

Synthesis of Anionic Iron(II) Complex Bearing an N-Heterocyclic Carbene Ligand and Its Catalysis for Aryl Grignard Cross-Coupling of Alkyl Halides

Huan-huan Gao, Chun-hui Yan, Xue-Ping Tao, Ying Xia, Hong-Mei Sun,* Qi Shen, and Yong Zhang

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

Received May 17, 2010

Summary: The reaction of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) with one equivalent of a novel imidazolium salt of iron(II), [FeBr₃(C_4H_8O)](HIPr)· C_4H_8O (1), afforded the anionic iron(II) complex bearing an N-heterocyclic carbene ligand [Fe(IPr)Br₃](HIPr)· C_7H_8 (2), which shows extremely high activity in comparison with the other iron(II)-based precatalysts in the cross-coupling reaction of 4-tolylmagnesium bromide with cyclohexyl bromide.

Introduction

During the past decade, N-heterocyclic carbenes (NHCs) have received increasing attention as alternative ligands for the development of late transition metal based homogeneous catalysts,¹ which is mostly due to their advantages over traditional phosphine ligands such as stronger σ -electron donation, tighter coordination, and more steric bulkiness.² In most cases, the replacement of phosphine ligands with electron-rich NHC ligands is of benefit to improve the stability and catalytic activity of their complexes. As a result, a large number of well-defined NHC complexes of Pd(II), especially singly ligated NHC complexes such as [(NHC)Pd(allyl)Cl]^{3a} and [(NHC)PdCl₂-(pyr)] (pyr = 3-chloropyridine),^{3b} have been found to show

*To whom correspondence should be addressed. Fax: (86)512-65880305. Tel: (86)512-65880330. E-mail: sunhm@suda.edu.cn.

(2) (a) Kühl, O. Chem. Soc. Rev. 2007, 36, 592–607. (b) Hahn, F. E.; Jahnke,
 M. C. Angew. Chem., Int. Ed. 2008, 47, 3122–3172. (c) Jacobsen, H.; Correa, A.;
 Poater, A.; Costabile, C.; Cavallo, L. Coord. Chem. Rev. 2009, 253, 687–703.

(3) For recent reviews see: (a) Christmann, U.; Vilar, R. Angew. Chem., Int. Ed. 2005, 44, 366–374. (b) Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G. Angew. Chem., Int. Ed. 2007, 46, 2768–2813. (c) Marion, N.; Nolan, S. P. Acc. Chem. Res. 2008, 41, 1440–1449.

(4) For recent reviews see: (a) Bolm, C.; Legros, J.; Paih, J. Le.; Zani,
L. Chem. Rev. 2004, 104, 6217–6254. (b) Fürstner, A.; Martin, R. Chem.
Lett. 2005, 34, 624–629. (c) Sherry, B. D.; Fürstner, A. Acc. Chem. Res.
2008, 41, 1500–1511. (d) Enthaler, S.; Junge, K.; Beller, M. Angew. Chem.,
Int. Ed. 2008, 47, 3317–3321. (e) Correa; Manchen, O. G.; Bolm, C. Chem.
Soc. Rev. 2008, 37, 1108–1117. (f) Plietker, B., Ed. Iron Catalysis in
Organic Chemistry; Wiley-VCH: Weinheim, 2008. (g) Czaplik, W. M.;
Mayer, M.; Jacobi von Wangelin, A. Angew. Chem., Int. Ed. 2009, 48, 607–610. (h) Czaplik, W. M.; Cwengoš, J.; Jacobi von Wangelin, A.
ChemSusChem 2009, 2, 396–417. (i) Nakamura, E.; Yoshikai, N. J. Org.
Chem. 2010, DOI: 10.1021/jo100693m.

outstanding catalytic activity for cross-coupling reactions and related transformations.³ However, in comparison with intensively studied palladium-based complexes, the NHC complexes of iron remain scarely considered in this respect, ^{li} even if the development of iron-based catalysts is of great interest due to iron being more cost-effective and environmentally benign compared to palladium.⁴

In fact, iron remains one of the least studied late transition metals with NHCs.¹ⁱ To date, only a few kinds of welldefined iron NHC complexes have been reported, which include hexacarbene complexes,⁵ tetracarbene complexes,⁶ tricarbene complexes,⁷ biscarbene complexes,⁸ and pianostool monocarbene complexes that are co-ligated by cyclopentadienyl and CO ligands.⁹ Among them, only two biscarbene complexes, i.e., $Fe(NHC)_2X_2^{8a}$ and $Fe(CNC)Br_2$ [CNC = 2,6-bis(imidazolylidene)pyridine],^{8b} have been found to show good catalytic activity for atom transfer radical polymerization of styrene and methyl methacrylate^{8a} and the cross-coupling reaction of 4-tolylmagnesium bromide with cyclohexyl bromide.¹⁰ Therefore, further study on the breadth of iron-based NHC complexes, in parallel with the growing interest for iron catalysis, is highly desired.¹¹

As a continuation of our research on the iron¹¹ and nickel¹² chemistry of NHCs, we herein report the synthesis

(5) Fränkel, R.; Kernbach, U.; Bakola-Christianopoulou, M.; Plaia, U.; Suter, M.; Ponikwar, W.; Nöth, H.; Moinet, C.; Fehlhammer, W. P. *J. Organomet. Chem.* **2001**, *617–618*, 530–545.

(6) McGuinness, D. S.; Gibson, V. C.; Steed, J. W. Organometallics 2004, 23, 6288–6292.

(7) (a) Nieto, I.; Cervantes-Lee, F.; Smith, J. M. *Chem. Commun.* **2005**, 3811–3813. (b) Vogel, C.; Heinemann, F. W.; Sutter, J.; Anthon, C.; Meyer, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 2681–2684.

(8) (a) Louie, J.; Grubbs, R. H. *Chem. Commun.* 2000, 1479–1480. (b) Danopoulos, A. A.; Tsoureas, N.; Wright, J. A.; Light, M. E. *Organometallics* 2004, *23*, 166–168. (c) Danopoulos, A. A.; Wright, J. A.; Motherwell, W. B. *Chem. Commun.* 2005, 784–786. (d) Liu, B.; Xia, Q. Q.; Chen, W. Z. *Angew. Chem., Int. Ed.* 2009, *48*, 5513–5516.

(9) (a) Buchgraber, P.; Toupet, L.; Guerchais, V. *Organometallics* **2003**, *22*, 5144–5147. (b) Llewellyn, S. A.; Green, M. L. H.; Green, J. C.; Cowley, A. R. *Dalton Trans.* **2006**, 2535–2541. (c) Mercs, L.; Labat, G.; Neels, A.; Ehlers, A.; Albrecht, M. *Organometallics* **2006**, *25*, 5648–5656.

(10) Bedford, R. B.; Betham, M.; Bruce, D. W.; Danopoulos, A. A.;
Frost, R. M.; Hird, M. J. Org. Chem. 2006, 71, 1104–1110.
(11) (a) Chen, M. Z.; Sun, H. M.; Li, W. F.; Wang, Z. G.; Shen, Q.;

(11) (a) Chen, M. Z.; Sun, H. M.; Li, W. F.; Wang, Z. G.; Shen, Q.; Zhang, Y. J. Organomet. Chem. **2006**, 691, 2489–2494. (b) Wang, Y. S.; Sun, H. M.; Tao, X. P.; Shen, Q.; Zhang, Y. Chin. Sci. Bull. **2007**, 52, 3193–3199.

(12) (a) Sun, H. M.; Shao, Q.; Hu, D. M.; Li, W. F.; Shen, Q.; Zhang, Y. Organometallics 2005, 24, 331–334. (b) Li, W. F.; Sun, H. M.; Chen, M. Z.; Wang, Z. G.; Hu, D. M.; Shen, Q.; Zhang, Y. Organometallics 2005, 24, 5925–5928. (c) Li, W. F.; Sun, H. M.; Wang, Z. G.; Chen, M. Z.; Shen, Q.; Zhang, Y. J. Organomet. Chem. 2005, 690, 6227–6232. (d) Sun, H. M.; Hu, D. M.; Wang, Y. S.; Shen, Q.; Zhang, Y. J. Organomet. Chem. 2007, 692, 903–907. (e) Li, W. F.; Sun, H. M.; Chen, M. Z.; Shen, Q.; Zhang, Y. J. Organomet. Chem. 2008, 693, 2047–2051.

Published on Web 08/26/2010

For recent reviews see: (a) Bourissou, D.; Guerret, O.; Gabbaï,
 F. P.; Bertrand, G. Chem. Rev. 2000, 100, 39–1203. (b) Herrmann, W. A. Angew. Chem., Int. Ed. 2002, 41, 1290–1309. (c) Peris, E.; Crabtree, R. H. Coord. Chem. Rev. 2004, 248, 2239–2246. (d) Crudden, C. M.; Allen, D. P. Coord. Chem. Rev. 2004, 248, 2247–2273. (e) Pugh, D.; Danopoulos, A. A. Coord. Chem. Rev. 2007, 251, 610–641. (f) Mata, J. A.; Poyatos, M.; Peris,
 E. Coord. Chem. Rev. 2007, 251, 841–859. (g) Würtz, S.; Glorius, F. Acc. Chem. Res. 2008, 41, 1523–1533. (h) Boeda, F.; Nolan, S. P. Annu. Rep. Prog. Chem. Sect. B 2008, 104, 184–210. (i) Diez-González, S.; Marion, N.; Nolan, S. P. Chem. Rev. 2009, 109, 3612–3676.



Figure 1. Crystal structure of 1 with thermal ellipsoids at the 30% probability level (only one disordered coordinating THF molecule shown). Hydrogen atoms and the cocrystallized non-coordinating THF molecule are omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe(1)-Br(1) 2.4267(17), Fe(1)-Br(2) 2.4128(16), Fe(1)-Br(3) 2.4148(16), Fe(1)-O(1) 2.062(16), H(6)-Br(2) 2.92, H(7)-Br(1) 2.95; O(1)-Fe(1)-Br(1) 104.4(4), O(1)-Fe(1)-Br(2) 98.9(4), O(1)-Fe(1)-Br(3) 106.1(4), Br(1)-Fe(1)-Br(2) 113.40(6), Br(1)-Fe(1)-Br(3) 115.21(6), Br(2)-Fe(1)-Br(3) 116.33(6).

Scheme 1

$$\begin{array}{rl} \mathsf{FeBr}_2 + & \mathsf{Ar} - \mathsf{N} \overset{\mathsf{H}}{\bigoplus} \mathsf{N}^{\mathsf{P}} - \mathsf{Ar} & \xrightarrow{\mathsf{THF}} & [\mathsf{FeBr}_3(\mathsf{C}_4\mathsf{H}_8\mathsf{O})](\mathsf{H}|\mathsf{Pr}) \cdot \mathsf{C}_4\mathsf{H}_8\mathsf{O} \\ & & \mathsf{H}|\mathsf{Pr} \cdot \mathsf{Br} & \mathbf{1} \\ \mathsf{Ar} = 2,6 \text{-diisopropylphenyl} \end{array}$$

and molecular structure of an anionic mononuclear iron(II) complex bearing one NHC ligand, $[Fe(IPr)Br_3](HIPr) \cdot C_7H_8$ (2), which represents the first example of singly ligated NHC complexes of iron(II). The preliminary results on its catalytic activity for the cross-coupling of 4-tolylmagnesium with cyclohexyl bromide and other alkyl halides bearing β -hydrogen are also described.

Results and Discussion

Our approach toward the target iron(II) complex starts from a novel N,N-diarylimidazolium salt of iron(II), **1**. At room temperature, anhydrous FeBr₂ reacted slowly with one equivalent of imidazolium salt HIPr·Br in THF (Scheme 1). After the mixture was stirred for 24 h, removal of the solvent *in vacuo* and recrystallization from THF produces yellow crystals of [FeBr₃(C₄H₈O)](HIPr)·C₄H₈O (**1**) in ca. 70% yield, as identified by elemental analysis and X-ray diffraction (Figure 1). Complex **1** is sensitive to air at room temperature, and its color changed gradually from yellow to red and to brown in air.

When one equivalent of IPr was added to the THF solution of **1** at room temperature, the resulting solution changed color from yellow to pale gray quickly, accompained by the appearance of white precipitates. After stirring for 6 h, the solution was filtered and evaporated to dryness. The residue was extracted with toluene. A white powder was



Figure 2. Crystal structure of $2 \cdot 2C_7H_8$ with thermal ellipsoids at the 30% probability level. Hydrogen atoms and three toluene molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe(1)-Br(1) 2.4356(9), Fe(1)-Br(2) 2.4600(12), Fe(1)-C(1) 2.110(7); C(1)-Fe(1)-Br(1) 108.18(9), C(1)-Fe(1)-Br(2) 116.11(18), Br(1)-Fe(1)-Br(2) 104.52(3), Br(1A)-Fe(1)-Br(2) 104.52(3).

Scheme 2

$$1 + Ar - N \xrightarrow{\bullet} N - Ar \xrightarrow{THF / Toluene} [Fe(IPr)Br_3](HIPr) \cdot C_7H_8$$

IPr 2
Ar = 2,6-diisopropylphenyl

isolated from a concentrated toluene solution in ca. 55% yield, which was identified to be $[Fe(IPr)Br_3](HIPr) \cdot C_7H_8$ (2) by elemental analysis (Scheme 2). Recrystallization from toluene afforded colorless crystals of $[Fe(IPr)Br_3](HIPr) \cdot 3C_7H_8$ (2 · 2C₇H₈) suitable for X-ray structure determination (Figure 2). Complex 2 is thermally stable, but is very sensitive to air compared to complex 1.

Complexes 1 and 2 were structurally determined by X-ray crystallography. The crystallographic and measurement data are shown in Table 1. Their crystal structures are depicted in Figures 1 and 2.

To date, complex 1 is the first structurally characterized imidazolium salt of iron(II).¹³ As shown in Figure 1, the iron center is coordinated by three Br atoms and one O atom from the solvated THF molecule in a distorted tetrahedral geometry with angles at iron in the range $98.9(4)-116.33(6)^{\circ}$. The Fe–Br^{8b,14} and Fe–O¹⁵ bond lengths are very close to other iron(II) complexes reported in the literature. Notably, two Br atoms of the anion form obvious hydrogen bonding

 ^{(13) (}a) Dupont, J.; de Souza, R. F.; Suarez, P. A. Z. Chem. Rev. 2002, 102, 3667–3692.
 (b) Pârvulescu, V. I.; Hardacre, C. Chem. Rev. 2007, 107, 2615–2665.

⁽¹⁴⁾ O'Reilly, R. K.; Shaver, M. P.; Gibson, V. C.; White, J. P. *Macromolecules* **2007**, *40*, 7441–7452.

⁽¹⁵⁾ Bartlett, R. A.; Ellison, J. J.; Power, P. P.; Shoner, S. C. Inorg. Chem. 1991, 30, 2888–2894.

Table 1. X-ray Crystallographic Data for 1 and 2

	1	$2 \cdot 2 C_7 H_8$
empirical formula	C35H53Br3FeN2O2	C75H97Br3FeN4
fw	829.37	1350.15
temperature (K)	223(2)	223(2)
λ(Mo Ka) (Å)	0.71075	0.71075
cryst syst	monoclinic	monoclinic
space group	P21/c	C2/m
unit cell dimens		
a(A)	12.221(2)	25.818(4)
$b(\mathbf{A})$	32.359(5)	17.062(2)
$c(\mathbf{A})$	10.1880(17)	20.125(3)
β (deg)	96.912(5)	127.016(4)
$V(Å^3)$	3999.7(11)	7078.8(19)
Z	4	4
$D_{\text{calc}} (\text{g cm}^{-3})$	1.377	1.267
$\mu (\mathrm{mm}^{-1})$	3.403	1.949
<i>F</i> (000)	1696	2824
cryst size (mm)	0.80 imes 0.80 imes 0.50	$0.80 \times 0.25 \times 0.20$
θ range (deg)	3.03-25.50	3.05-25.50
no. of reflns collected	20 224	18 183
no. of reflns unique, R_{int}	7417, 0.0692	6762, 0.0389
goodness-of-fit on F^2	1.126	1.070
$R_1, wR_2 \left[I > 2\sigma(I) \right]$	0.0917, 0.2160	0.0780, 0.2052
R_1, wR_2 (all data)	0.1516, 0.2449	0.1009, 0.2218

with the H6 and H7 protons of the imidazolium ring, respectively.¹⁶ Thus, complex **1** can be described as a simple collection of ion pairs, which is quite different from those found in N,N'-dialkylimidazolium-based salts; that is, the general formula [HNHC]₂[MCl₄] (M = Pd¹⁷ and Ni¹⁸) was reported. This unique pattern in **1** is mostly attributed to the steric bulkiness of the aryl-substituted imidazolium cation.

X-ray structure determination revealed that complex 2 is an anionic mononuclear iron(II) complex. As seen from Figure 2, the iron center is coordinated by a carbene carbon atom and three Br atoms in a distorted tetrahedral geometry with angles in the range $104.52(3)-116.11(18)^\circ$. The bond length of Fe- $C_{carbene}$ in 2 is 2.110(7) Å, which falls within the range of previously reported values in iron NHC complexes, i.e., shorter than those in Fe(CNC)Br₂ (2.166(10) and 2.193(10) Å),^{8b} HB(^tBuIm)₃FeBr (^tBuIm = 1-*tert*-butylimidazol, 2.123(3)-2.135(3) Å),^{7a} and *trans*-Fe(NHC)₂Cl₂ (2.1363(15) Å),^{8a} while longer than those in Fe(aryloxo-functionalized NHC)₂ (2.076(4)-2.094(4) Å),^{11a} Fe(alkenyloxofunctionalized NHC)₂ (2.023(7)-2.047(5) Å),^{11b} CpFe(CO)₂-(NHC)I (1.980(5) Å),^{9a} [Fe(2,6-bis(NHC)pyridine)(MeCN)₃]-[BPh₄]₂ (1.944(5) and 1.947(5) Å),^{8b} and [Fe(bis(pyridylimidazolidene)methane)₂](PF₆)₂ (1.801(6) Å).^{8d} A notable feature in this structure is that there is no discrete hydrogen bonding interaction between the Br atoms of the anion and any proton of the imidazolium ring, which is quite different from the interaction between the anion and the cation present in 1. The Fe-Br bond lengths of 2.4356(9) and 2.4600(12) A in 2 are significantly longer than those found in 1, which reflects a bulky hindrance around the center metal exerted by the IPr ligand and/or a strong σ -electron donation of the IPr ligand. Additionally, the carbene ring plane is oriented nearly perpendicular to that occupied by three bromide ligands.

 Table 2. Activities of Catalytic Systems Based on Iron(II)

 Complexes^a

run ^b	precatalyst	precatalyst loading (mol %)	yield ^c
1	FeBr ₂	5	41
2	1	3	74
3	$1 + HIPr \cdot Br$	3	80
4	2	1	96
5	2	0.5	89
6^d	2	1	83
7^e	2	1	90
8 ^f	2	1	86
9^g	Fe(CNC)Br ₂	5	94 ^h

^{*a*} Cyclohexyl bromide (1.0 mmol), 4-MeC₆H₄MgBr (1.5 mmol), Et₂O, reflux, 30 min, Ar. ^{*b*} 4-MeC₆H₄MgBr was added in one portion at 0 °C, the reaction solution was stirred for 2 min and then refluxed for 30 min. ^{*c*} Yield of the isolated product after column chromatography, average of 2 trials. ^{*d*} Cyclopentyl bromide (1.0 mmol). ^{*e*} 2-Bromohexane (1.0 mmol). ^{*f*} 1-Bromooctane. ^{*g*} Cyclohexyl bromide (2.0 mmol), 4-MeC₆H₄MgBr (4.0 mmol), Et₂O, reflux, 30 min. ^{*h*} Conversion.

During the past few years, one of the most notable successes in iron-based catalysis is that several well-defined iron complexes have been developed for the cross-coupling reaction of aryl Grignard reagents with primary or secondary alkyl halides bearing β -hydrogens, which is mostly due to their ability to suppress the undesired β -hydrogen elimination efficiently as well as their potential from a mechanistic point of view.¹⁹ To assess the catalytic activity of complex **2** and related iron(II)-based salts, the reaction shown in eq 1 was chosen, as it is a prototype cross-coupling of aryl Grignard reagents with alkyl halides bearing β -hydrogens.^{10,19}

$$-\underbrace{H}_{1.5 \text{ equiv.}}^{\text{Br}} + \underbrace{\frac{2: 0.5 \sim 1 \text{ mol }\%}{\text{Et}_2 \text{O}, \text{ reflux, 30 min}}}_{\text{Et}_2 \text{O}, \text{ reflux, 30 min}} \tag{1}$$

It is worth noting that the present cross-coupling reaction can be performed successfully at elevated temperature, and the Grignard reagent can be added in one portion at room temperature without the requirement of slow addition via a syringe pump. The preliminary results are listed in Table 2. Complex 2 showed the highest activity. Almost a quantitative yield of the coupling product was obtained at 1 mol % loading, and the yield still reached 89% even when the loading was reduced to 0.5 mol % (runs 4, 5). Meanwhile, 1 exhibited moderate activity and provided a coupling product in 74% yield with a 3 mol % loading (run 2), and FeBr₂ was the least active one, affording the product merely in 41% yield with a 5 mol % loading (run 1). The difference in activity between 1 and FeBr₂ may be attributed to the more stable active species in 1 stabilized by imidazolium salts. 13b, 19c Considering the suggestion that the NHC ligand could be formed *in situ* via the deprotonation of an imidazolium salt by Grignard reagents,^{11,10} the same reaction with a mixture of 1 and HIPr.Br was conducted. However, this reaction gave the product in a yield almost the same as that obtained by 1, indicating that it is not as easy as expected to form a IPr ligand in situ under the present reaction conditions (run 3). Alternatively, it is not easy to form a Fe-Ccarbene bond in situ. The same situation was also recently

⁽¹⁶⁾ Taylor, R.; Kennard, O. J. Am. Chem. Soc. 1982, 104, 5063-5070.

^{(17) (}a) Ortwerth, M. F.; Wyzlic, M. J.; Baughman, R. G. Acta Crystallogr. **1998**, C54, 1594–1596. (b) Yang, X.; Fei, Z.; Geldbach, T. J.; Phillips, A. D.; Hartinger, C. G.; Li, Y.; Dyson, P. J. Organometallics **2008**, 27, 3971–3977.

⁽¹⁸⁾ Hitchcock, P. B.; Seddon, K. R.; Welton, T. J. Chem. Soc., Dalton Trans. 1993, 2639–2643.

^{(19) (}a) Martin, R.; Fürstner, A. Angew. Chem., Int. Ed. 2004, 43, 3955–3957. (b) Bedford, R. B.; Bruce, B. W.; Frost, R. M.; Goodby, J. W.; Hird, M. Chem. Commun. 2004, 2822–2823. (c) Bica, K.; Gaertner, P. Org. Lett. 2006, 8, 733–735. (d) Chowdhury, R. R.; Crane, A. K.; Fowler, C.; Wong, P. K.; Kozak, C. M. Chem. Commun. 2008, 94–96.

reported by Nakamura et al..²⁰ Thus, it is reasonable that the high activity shown by **2** in the present cross-coupling reaction is related to the presence of a Fe- $C_{carbene}$ bond in complex **2**. In addition, complex **2** also showed good catalytic activity for the cross-coupling reaction of 4-tolylmagnesium bromide with other alkyl bromides, such as cyclopentyl bromide, 2-bromohexane, and 1-bromooctane (runs 6–8).

Notably, the catalytic activity of **2** is found to be much higher than that of a biscarbene complex of iron(II) Fe-(CNC)Br₂ reported by Bedford et al. (run 9).¹⁰ Normally, 2–5 mol % or higher loadings of iron complexes are usually required to achieve satisfactory yields for the reaction shown in eq 1.^{10,19} Therefore, the present results suggest that complex **2** might be among the most efficient precatalysts for the cross-coupling reaction of aryl Grignard reagents with alkyl halides bearing β -hydrogens, possibly due to a singly ligated NHC active species with high nucleophilicity.³

Conclusions

A novel anionic iron(II) complex bearing a bulky NHC ligand, $[Fe(IPr)Br_3](HIPr) \cdot C_7H_8$ (2), has been easily synthesized for the first time by the reaction of a new imidazolium salt of iron(II), $[FeBr_3(C_4H_8O)](HIPr) \cdot C_4H_8O$ (1), with an equivalent of carbene ligand IPr. Complex 2 has been found to show potential application as a precatalyst in the cross-coupling reaction of aryl Grignard reagents with alkyl halides bearing β -hydrogens under mild reaction conditions. Further studies on the scope of this reaction and the application of this new strategy in the synthesis of NHC complexes of other transition metals are ongoing in our laboratory.

Experimental Section

General Considerations. 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. Organic reagents used for cross-coupling reactions were purchased from Aldrich, and phenylmagnesium bromide was diluted prior to use. Anhydrous FeBr₂ was isolated from the reaction of HBr (40%) with excess iron powder in Ar as a yellowish-brown powder. 1,3-Bis(2,6-diisopropylphenyl)imidazolium bromide (HIPr·Br)²¹ and IPr²² 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 Unity Inova-400 spectrometer at 25 °C.

Structure Determination. For 1 or 2, a suitable crystal was mounted in a thin-walled glass capillary for X-ray structural

analysis. Diffraction data were collected on a Rigaku Mercury CCD area detector at 193(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.

Synthesis of $[FeBr_3(C_4H_8O)](HIPr) \cdot C_4H_8O$ (1). A Schlenk flask was charged with bis(2,6-diisopropylphenyl)imidazolium bromide (1.9062 g, 4.06 mmol), THF (20 mL), and a stirring bar. To this suspension solution was added FeBr₂ (0.8770 g, 4.06 mmol) in 60 mL of THF. The reaction mixture was stirred for 24 h at room temperature, filtered, and evaporated to dryness. The residue was extracted with THF, and recrystallization from concentrated THF yielded yellow crystals (2.36 g, 70%) suitable for elemental analysis and X-ray diffraction determination. Mp: 95–97 °C. Anal. Calcd for C₂₇H₃₇Br₃FeN₂(C₄H₈O)₂: C, 50.69; H, 6.44; N, 3.38. Found: C, 50.29; H, 6.87; N, 3.08.

Synthesis of $[Fe(IPr)Br_3](HIPr) \cdot C_7H_8$ (2). A Schlenk flask was charged with 1 (1.9072 g, 2.30 mmol), THF (15 mL), and a stirring bar. To this solution was added IPr (0.8878 g, 2.30 mmol) in 15 mL of THF. The resulting solution changed color from yellow to pale gray quickly, accompanied by the appearance of white precipitates. After stirring for 6 h at room temperature, the suspension solution was filtered and evaporated to dryness. The residue was extracted with toluene. The product 2 was obtained as a white powder from concentrated toluene in ca. 55% yield (1.47 g), which was suitable for elemental analysis. Mp: 119–121 °C. Anal. Calcd for $C_{54}H_{73}Br_3$ -FeN₄(C_7H_8): C, 62.84; H, 7.00; N, 4.81. Found: C, 62.94; H, 7.02; N, 4.46.

General Procedure for the Cross-Coupling of 4-Tolylmagnesium Bromide with Alkyl Bromides. A Schlenk tube was charged with iron(II)-based precatalyst (0.05 mmol), alkyl bromide (1.00 mmol), diethyl ether (0.8 mL), and a stirring bar. The mixture was stirred at 0 °C for 2 min. 4-Methylphenylmagnesium bromide (1.50 mmol, 0.89 M solution in diethyl ether) was added to this solution at 0 °C. The resulting solution changed color to black and was then stirred for 30 min at reflux (oil bath temperature was ca. 45 °C). After the reaction was quenched by adding dilute hydrochloric acid (1 M, 0.5 mL), the mixture was extracted with diethyl ether and dried with MgSO₄. The solvents were removed under reduced pressure, and the residual mixture was separated by column chromatography by eluting with petroleum ether (60-90 °C) to give the desired coupling product. The identity of the product was confirmed by ¹H NMR spectroscopy and TLC.

Acknowledgment. We are grateful to the National Natural Science Foundation of China (Grant 20772089) for the financial support.

Supporting Information Available: Crystallographic data, in CIF format, for the structure analyses of **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

⁽²⁰⁾ Hatakeyama, T.; Hashimoto, S.; Ishizuka, K; Nakamura, M. J. Am. Chem. Soc. 2009, 131, 11949–11963.

⁽²¹⁾ Arduengo, A. J., III. U.S. Patent 5 077 414, 1991.

⁽²²⁾ Arduengo, A. J., III; Dias, H. V. R.; Harlow, R. L.; Kline, M. J. Am. Chem. Soc. **1992**, 114, 5530–5534.