$_3$ or PCy$_3$, affording the corresponding target iron(II) complex **2** or **3**, respectively. All these complexes were characterized by elemental analysis, electrospray ionization mass spectrometry (ESI-MS), ^{1}H NMR spectroscopy and X-ray crystallography. These air-insensitive complexes **2**-**6** showed high catalytic activities in the cross-coupling of aryl phosphates with primary and secondary alkyl Grignard reagents with broad substrate scope, wherein [HIPr][Fe(PCy$_3$)Br$_3$] (**5**) is the most effective. Complex **5** also catalyzes the reductive cross-coupling of aryl phosphates with unactivated alkyl bromides in the presence of magnesium turnings and LiCl, as well as the corresponding one-pot acylation/cross-coupling sequence under mild conditions.

Introduction

Transition metal-catalyzed Grignard cross-coupling reactions are a powerful tool in organic synthesis to construct C–C bonds.[1] In the past decades, significant efforts have been made to development more efficient catalytic systems as well as more economic and eco-friendly coupling partners for this transformation.

Recently, iron-catalyzed Grignard cross-coupling using phenolic derivatives as potential electrophiles has been highlighted as an appealing reaction from a sustainable point of view.[2] This is not only ascribed to the fact that iron is one of the most abundant, inexpensive, non-toxic, and environmentally benign metals on earth,[3] but also to its combination with C–O electrophiles, which possess many advantages compared with the corresponding halides.[2] In this context, several kinds of C–O electrophiles, including aryl/alkenyl triflates,[4a-d] aryl/alkenyl tosylates,[4a-b,4f] aryl/alkenyl pivalates,[4e] 2-pyrone derivatives,[4i] aryl carbamates,[4g] aryl sulfamates,[4g-h] and alkenyl acetates,[4j] have been shown to work well, and generally associated with the use of simple iron salts, *i.e.* FeCl$_n$ and Fe(acac)$_3$, as the catalysts in the presence of appropriate ligands.

In addition to the above-mentioned substrates, phosphates represent another kind of attractive electrophile because they are the most abundant esters in living organisms. Moreover, phosphates boast simple and inexpensive preparation, and are more environmentally benign and stable than other kinds of phenolic derivatives.[5] In this context, alkenyl phosphates[6a-b] and terminal conjugated dienyl phosphates[6c] have been found to react readily with Grignard reagents in the presence of both Fe(acac)$_3$ and an appropriate additive. Pyrimidin-2-yl phosphates have also been successfully applied to Grignard coupling using a catalyst system composed of Fe(acac)$_3$ and biphosphine ligands.[4f,6d] However, aryl phosphates, which are derived from unactivated phenols, remain challenging substrates in iron-catalyzed Grignard cross-coupling reactions.[7] Furthermore, only a few examples of other transition metal-catalyzed cross-coupling reactions involving an aryl phosphate have been reported,[7,8] although nickel-catalyzed Grignard cross-coupling of aryl phosphates has been known since the beginning of cross-coupling reactions.[7a] The main difficulty is that aryl phosphates possess a less reactive aromatic C-O bond compared with that of alkenyl phosphates.[2a] Therefore, an alternative iron-based catalyst is of great interest to address this challenge.

Based on the fact that bulky electron-donating ligands, *i.e.*, PCy$_3$[7c,7e] or [HIPr]Cl [1,3-bis(2,6-diisopropylphenyl)imidazolium chloride, which may free an *N*-heterocyclic carbene (NHC) ligand IPr under basic conditions],[7d] are usually required in nickel-based catalytic systems to overcome this issue,[2a] we decided to explore the possibility of constructing highly efficient iron-based catalysts

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[a] *The Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, People's Republic of China. E-mail: sunhm@suda.edu.cn.*

†Electronic Supplementary Information (ESI) available: crystallographic data and spectral data (^{1}H NMR and ^{13}C NMR). CCDC reference numbers 1485930, 1485924, 1485927, 1485926, 1485929, 1485931 for **1–6**, respectively. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x.

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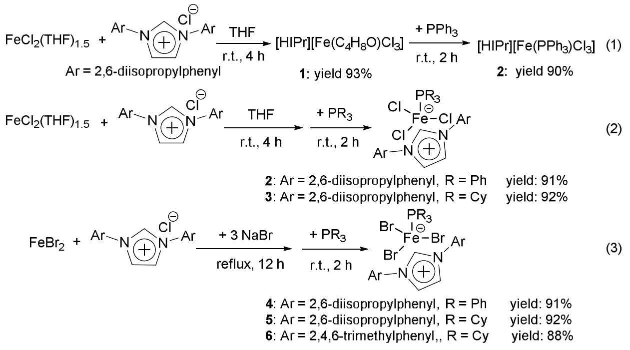
DOI: 10.1039/C6DT02995G

by simultaneously employing two types of ligands. In fact, this strategy has already been successful in the design of palladium-[9] and nickel[10]-based catalysts for several cross-coupling reactions, offering the distinct features of the reversible dissociation of a labile phosphine ligand as well as the tight binding of a robust NHC ligand to the central metal, which can aid both the oxidative addition and reductive elimination steps in the generally accepted mechanism as well as stabilizing the metal center at different stages of the catalytic cycle.[2a] However, its application in iron catalysis is still poorly explored,[11c] even if the research on the chemistry of NHC complexes of iron has received substantial attention over the past decade.[11]

Considering the available synthesis of NHC ligands by *in situ* dehydrohalogenation of the corresponding imidazolium salt with various bases[12] and our previous work on mixed phosphine/imidazolium cation nickel(II) complexes,[13] we report here the facile synthesis of a new type of ionic iron(II) complexes containing a phosphine ligand and an imidazolium cation (**2**-**6**), and their catalytic potential in the cross-coupling of aryl phosphates with primary and secondary alkyl Grignard reagents and the corresponding reductive cross-coupling.

Results and discussion

Synthesis and characterization of ionic iron(II) complexes



Scheme 1. Synthesis of ionic iron(II) complexes **1**–**6**

The synthesis of target ionic iron(II) complexes **2**–**6** is summarized in Scheme 1. According to a published procedure,[14] $FeCl_2(THF)_{1.5}$ reacted smoothly with one equivalent of 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride ([HIPr]Cl) in THF at room temperature (Scheme 1, eqn 1). Although both $FeCl_2(THF)_{1.5}$ and [HIPr]Cl were insoluble in THF, the mixture changed from a suspended state to a colorless transparent liquid when their THF suspensions were mixed. After this workup, iron(II) complex [HIPr][Fe(C_4H_8O)Cl_3] (**1**) was obtained as colorless crystals in *ca.* 93% yield. Subsequent reaction of **1** with one equivalent of PPh_3 occurred quickly in THF at room temperature, resulting in the target ionic iron(II) complex [HIPr][Fe(PPh_3)Cl_3] (**2**) as colorless crystals in *ca.* 90% yield. Of note, complex **1** is very sensitive to air at room temperature in solid state, and its color changed quickly from colorless to yellowish in air. Its derived complex **2**, by contrast, is more tolerant to air, and can remain unchanged for at least one hour in open air.

Detailed examination revealed that complex **2** could be easily synthesized by a stepwise approach in *ca*. 91% yield (Scheme 1, eqn 2). The notable advantage of the stepwise approach is the needlessness to isolate and purify the monoimidazolium cation-supported iron(II) complex **1**. Similar protocol involving PCy_3 ligand leads to the formation of complex **3** as colorless crystals in *ca.* 92% yield. The exchange of the anion from Cl to Br also works smoothly by the addition of excess amounts of NaBr during the procedure (Scheme 1, eqn 3), affording the desired ionic iron(II) complexes **4**–**6** as pale yellow crystals in yields of 91%, 92% and 88%, respectively. The air tolerance of 3–**6** is closely similar to that of **2**, which provides a great convenience for their handle and application in catalysis. However, the color of their THF solutions changed slowly from colorless to yellow (for **2** and **3**) or color deepened (for **4**–**6**) in one hour upon expositing to open air.

Further attempts to synthesize the corresponding neutral iron(II) complex containing both a phosphine ligand and an NHC ligand by dehydrohalogenation of **4** or **5** with various bases, such as ^{n}BuLi[10a-b] or KO^{t}Bu,[10c] were investigated. Typically, the addition of one equivalent of base to a THF solution of **4** or **5** induced a color change to pale gray immediately. Unfortunately, our attempts to isolate the target iron(II) complex Fe(PPh_3)(IPr)Br_2 were unsuccessful, and only pure ionic iron(II) complex [Fe(IPr)Br_3](HIPr)·C_7H_8[14] was identified in this study.[15]

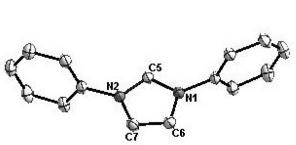


Figure 1. Molecular structure of **1** with thermal ellipsoids at the 30% probability level. Hydrogens and isopropyl groups are omitted for clarity. Selected bond lengths (Å) and angles (°): Fe(1)-O(1) 2.071(3), Fe(1)-Cl(1) 2.2857(13), Fe(1)-Cl(2) 2.2774(12), Fe(1)-Cl(3) 2.2684(10); O(1)-Fe(1)-Cl(1) 101.89(10), O(1)-Fe(1)-Cl(2) 100.38(8), O(1)-Fe(1)-Cl(3), 105.08(10), Cl(1)-Fe(1)-Cl(2) 114.61(4), Cl(1)-Fe(1)-Cl(3) 113.21(5), Cl(2)-Fe(1)-Cl(3) 118.61(4).

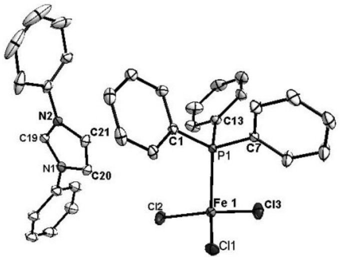


Figure 2. Molecular structure of **2** with thermal ellipsoids at the 30% probability level. Hydrogens and isopropyl groups are omitted for clarity. Selected bond lengths (Å) and angles (°): Fe(1)-P(1) 2.4604(8), Fe(1)-Cl(1) 2.3020(10), Fe(1)-Cl(2) 2.2692(9), Fe(1)-Cl(3) 2.2698(10); P(1)-Fe(1)-Cl(1) 102.33(4), P(1)-Fe(1)-Cl(2) 107.04(3), P(1)-Fe(1)-Cl(3) 119.50(4), Cl(1)-Fe(1)-Cl(2) 111.01(5), Cl(1)-Fe(1)-Cl(3) 119.50(4), Cl(2)-Fe(1)-Cl(3) 114.97(5).

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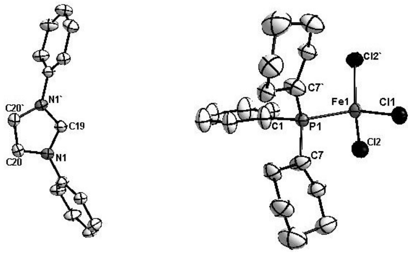

Figure 3. Molecular structure of **3** with thermal ellipsoids at the 30% probability level. Hydrogens and isopropyl groups are omitted for clarity. Selected bond lengths (Å) and angles (°): Fe(1)-P(1) 2.457(2), Fe(1)-Cl(1) 2.301(2), Fe(1)-Cl(2) 2.2777(16), Fe(1)-Cl`(2) 2.2777(16); P(1)-Fe(1)-Cl(1) 100.58(8), P(1)-Fe(1)-Cl(2) 110.33(5), P(1)-Fe(1)-Cl(2)` 110.33(5), Cl(1)-Fe(1)-Cl(2) 111.69(6), Cl(1)-Fe(1)-Cl(2)` 111.69(6), Cl(2)-Fe(1)-Cl(2)` 111.70(10).

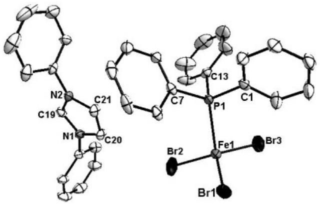

Figure 4. Molecular structures of **4** with thermal ellipsoids at the 30% probability level. Hydrogens and isopropyl groups are omitted for clarity. Selected bond lengths (Å) and angles (°): Fe(1)-P(1) 2.463(2), Fe(1)-Br(1) 2.4327(16), Fe(1)-Br(2) 2.3769(14), Fe(1)-Br(3) 2.4082(14); P(1)-Fe(1)-Br(1) 102.24(7), P(1)-Fe(1)-Br(2) 109.58(6), P(1)-Fe(1)-Br(3) 99.57(6), Br(1)-Fe(1)-Br(2) 111.27(6), Br(1)-Fe(1)-Br(3) 119.83(5), Br(2)-Fe(1)-Br(3) 112.66(7).

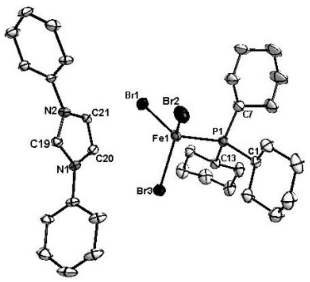

Figure 5. Molecular structures of **5** with thermal ellipsoids at the 30% probability level. Hydrogens and isopropyl groups are omitted for clarity. Selected bond lengths (Å) and angles (°): Fe(1)-P(1) 2.4566(14), Fe(1)-Br(1) 2.4393(9), Fe(1)-Br(2) 2.4062(10), Fe(1)-Br(3) 2.4473(9); P(1)-Fe(1)-Br(1) 108.31(4), P(1)-Fe(1)-Br(2) 114.80(4), P(1)-Fe(1)-Br(3) 97.54(4), Br(1)-Fe(1)-Br(2) 110.67(3), Br(1)-Fe(1)-Br(3) 111.15(4), Br(2)-Fe(1)-Br(3) 113.67(4).

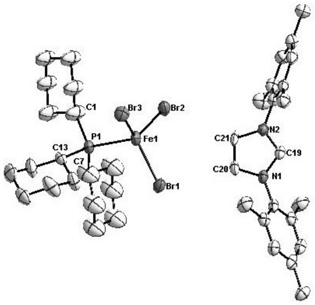

Figure 6. Molecular structures of **6** with thermal ellipsoids at the 30% probability level. Hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (°): Fe(1)-P(1) 2.441(2), Fe(1)-Br(1) 2.4428(13), Fe(1)-Br(2) 2.4272(11), Fe(1)-Br(3) 2.4095(12); P(1)-Fe(1)-Br(1) 108.65(6), P(1)-Fe(1)-Br(2) 106.04(5), P(1)-Fe(1)-Br(3) 102.89(6), Br(1)-Fe(1)-Br(2) 112.16(5), Br(1)-Fe(1)-Br(3) 112.28(5), Br(2)-Fe(1)-Br(3) 114.05(4).

These ionic iron(II) complexes **1**–**6** have been fully characterized by elemental analysis, electrospray ionization mass spectrometry (ESI-MS), ^{1}H NMR spectroscopy and X-ray crystallography. The positive ion ESI-MS of **1**–**6** were used to establish the presence of the imidazolium cation, and in all cases a peak with an intensity of almost 100% indicative of the imidazolium cation was observed. The ^{1}H NMR spectra of complexes **1**–**6** exhibited characteristic resonances similar to those of the corresponding imidazolium salts, except for the slight differences and broadening in the chemical shifts, together with one broad peak assigned to the signals of the protons of tetrahydrofuran appeared at 4.22 ppm for **1** and multiple broad and/or weak peaks assigned to the signals of the protons of phosphine ligands appeared at ranges of 0.37–10.54 ppm for **2**–**6**. The ^{13}P NMR spectra of **2**–**6** exhibited no signal in CD_3OCD_3, indicating the direct bonding of the phosphine ligand to the paramagnetic iron(II) center.[16] The more direct evidence of the formation of **1** and desired ionic iron(II) complexes **2**–**6** comes from X-ray structure determination.

The crystallographic and measurement data are listed in Tables S1 and S2 (see ESI†). The molecular structures of these complexes are shown in Figures **1**–**6**, along with key distances and angles.

To date, complex **1** is the second structural characterized ionic iron(II) complex bearing one imidazolium cation.[17] As shown in Figure 1, the solid-state structure of **1** consists of one $[Fe(C_4H_8O)Cl_3]^-$ anion and one $[HIPr]^+$ cation. The iron center is coordinated by three Cl atoms and one O atom from solvated THF molecule in a distorted tetrahedral geometry with angles at iron in the range 100.38(8)–118.61(4)°. The Fe-Cl[18] and Fe-O[14] bond lengths are very close to other ionic iron(II) complexes reported in literatures. The mean value of the Fe-Cl bond length is 2.277 Å. The bond distances and angles within the imidazolium ring and side chain differed only slightly, corresponding well with the related imidazolium salt [HIPr]Cl reported previously.[19c]

For complexes **2**–**6**, each of the five molecular structures contains one $[Fe(PR_3)X_3]^-$ anion and one imidazolium $[HL]^+$ cation. Similar to that of **1**, the structure of $[HIPr]^+$ or $[HIMes]^+$ cation do not change significantly on the reaction of the corresponding imiazolium salt with simple iron(II) salt and the phosphine ligand, and is also comparable to those of previously reported imidazolium salts, *i.e.* [HIPr]Cl and [HIMes]Cl,[19] respectively. In all five $[Fe(PR_3)X_3]^-$ anions, each iron atom is coordinated by three halogen atoms and one phosphorus atom in a distorted tetrahedral geometry with angles at iron in the range 102.33(4)–119.50(4)° for **2**, 100.58(8)–111.70(10)° for **3**, 99.57(6)–119.83(5)° for **4**, 97.54(4)–114.80(4)° for **5**, and 102.89(6)–114.05(4)° for **6**. The Fe–Cl, Fe–Br, and Fe–P bond lengths were found to lie in the ranges of 2.2692(9)–2.3020(10) Å, 2.3769(14)–2.4473(9) Å, and 2.441(2)–2.463(2) Å, respectively. The mean values of the Fe–Cl bond lengths are 2.280 Å for **2** and 2.285 Å for **3**, whereas the mean values of the Fe–Br bond lengths are 2.406 Å, 2.431 Å and 2.427 Å for **4–6**, respectively. The Fe–P bond length of 2.457(2) Å in **3** is almost the same as that of 2.4566(14) Å in **5**, even if they bear different halide atoms. The similar trend in the variation of Fe–

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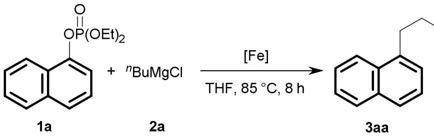
P bond lengths [2.4604(8) and 2.463(2) Å in **2** and **4**, respectively] is observed in the structures of **2** and **4**. These values are unexceptional and lie within the ranges found for other complexes containing $[Fe(PR_3)Cl_3]^-$ anion[18a-d] or other ionic iron(II) bromides.[14,16f]

Nevertheless, a detailed structural analysis reveals that there are some structural differences among these complexes. For example, the complex bearing a PCy_3 ligand has a slightly longer Fe-X bond and a slightly shorter Fe–P bond (compare **3** with **2**, and **5** with **4**), which mostly be consistent both with the larger steric bulkiness and the stronger σ-donor ability of the PCy_3 ligand relative to the PPh_3 ligand.[13b] With respect to the imidazolium cation, the complex containing a $[HIPr]^+$ cation has a longer Fe−P bond as well as a slightly longer Fe−Br bond (compare **5** with **6**), mostly due to the larger steric bulkiness of $[HIPr]^+$ cation relative to $[HIMes]^+$ cation.[19]

As expected, in structures of **1**, **2**, **4**, **5** and **6** described above, the imidazolium cation and the iron(II)-containing anion is held in place by extensive C–H···X interactions (general in contact below 3 Å),[14,17] together with extensive C–H···O interactions between imidazolium cation and solvated THF molecule for **1**, **3**, **5** and **6**. The shortest hydrogen bond of C–H···X interaction is found in **2**, stemming from H(19) to Cl(1) (2.513 Å).

Catalysis of ionic iron(II) complexes

Table 1. Iron-Catalyzed Cross-Coupling of **1a** with **2a**[a]

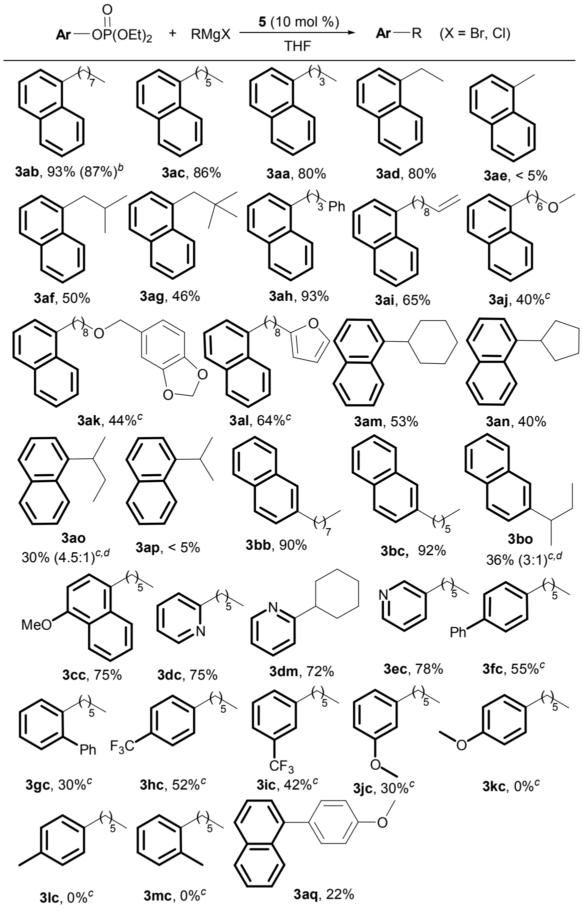


Entry	Catalyst (10 mol %)	Conversion (%)	Yield **3aa** (%)
1	**2**	99	76
2	**3**	99	84
3	**4**	99	82
4	**5**	99	90(80)[b](< 5%)[c]
5	**6**	99	81
6	**1**	99	65(76)[d]
7	$[HIPr][Fe(C_4H_8O)Br_3]$	99	72(80)[d]
8[e]	$FeCl_2$, [HIPr]Cl, PCy_3	99	80
9[e]	FeF_2, [HIPr]Cl, PCy_3	99	65
10	$Fe(PPh_3)_2Cl_2$	97	21
11	$Fe(PCy_3)_2Cl_2$	99	43
12	$FeCl_2$	99	34
13	$FeBr_2$	99	40

[a] Reaction conditions: 1-naphthyl diethyl phosphate (0.5 mmol), ${}^nBuMgCl$ (2 mmol), THF (total volume: 6 mL), 85 °C, 8 h, GC yields using *n*-hexadecane as internal standard; an average of two runs. [b] **5** (5 mol %). [c] Dibutylzinc (1 mmol). [d] PCy_3 (10 mol %) was added. [e] [HIPr]Cl (10 mol%) and PCy_3 (10 mol %).

The catalytic performances of complexes **1**–**6** were then investigated by reaction of **1a** with *n*-butylmagnesium chloride **2a**. In general, quantitative transformation of **1a** was observed under the optimal conditions. As shown in Table 1, **2**–**6** are capable of catalyzing the alkylation of **1a**, producing **3aa** in 76%–90% yields along with naphthalene byproduct in 23%–9% yields.[20] Among these catalysts, the bulky and more electron-rich complex **5**, $[HIPr][Fe(PCy_3)Br_3]$, is the most effective, affording **3aa** in 90% yield. Furthermore, the yield was 80% when the loading of **5** was lowered to 5.0 mol %. However, replacing ${}^nBuMgCl$ with ${}^nBu_2Zn$ resulted in the yield of **3aa** being less than 5%. In comparison, **1** and $[HIPr][Fe(C_4H_8O)Br_3]$ showed moderate catalytic activity in the cross-coupling, respectively furnishing yields of **3aa** of 65% (entry 5) and 70% (entry 6). The addition of PCy_3 (10 mol %) induced some acceleration of the cross-coupling reaction. A mixture of $FeCl_2$/[HIPr]Cl/PCy_3 afforded **3aa** in a 80% yield (entry 8). By the way, replacing $FeCl_2$ with FeF_2 led to a lower yield of 65% for desired product (entry 9), even if FeF_2 had successfully been employed in Grignard cross-coupling reactions with NHC ligands.[4h,21] The least effective complexes were $Fe(PPh_3)_2Cl_2$ and $Fe(PCy_3)_2Cl_2$ (entries 10 and 11). Similarly, simple iron salts $FeCl_2$ and $FeBr_2$ also provided **3aa** in low yields (entries 12 and 13). These results suggest that the combination of an electron-rich PCy_3 ligand with a bulky HIPr cation in an iron(II) complex makes the complex a more reactive catalyst in subsequent cross-coupling,[22] similar to the results obtained for palladium-[9] and nickel-[10] based systems.

Table 2. Representative Aryl–Alkyl Couplings[a]



[a] Reaction conditions: **5** (10 mol %), aryl phosphates (0.5 mmol), RMgCl (2 mmol), THF (total volume: 6 mL), 85 °C, 8 h, isolated yields. [b] RMgBr (2 mmol). [c] RMgCl (2.5 mmol). [d] Branched/linear ratio in parentheses.

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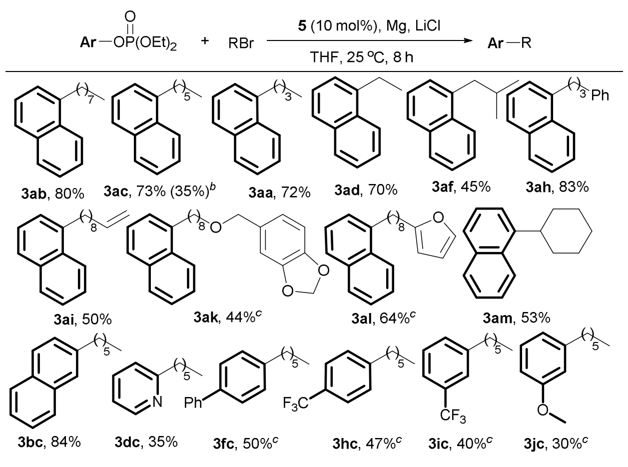
Table 2 presents the scope of this cross-coupling reaction using **5**, as reflected by a number of representative aryl phosphates **1** with diverse alkylation patterns. The nature of the nucleophile strongly influences the reaction. For example, **1a** coupled well with primary alkyl Grignard reagents with ≥ 2 carbon atoms to give the desired products (**3aa**–**3ad**) in 73%–93% yields. In contrast, methylmagnesium chloride failed to give the desired product **3ae**, which possibly indicates the *in situ* generation of low-valent iron species *via* β–H elimination.[4b,4e] In addition, the counteranion of the Grignard reagent also has some effect on the reaction. For example, *n*-octylMgCl provided a slightly higher yield of **3ab** than *n*-octylMgBr. Notably, steric bulk at the β-position of the alkyl spacer in the Grignard reagents **3af** and **3ag** was tolerated. Functional groups in the Grignard reagents such as phenyl (**3ah**), vinyl (**3ai**), ether (**3aj**), and ketal (**3ak**) survived in the reaction. In addition, a furan-containing Grignard reagent gave **3al** in a yield of 64%. Secondary cyclic Grignard reagents, *i.e.*, cyclohexyl and cyclopentylmagnesium chloride, coupled somewhat slowly to give the corresponding coupling products in 53% (**3am**) and 40% (**3an**) yield. In comparison, 2-butylmagnesium chloride provided the desired **3ao** in a lower yield of 30% with a moderate branch selectivity. Nevertheless, these latter three results reveal the potential of **5** in C–C bond formation *via* the cross-coupling between secondary C_{sp3} organometallic species and aryl C_{sp2} centers, which is still a challenging research topic in transition metal-catalyzed cross-coupling reactions.[23] However, the attempt to extend the substrate to an isopropyl Grignard reagent was unsuccessful (**3ap**), as Shi *et al.*[4e] reported. To date, only two papers have described the use of isopropylmagnesium chloride[4g] or bromide[6d] in iron-catalyzed cross-couplings with C-O electrophiles.

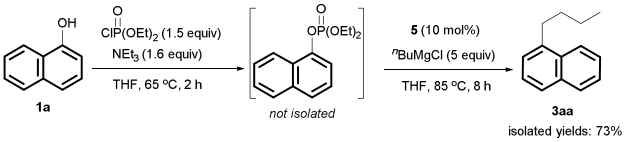
Table 3. Reductive Cross-Couplings of Aryl Phosphates with Alkyl Bromides[a]



[a] Reaction conditions: **5** (10 mol %), aryl phosphates (0.5 mmol), RBr (2.5 mmol), magnesium turnings (2.6 mmol), LiCl (2.6 mmol), isolated yields. [b] RCl (2.5 mmol). [c] RBr (3.0 mmol).

The scope of the methodology also includes a variety of aryl phosphates that are compatible with the cross-coupling reaction. For 2-naphthyl phosphate, the reaction with *n*-octyl and *n*-hexyl Grignard reagents afforded the corresponding desired products in 90% (**3bb**) and 92% (**3bc**) yields, respectively. Conversely, a lower yield of 36% was obtained with 2-buylmagnesium chloride (**3bo**). A strongly electron-donating OMe group on the aryl ring of phosphate does not greatly affect the product yield (**3cc**). Notably, 2-pyridyl and 3-pyridyl phosphates coupled efficiently with primary or secondary Grignard reagents under standard reaction conditions to give the coupling products in 72%–78% yields (**3dc**, **3dm** and **3ec**). In addition, 4-biphenyl phosphate, a rare used C–O electrophile, also gave a moderate yield of the desired product (**3fc**) by increasing the dosage of Grignard reagent, meanwhile its *ortho*-analogue gave a lower yield of 30% (**3gc**). Under the same reaction conditions, less reactive non-fused phenyl substrates, such as 4-trifluoromethylphenyl, 3-trifluoromethylphenyl, and 3-methoxyphenyl phosphates, are capable of giving the coupling products in 35%–52% yields (**3hc**, **3ic** and **3jc**). However, non-fused phenyl phosphates possessing electron-rich substituents at either *ortho*- or *para*-position (**3kc**, **3lc** and **3mc**) were inert in this study, which are quite similar to those reported previously for a $Fe(acac)_3$-catalyzed aryl tosylates-involved approach.[4a] The cross-coupling of **3a** with 4-methoxyphenylmagnesium chloride provided the desired **3aq** in a low yield of 22%.

Recently, iron-catalyzed reductive cross-coupling reactions between two electrophiles have received increasing attention as an attractive alternative strategy to traditional Grignard reactions.[24] This new reaction pattern features the *in situ* generation of Grignard reagents, and thus exhibits lower hazard potential, better operational simplicity and cost savings compared with conventional Grignard reactions.[24a] In this context, von Wangelin and co-workers achieved the reductive cross-coupling reaction of allyl phosphates and aryl bromides with a $FeCl_3$/TMEDA/Mg/LiCl system.[24b] However, the related cross-coupling of aryl phosphates and alkyl halides has not been explored. Thus, we decided to investigate the possibility of extension of the cross-coupling of **1** and **2** to a reductive version. To our delight, iron(II) complex **5** is also capable of catalyzing the reductive cross-coupling of aryl phosphates with alkyl bromides in the presence of stoichiometric Mg and LiCl.[25] As seen from Table 3, the desired products were obtained in yields very close to those achieved from the traditional reactions (see Table 2). Nevertheless, it is worth noting that alkyl chlorides showed low activity toward the reductive cross-coupling (**3ac**), possibly because of their relatively low activity in the initiation stage of Grignard reagent formation compared with alkyl bromides.



Scheme 2. One-Pot Acylation/Cross-Coupling Sequence

Scheme 2 presents another powerful version of the cross-coupling reaction described herein. Because the pivalylation of phenolic substrates typically proceeds quantitatively with minimal byproduct formation,[26] a one-pot acylation/cross-

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coupling sequence from 1-naphthol was successful, affording the desired **3aa** in 73% yield.

Conclusions

In summary, we synthesized a new type of ionic iron(II) complex containing both a phosphine ligand and an imidazolium cation. We demonstrated their great catalytic potential in the cross-coupling of aryl phosphates with alkyl Grignard reagents, as well as in both the corresponding reductive cross-coupling and the one-pot acylation/cross-coupling sequence. Thus, this work disclosed the great potential to utilize an aryl phosphate as an electrophile in iron-catalyzed C-C bond formation. Since a variety of phosphine ligands as well as imidazolium cations are available, this work also provides an attractively alternative strategy for building highly active and, yet somewhat robust catalysts of iron. Investigations aimed at further fine-tuning their catalytic activity by surveying well-matched pairs of phosphine ligands and imidazolium cations, probing mechanistic aspects of these findings, and synthesizing the corresponding mixed phosphine/*N*-heterocyclic carbene iron(II) complexes are on going.

Experimental section

General procedures

All manipulations were performed under pure argon with exclusion of air and moisture using standard Schlenk techniques. Solvents were distilled from Na/benzophenone ketyl under pure argon prior to use. All the substrates, reagents and materials were purchased from Sigma Aldrich, Alfa Aesar and TCI Chemicals. 1,3-Bis(2,6-diisopropylphenyl)-imidazolium chloride ([HIPr]Cl),[19c] 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride ([HIMes]Cl),[19c] [HIPr][Fe(C_4H_8O)Br_3],[14] Fe(PPh_3)$_2$$Cl_2$[27] and Fe($PCy_3$)$_2$$Cl_2$[28] were prepared by published methods. Elemental analysis was 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 melt points were determined on a Diamond DSC (Perkin Elmer) using powder samples under N_2 atmosphere (50 mL/min). The system was heated from 50 to 350 °C at 20 °C /min. Gas chromatographic (GC) analysis was performed on a Varian CP-3800 instruments equipped with an FID detector and a capillary column AT.OV-101 (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. High resolution mass spectra were obtained using GCT-TOF instrument with ESI or CI source.

[HIPr][Fe(C_4H_8O)Cl_3] (**1**). Following a procedure similar to the synthetic procedure of [HIPr][Fe(C_4H_8O)Br_3][14], a Schlenk flask was charged with [HIPr]Cl (0.76 g, 1.80 mmol), THF (40.0 mL), and a stirring bar. To this suspension was added a THF (10 mL) suspension of $FeCl_2(THF)_{1.5}$ (0.42 g, 1.80 mmol). The reaction mixture was stirred for 4 h at room temperature, during which time the mixture became a homogeneous colorless solution. The reaction solution was filtered, and evaporated to dryness. The residue was washed with hexane (3 × 10.0 mL), extracted with THF (3 × 10.0 mL), and crystallized from concentrated THF at 0 °C. The product **1** was precipitated as colorless crystals in a yield of 93% (1.04 g), mp 170 °C. Anal. calcd for $C_{31}H_{45}Cl_3FeN_2O$: C, 59.68; H, 7.27; N, 4.49. Found: C, 59.66; H, 7.30; N, 4.45. ^{1}H NMR (δ, 400 MHz, $(CD_3)_2CO$): 1.24 (s, 24H, $CH(CH_3)_2$), 2.55 (s, 4H, $CH(CH_3)_2$), 4.22 (br s, $O(CH_2CH_2)_2$), 7.47 (s, 4H, *m*-C_6H_3), 7.62 (s, 2H, *p*-C_6H_3), 8.18 (s, 2H, NCHCHN), 9.66 (s, 1H, NCHN). MS (ESI+): *m/z* 389.2954 $[C_{27}H_{37}N_2]^+$ (100%).

[HIPr][Fe(PPh_3)Cl_3] (**2**). Procedure A: a Schlenk flask was charged with [HIPr][Fe(C_4H_8O)Cl_3] (0.12 g, 1.93 mmol), THF (40.0 mL), and a stirring bar. To the colorless solution was then added PPh_3 (0.510 g, 1.93 mmol). After stirred for 2 h at room temperature, the reaction solution was filtered, and evaporated to dryness. The residue was washed with hexane (3 × 10.0 mL), extracted with THF (3 × 10.0 mL), and crystallized from concentrated THF at 0 °C. The product was precipitated as colorless crystals in a yield of 90% (1.42 g), mp 185 °C. Anal. calcd for $C_{45}H_{52}Cl_3FeN_2P$: C, 66.39; H, 6.44; N, 3.44. Found: C, 66.37; H, 6.40; N, 3.41. ^{1}H NMR (δ, 400 MHz, $(CD_3)_2CO$): 1.22 (s, 24H, $CH(CH_3)_2$), 2.54 (s, 4H, $CH(CH_3)_2$), 5.33 (br s, $P(C_6H_5)_3$), 6.66 (br s, $P(C_6H_5)_3$), 7.44 (s, 4H, *m*-C_6H_3), 7.58 (s, 2H, *p*-C_6H_3), 8.14 (s, 2H, NCHCHN), 9.27 (br s, $P(C_6H_5)_3$), 9.65 (s, 1H, NCHN). MS (ESI+): *m/z* 389.2954 $[C_{27}H_{37}N_2]^+$ (100%).

Procedure B: a Schlenk flask was charged with [HIPr]Cl (0.82 g, 1.93 mmol), THF (40 mL), and a stirring bar. To this suspension solution was added a THF (10 mL) suspension of $FeCl_2(THF)_{1.5}$ (0.45 g, 1.93 mmol). The reaction mixture was stirred for 4 h at room temperature. To the resulting colorless solution was then added PPh_3 (0.510 g, 1.93 mmol). The reaction mixture was stirred for 2 h at room temperature. After workup, the product was precipitated as colorless crystals in a yield of 91% (1.43 g).

[HIPr][Fe(PCy_3)Cl_3] (**3**). Following a procedure similar to the procedure B of **2** except that PCy_3 was used instead of PPh_3, the product **3** was precipitated as colorless crystals in a yield of 92% (1.45 g), mp 172 °C. Anal. calcd for $C_{45}H_{70}Cl_3FeN_2P$: C, 64.94; H, 8.48; N, 3.37. Found: C, 64.93; H, 8.46; N, 3.36. ^{1}H NMR (δ, 400 MHz, $(CD_3)_2CO$): 0.37 (br s, $P(C_6H_{11})_3$), 0.95–0.97 (m, $P(C_6H_{11})_3$), 1.34 (s, 24H, $CH(CH_3)_2$), 1.60 (br s, $P(C_6H_{11})_3$), 2.73 (s, 4H, $CH(CH_3)_2$), 3.95 (br s, $P(C_6H_{11})_3$), 4.16 (s, $P(C_6H_{11})_3$), 5.65 (br s, $P(C_6H_{11})_3$), 7.53 (s, 4H, *m*-C_6H_3), 7.63 (s, 2H, *p*-C_6H_3), 8.47 (s, 2H, NCHCHN), 9.79 (s, 1H, NCHN). MS (ESI+): *m/z* 389.2966 $[C_{27}H_{37}N_2]^+$ (100%).

[HIPr][Fe(PPh_3)Br_3] (**4**). A Schlenk flask was charged with [HIPr]Cl (0.848 g, 2.03 mmol), THF (40 mL), NaBr (0.627 g, 6.09 mmol) and a stirring bar. To this suspension was added a THF (10 mL) solution of $FeBr_2$ (0.439 g, 2.03 mmol). The reaction mixture was stirred for 12 h at the reflux temperature of THF. To this cooled suspension was then added PPh_3 (0.532 g, 2.03 mmol). After stirred for 2 h at room temperature, the reaction solution was filtered, and evaporated to dryness. The residue was washed with hexane (3 × 10.0 mL), extracted with THF (3 × 10.0 mL), and crystallized from

DOI: 10.1039/C6DT02995G

concentrated THF at 0 °C. The product was precipitated as pale yellow crystals in a yield of 91% (1.74 g), mp 193 °C. Anal. calcd for $C_{45}H_{52}Br_3FeN_2P$: C, 57.05; H, 5.53; N, 2.96. Found: C, 57.03; H, 5.50; N, 2.94. ^{1}H NMR (δ, 400 MHz, $(CD_3)_2CO$): 1.29–1.35 (m, 24H, $CH(CH_3)_2$), 2.64 (s, 4H, $CH(CH_3)_2$), 4.38 (br s, $P(C_6H_5)_3$), 7.12 (br s, $P(C_6H_5)_3$), 7.52 (s, 4H, *m*-C_6H_3), 7.66 (s, 2H, *p*-C_6H_3), 8.29 (s, 2H, NCHCHN), 9.73 (s, 1H, NCHN), 10.54 (br s, $P(C_6H_5)_3$). MS (ESI+): *m/z* 389.2959 $[C_{27}H_{37}N_2]^+$ (100%).

[HIPr][Fe(PCy$_3$)Br$_3$] (**5**). Following a procedure similar to that of **4** except that PCy_3 was used instead of PPh_3, the product **5** was precipitated as pale yellow crystals in a yield of 92% (2.21 g), mp 180 °C. Anal. calcd for $C_{45}H_{70}Br_3FeN_2P$: C, 55.97; H, 7.31; N, 2.90. Found: C, 55.95; H, 7.30; N, 2.89. ^{1}H NMR (δ, 400 MHz, $(CD_3)_2CO$): 0.46 (br s, $P(C_6H_{11})_3$), 1.32–1.36 (m, 24H, $CH(CH_3)_2$), 1.70 (br s, $P(C_6H_{11})_3$), 1.86 (br s, $P(C_6H_{11})_3$), 2.77 (m, 4H, $CH(CH_3)_2$), 3.76 (s, $P(C_6H_{11})_3$), 4.48 (br s, $P(C_6H_{11})_3$), 5.78 (br s, $P(C_6H_{11})_3$), 7.54–7.56 (m, 4H, *m*-C_6H_3), 7.66–7.68 (m, 2H, *p*-C_6H_3), 8.91 (s, 2H, NCHCHN), 9.91 (s, 1H, NCHN). MS (ESI+): *m/z* 389.2959 $[C_{27}H_{37}N_2]^+$ (100%).

[HIMes][Fe(PCy$_3$)Br$_3$] (**6**). Following a procedure similar to that of **4** except that [HIMes]Cl was used instead of [HIPr]Cl, the product **6** was precipitated as pale yellow crystals in a yield of 88% (1.18 g), mp 179 °C. Anal. calcd for $C_{39}H_{58}Br_3FeN_2P$: C, 53.14; H, 6.63; N, 3.18. Found: C, 53.10; H, 6.66; N, 3.16. ^{1}H NMR (δ, 400 MHz, $(CD_3)_2CO$): 0.48 (br s, $P(C_6H_{11})_3$), 0.93 (br s, $P(C_6H_{11})_3$), 1.32 (br s, $P(C_6H_{11})_3$), 1.70 (br s, $P(C_6H_{11})_3$), 2.33 (s, 12H, CH_3), 2.46 (s, 6H, CH_3), 3.77 (s, $P(C_6H_{11})_3$), 4.42 (br s, $P(C_6H_{11})_3$), 5.71 (br s, $P(C_6H_{11})_3$), 7.30 (s, 4H, *m*-C_6H_2), 8.49 (s, 2H, NCHCHN), 9.50 (s, 1H, NCHN). MS (ESI+): *m/z* 305.2002 $[C_{21}H_{25}N_2]^+$ (100%).

General Procedure for the Cross-Coupling of Aryl Phosphates with Alkyl Grignard Reagents.

A Schlenk flask was charged with complex **5** (0.05 g, 0.05 mmol), aryl phosphates (0.5 mmol), THF (3 mL) and a stirring bar. The mixture was stirred at 0 °C for 2 min. To this stirred mixture was added the solution of alkyl Grignard reagents (2.0 mL, 1.0 M in THF) at 0 °C via syringe. The resulting solution turned black immediately and was then stirred for 8 h in an oil bath at 85 °C. The reaction was quenched by addition of saturated ammonium chloride solution, the mixture was extracted with ethyl acetate (3 × 3.0 mL) and dried over Na_2SO_4. The GC yield of the desired product is determined by GC analysis, using *n*-hexadecane as an internal standard. 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 NMR spectroscopy and TLC.

General Procedure for the Cross-Coupling of Aryl Phosphates with Alkyl Bromides.

A Schlenk flask was charged with complex **5** (0.05 g, 0.05 mmol), magnesium turnings (62.4 mg, 2.6 mmol), aryl phosphates (0.5 mmol) and a stirring bar. To this flask was added than 5.2 mL of a solution of LiCl (0.5 M in THF) via syringe. The mixture was cooled down to 0 °C in an ice-water bath. To this stirred mixture, alkyl bromides (2.5 mmol) were added at 0 °C via syringe. The reaction mixture was then stirred for 10 h at 25 °C. The reaction was quenched by addition of saturated ammonium chloride solution, the mixture was extracted with ethyl acetate (3 × 3.0 mL) and dried over Na_2SO_4. The GC yield of the desired product is determined by GC analysis, using *n*-hexadecane as an internal standard. 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 NMR spectroscopy and TLC.

General Procedure for the One-Pot Acylation/Cross-Coupling Sequence.

A Schlenk flask was charged with 1-naphthol (0.07 g, 0.5 mmol), THF (4 mL) and a stirring bar. To the solution was added dropwise diethyl chlorophosphate (108 μL, 0.75 mmol) at 0 °C via syringe with stirring. The mixture was stirred at 0 °C for 2 min. To this stirred mixture was then added dropwise triethylamine (112 μL, 0.8 mmol) at 0 °C via syringe. The reaction mixture was stirred for 2 h in an oil bath at 65 °C. After cooling the mixture to 0 °C (ice water bath), *n*-butylmagnesium chloride (2.5 mL, 1.0 M in THF) and complex **5** (0.05 g, 0.05 mmol) were added sequentially. The reaction mixture was stirred for 8 h in an oil bath at 85 °C. The reaction was quenched by addition of saturated ammonium chloride solution, the mixture was extracted with ethyl acetate (3 × 3.0 mL) and dried over Na_2SO_4. The GC yield of the desired product is determined by GC analysis, using *n*-hexadecane as an internal standard. 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 NMR spectroscopy and TLC.

Acknowledgements

We are grateful to the National Natural Science Foundation of China (Grants 21472134 and 21172164), the Key Laboratory of Organic Chemistry of Jiangsu Province, and the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD) for financial support.

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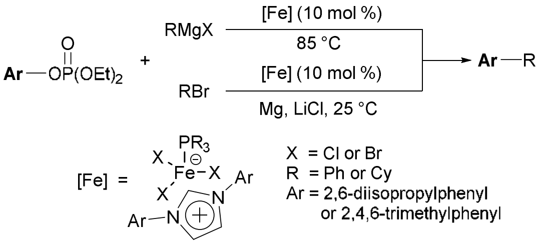
DOI: 10.1039/C6DT02995G

Alkyl Grignard cross-coupling of aryl phosphates catalyzed by new, highly active ionic iron(II) complexes containing a phosphine ligand and an imidazolium cation

Zhuang Li, Ling Liu, Hong-mei Sun,* Qi Shen and Yong Zhang



Ionic iron(II) complexes, [HL][Fe(PR_3)X_3], showed high catalytic activities in alkyl Grignard cross-coupling of aryl phosphates, and the corresponding reductive cross-coupling.