

Accepted Article

Title: Cross-coupling Reactions of Alkyl Halides with Aryl Grignard Reagents using a Tetrachloroferrate with an Innocent Countercation

Authors: Toru Hashimoto, Tsubasa Maruyama, Takamichi Yamaguchi, Yutaka Matsubara, and Yoshitaka Yamaguchi

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Adv. Synth. Catal. 10.1002/adsc.201900568

Link to VoR: http://dx.doi.org/10.1002/adsc.201900568

COMMUNICATION

DOI: 10.1002/adsc.201((will be filled in by the editorial staff))

Cross-coupling Reactions of Alkyl Halides with Aryl Grignard Reagents using a Tetrachloroferrate with an Innocent Countercation

Toru Hashimoto,^{a,*} Tsubasa Maruyama,^a Takamichi Yamaguchi,^a Yutaka Matsubara,^a and Yoshitaka Yamaguchi^{a,*}

 ^a Department of Advanced Materials Chemistry, Graduate School of Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan Phone:(+81)-45-339-3932 Fax: (+81)-45-339-3932 E-mail: hashimoto-toru-kh@ynu.ac.jp and yamaguchi-yoshitaka-hw@ynu.ac.jp

Received: ((will be filled in by the editorial staff))

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201#######.

Abstract. Bis(triphenylphosphoranylidene)ammonium tetrachloroferrate, (PPN)[FeCl₄] (1), was evaluated as a catalyst for cross-coupling reactions. 1 exhibits high stability toward air and moisture and is an effective catalyst for the reaction of secondary alkyl halides with aryl Grignard reagents. The PPN cation is considered as an innocent counterpart to the iron center. We have developed an easy-to-handle iron catalyst for "ligand-free" cross-coupling reactions.

Keywords: Iron; ferrate salt; cross-coupling reaction; alkyl halide; Grignard reagent

Transition-metal-catalyzed cross-coupling reactions between organic electrophiles and organometallic reagents represent one of the most powerful strategies for the construction of carbon–carbon bonds.^[1] Since the discovery of cross-coupling reactions, palladium and nickel complexes have been extensively studied as catalysts, and continuous improvements have resulted in the development of highly efficient catalytic systems. Considerable attention has also been focused on the use of iron catalysts in these reactions, given that iron is an ideally suited practical transition metal owing to its low cost, low toxicity, and abundance.^[2] The first discovery of FeCl₃catalyzed cross-coupling reactions was reported by Kochi in 1971.^[3] In 1998, Cahiez used an iron/NMP (NMP = N-methylpyrrolidinone) system, in which NMP serves as a co-solvent that has a beneficial impact on reactions involving alkenyl electrophiles.^[4] Subsequently, Fürstner improved this Fe(acac)₃/NMP (acac = 2,4-pentanedionato) system for reactions using aryl chlorides and triflates.^[5, 6]

So far, various catalyst systems have been developed combining iron sources such as FeCl₃ and $Fe(acac)_3$ with donor molecules such as amines,^[7] phosphines,^[7h, 8] or N-heterocyclic carbenes (NHCs)^{[8a,} ^{9, 10]} as ligands and/or additives.^[11] In addition, welldefined iron complexes also have been developed as catalysts for the coupling reactions.^{[7h-7j, 8b-8i, 9d-9g, 11e,} ^{11g]} Moreover, it has been reported that Fe(acac) itself acts as an effective catalyst for the coupling reactions. Fe(acac)₃ is commercially available and stable toward air and moisture. It is thus an easy-tohandle iron source for the preparation of iron. complexes and catalysts. While FeCl₃ is arguably one of the most basic iron sources, it is unfortunately hydroscopic. Therefore, the development of easy-tohandle iron sources for large-scale industrial processes remains highly desirable.

Iron-containing imidazolium salts, generally classified as ionic liquids, show high stability toward air and moisture. In addition, these salts act as efficient catalysts for cross-coupling reactions.^[12, 13] In these catalytic systems, the formation of iron-NHC species as the catalytically active species by *in-situ* deprotonation of the azolium cation with a Grignard reagent cannot be ruled out.^[8a, 9, 10] Therefore, we were interested in the development of easy-to-handle iron catalysts and the realization of "ligand-free" iron catalysis for cross-coupling reactions. Herein, we report the cross-coupling of alkyl halides with aryl



Scheme 1. The cross-coupling reactions catalyzed by (PPN)[FeCl₄] (1) reported in this work.

Grignard reagents catalyzed by (PPN)[FeCl₄] (1), i.e., a tetrachloroferrate bearing the innocent cation bis(triphenylphosphoranylidene)ammonium (PPN), (Scheme 1).

Tetrachloroferrate 1 was prepared according to a literature method,^[14] i.e., by treating anhydrous FeCl₃ equimolar with an amount of bis(triphenylphosphoranylidene)ammonium chloride ((PPN)Cl) in MeOH at room temperature. Salt 1 was obtained in 91% yield as a yellow solid (Scheme 2) and characterized by elemental analyses and X-ray diffraction study (Figure 1). Interestingly, 1 is not hydroscopic and highly stable toward atmospheric air and moisture.^[15, 16] Moreover, 1 showed good solubility in THF and NMP, whereas it was poorly soluble in ethereal solvents such as Et₂O, tert-butyl methyl ether (MTBE), 1,2-dimethoxyethane (DME), and cyclopentyl methyl ether (CPME).

$$\begin{pmatrix} PPh_3 \\ N' \\ PPh_3 \end{pmatrix}$$
Cl + FeCl₃ \longrightarrow $\begin{pmatrix} PPh_3 \\ N' \\ PPh_3 \end{pmatrix}$ [FeCl₄]
1, 91%

Scheme 2. Preparation of catalyst (PPN)[FeCl₄] (1).



Figure 1. ORTEP drawing of (PPN)[FeCl₄] (1) with thermal ellipsoids at 30% probability. All hydrogen atoms have been omitted for clarity.

In order to evaluate the catalytic activity of 1, the cross-coupling reaction of bromocyclohexane (2a) with 1.2 equivalents of phenylmagnesium bromide was carried out in the presence of 5 mol% of 1 in various solvents (Table 1). In the case of THF, the cross-coupled product, phenylcyclohexane (3a), was obtained in 26% yield, together with the homocoupled product from phenylmagnesium bromide (biphenyl) in 36% yield (entry 1). In this case, 33% of the starting material (2a) was recovered. When the mixed solvent THF/NMP (9/1; v/v) was used, 3a was obtained in 27% yield (entry 2). Using NMP as the

Table 1. Optimization of the conditions for the crosscoupling of bromocyclohexane (2a) with phenylmagnesium bromide catalyzed by $1^{[a]}$



^[a] The reaction was carried out using **2a** (0.5–1.0 mmol) and PhMgBr (0.6–1.2 mmol, 1.2 equiv) in the presence of **1** (5 mol%) at room temperature. ^[b] The yield of **3a** is based on **2a** and wau determined by gas-liquid chromatography (GLC) analysis using undecane as the internal standard. ^[c] The yield of biphenyl is based on PhMgBr and was determined by GLC analysis using undecane as the internal standard. ^[d] THF/NMP = 9/1 (v/v). ^[e] The reaction (7.0 mmol scale) was carried out for 1.5 h using 1 mol% of **1**.

 Table 2. Substrate scope of the cross-coupling reaction of alkyl halides with aryl Grignard reagents catalyzed by 1^[a]



^[a] The reaction was carried out using alkyl halides 2 (0.5–1.0 mmol) and an aryl Grignard reagent (1.2–1.5 equiv) in the presence of 1 (5 mol%) at room temperature. ^[b] Isolated yield. ^[c] The yield of **3a** is based on **2b** or **2c** and was determined by GLC analysis using undecane as the internal standard.

solvent furnished 3a in 22% yield (entry 3). Subsequently, we investigated the reaction the aforementioned ethereal, albeit that 1 is poorly soluble in these solvents. In Et₂O, the yield of 3a increased to 58% yield, but the reaction did not reach completion (entry 4). MTBE and DME were not suitable solvents, i.e., **3a** was obtained merely in low yield (28% and 34%; entries 5 and 6). As shown in entry 7, CPME provided the best results, affording **3a** in 94% yield together with small amounts of biphenyl (10% yield based on PhMgBr). This catalytic protocol based on **1** was also successful on the gramscale (7 mmol of **2a**). In this case, the reaction proceeded efficiently to give **3a** in 88% yield, even when the amount of **1** was reduced to 1 mol% (entry 8).

To demonstrate the efficiency of **1** as a catalyst for such cross-coupling reactions, we investigated the substrate scope with a variety of alkyl halides and aryl Grignard reagents under the optimized reaction conditions, and the results are summarized in Table 2. Using *p*-tolylmagnesium bromide, **3b** was obtained in 95% yield (entry 1). p-Methoxyphenylmagnesium bromide afforded 3c in 90% yield (entry 2), while pdimethylaminophenylmagnesium bromide furnished a slightly lower yield of 3d (78%, entry 3). p-Fluorophenylmagnesium bromide, which bears an electron-withdrawing substituent, afforded **3e** in 63% yield (entry 4). Next, we investigated the influence of different electrophiles. The reaction between iodocyclohexane (2b) and PhMgBr furnished 3a in 69% yield (entry 5). In the case of chlorocyclohexane (2c), the yield of 3a decreased to 41% (entry 6). Bromocycloheptane (2d) was also tolerated as a coupling partner, affording **3f** in 50% yield (entry 7). The reaction of acyclic alkyl bromide 2e generated 3g in 81% yield, whereas the iodo analogue 2f provided 3g in 53% yield (entries 8 and 9). As shown in entry 10, the siloxy substituent on the alkyl chain remained intact and the product was obtained in 72% yield. o-Tolylmagnesium bromide gave the corresponding product **3i** in moderate yield^[7h] (entry 11). We next examined the reaction with primary alkyl halides. The reaction using 1-bromodecane (2h) proceeded sluggishly to give coupling product 3j in 30% yield under concomitant formation of decane (15%) and 1decene (40%). Furthermore, 15% of bromide 2h was recovered (entry 12). In the case of 1-iododecane (2i), the corresponding product (3j) was obtained in 32% vield.^[17] Moreover, benzylmagnesium bromide furnished 3k in 75% yield (Scheme 3).^[8b, 8g-8i]



Scheme 3. Coupling reaction of 2a with benzylmagnesium bromide catalyzed by 1.

To gain insight into the reaction mechanism,^[18] we investigated the coupling reaction using *trans*-4-benzyloxycyclohexyl bromide (2j) and (bromomethyl)cyclopropane (2k) as electrophiles under standard conditions (Schemes 4 and 5). Treatment of 2j with PhMgBr afforded a mixture of

stereoisomers **31** in 69% yield (*trans:cis* = 74:26). In the case of **2k**, the simple coupled product **3m** was not detected, whereas ring-opened product **3n** was obtained in 13% yield. Overall, these results indicated that the cross-coupling reaction catalyzed by **1** likely involves radical species.^[7b, 8a, 8c, 8e, 8g]



Scheme 4. Coupling reaction of 2j with PhMgBr catalyzed by 1.



Scheme 5. Coupling reaction of 2k with PhMgBr catalyzed by 1: radical clock experiment.

Furthermore, we examined the isolation of any potentially formed iron species. However, all attempts to obtain such species were unsuccessful. Although the actual structure of the intermediates in our catalytic system is not clear at this point, we assume that the [FeCl₄]⁻ anion of **1** plays an important role in the catalytic cycle. When other iron salts such as FeCl₃, FeCl₂, or Fe(acac)₃ were employed as catalysts under otherwise identical reaction conditions, the coupled product 3a was obtained in 90%, 93%, and 94% yield, respectively (Scheme 6). These results indicate that both 1 and these other iron compounds afford similarly active iron species via the reduction of a Grignard reagent in the catalytic cycle. Accordingly, we assume that the PPN cation in 1 does not engage in the catalytic reaction, i.e., the PPN cation can be considered as an innocent counterpart to the iron center.



Scheme 6. Cross-coupling reactions using iron salts in CPME.

In conclusion, we have reported (PPN)[FeCl₄] (1) as an efficient catalyst for the coupling of secondary alkyl halides with aryl and benzyl Grignard reagents under mild reaction conditions. 1 exhibits high stability toward air and atmospheric moisture. The

results described in this paper may thus promote the development of "ligand-free" iron-catalyzed reactions. Further investigations into the (i) mechanistic aspects of this catalytic system, including the role of the countercation, ferrate, and the solvent, (ii) the coupling of various organometallic reagents with organic electrophiles, and (iii) the development of novel organic transformations are currently in progress in our group.

Experimental Section

Preparation for (PPN)[FeCl4] (1): A Schlenk tube was charged with anhydrous FeCl₃ (0.608 g, 3.75 mmol), bis(triphenylphosphoranylidene)ammonium chloride ((PPN)Cl, 2.18 g, 3.80 mmol) and dry MeOH (45 mL) at room temperature. After stirring overnight, the solvent was removed *in vacuo* to give a yellow residue that was washed with Et₂O (4×10 mL) and dissolved in THF (20 mL). The solution was filtered through a pad of Celite and concentrated *in vacuo*. The residue was washed with hexane to give **1** as a yellow solid (2.50 g, 91%). IR (Diamond-ATR, neat): 2359, 1436, 1264, 1182, 1112, 1027, 997, 720, 688, 530, 495, 373 cm⁻¹. Anal. calcd for C₃₆H₃₀Cl₄FeNP₂, C, 58.73; H, 4.11; N, 1.90, found C, 58.74; H, 4.12; N, 1.84.

General procedure for the cross-coupling reactions: A Schlenk tube was charged with 1 (5 mol%), CPME (5 mL), the respective alkyl halide (0.50 mmol), and a Grignard reagent (1.2–1.5 equiv) at room temperature. The coupling reaction was carried out at room temperature for 1–24 h. After quenching with HCl (1 M, 2.0 mL), the aqueous layer was extracted with Et_2O (5 × 3 mL). The combined organic layers were washed with brine (5 mL) and dried over anhydrous MgSO4. After filtration and removal of all volatiles from the filtrate, the residue was purified by column chromatography on silica gel.

Acknowledgements

This work was supported by a Chugai Award in Synthetic Organic Chemistry, Japan, and JSPS KAKENHI grant JP17K05805. This work was also supported by the Collaborative Research Program of the Institute for Chemical Research, Kyoto University (grant 2018-24). The authors are grateful to Mr. Shinji Ishihara (Yokohama Natl. Univ.) for carrying out the elemental analyses and Dr. Takahiro Iwamoto and Prof. Masaharu Nakamura (Kyoto Univ.) for their kind help with the HRMS measurements. We thank Zeon Co., Ltd. for their generous donation of CPME. We also thank Hokko Chemical Industry Co., Ltd. for the generous supply of 4-fluorophenylmagnesium bromide.

References and Notes

- Metal-Catalyzed Cross-Coupling Reactions, 2nd ed. (Eds.; A. de Meijere, F. Diederich), Wiley-VCH: Weinheim, 2004.)
- [2] For reviews, see: a) C. Bolm, J. Legros, J. L. Paih, L. Zani, *Chem. Rev.* 2004, 104, 6217–6254; b) B. D. Sherry, A. Fürstner, *Acc. Chem. Res.* 2008, 41, 1500–1511; c) W. M. Czaplik, M. Mayer, J. Cvengros, A. J. von Wangelin, *ChemSusChem* 2009, 2, 396–417; d) R. Jana, T. P. Pathak, M. S. Sigman, *Chem. Rev.* 2011, 111, 1417–1492; e) A. Fürstner, *ACS Cent. Sci.* 2016, 2,

778–789. f) A. Piontek, E. Bisz, M. Szostak, Angew. Chem. **2018**, 130, 11284–11297; Angew. Chem., Int. Ed. **2018**, 57, 11116–11128.

- [3] a) M. Tamura, J. K. Kochi, J. Am. Chem. Soc. 1971, 93, 1487–1489; b) S. M. Smith, J. K. Kochi, J. Org. Chem. 1975, 40, 599–606; c) R. S. Smith, J. K. Kochi, J. Org. Chem. 1976, 41, 502–509.
- [4] G. Cahiez, H. Avedissian, Synthesis 1998, 119-1205.
- [5] a) A. Fürstner, A. Leitner, Angew. Chem. 2002, 114, 632–635; Angew. Chem., Int. Ed. 2002, 41, 609–612;
 b) A. Fürstner, A. Leitner, M. Méndez, H. Krause, J. Am. Chem. Soc. 2002, 124, 13856–13863; c) A. Fürstner, H. Krause, C. W. Lehmann, Angew. Chem. 2006, 118, 454–458; Angew. Chem., Int. Ed. 2006, 45, 440–444.
- [6] It has been reported that NMP can interact with the magnesium centers in iron-catalyzed cross-coupling reactions; for details, see: S. B. Muñoz III, S. L. Daifuku, J. D. Sears, T. M. Baker, S. H. Carpenter, W. W. Brennessel, M. L. Neidig, Angew. Chem. 2018, 130, 6606–6610; Angew. Chem., Int. Ed. 2018, 57, 6496– 6500.
- [7] a) M. Nakamura, K. Matsuo, S. Ito, E. Nakamura, J. Am. Chem. Soc. 2004, 126, 3686-3687; b) R. B. Bedford, D. W. Bruce, R. M. Frost, M. Hird, Chem. Commun. 2005, 4161-4163; c) G. Cahiez, V. Habiak, C. Duplais, A. Moyeux, Angew. Chem. 2007, 119, 4442-4444; Angew. Chem. Int. Ed. 2007, 46, 4364-4366.; d) A. Guérinot, S. Reymond, J. Cossy, Angew Chem. 2007, 119, 6641-6644; Angew. Chem. Int. Ed. 2007, 46, 6521–6524.; e) S. Ito, Y. Fujiwara, F Nakamura, M. Nakamura, Org. Lett. 2009, 11, 4306-4309; f) T. Hatakeyama, N. Nakagawa, M. Nakamura. Org. Lett. 2009, 11, 4496–4499; g) S. E. Denmark, A. J. Cresswell, J. Org. Chem. 2013, 78, 12593-12628; h) C.-L. Sun, H. Krause, A. Fürstner, Adv. Synth. Catal. 2014, 356, 1281–1291; i) R. B. Bedford, P. B. Brenner, D. Elorriaga, J. N. Harvey, J. Nunn, Dalton Trans. **2016**, 45, 15811–15817; j) Y. Matsubara, T. Yamaguchi, T. Hashimoto, Y. Yamaguchi, Polyhedron, 2017, 128, 198-202.
- [8] a) R. B. Bedford, M. Betham, D. W. Bruce, A. A. Danopoulos, R. M. Frost, M. Hird, J. Org. Chem. 2006, 71, 1104-1110; b) R. B. Bedford, M. Huwe, M. C. Wilkinson, Chem. Commun. 2009, 600-602; c) T. Hatakeyama, Y. Kondo, Y. Fujiwara, H. Takaya, S. Ito, E. Nakamura, M. Nakamura, Chem. Commun. 2009 1216-1218; d) R. B. Bedford, M. A. Hall, G. R. Hodges, M. Huwe, M. C. Wilkinson, Chem. Commun. 2009, 6430-6432; e) T. Hatakeyama, Y. Fujiwara, Y. Okada, T. Itoh, T. Hashimoto, S. Kawamura, K. Ogata, H. Takaya, M. Nakamura, Chem. Lett. 2011, 40, 1030-1032; f) S. Kawamura, T. Kawabata, K. Ishizuka, M. Nakamura, Chem. Commun. 2012, 48, 9376-9378; g) T. Hatakeyama, T. Hashimoto, Y. Kondo, Y. Fujiwara, H. Seike, H. Takaya, Y. Tamada, T. Ono, M. Nakamura, J. Am. Chem. Soc. 2010, 132, 10674-10676; h) R. B. Bedford, P. B. Brenner, E. Carter, T. W. Carvell, P. M. Cogswell, T. Gallagher, J. N. Harvey, D. M. Murphy, E.

C. Neeve, J. Nunn, D. R. Pye, *Chem.-Eur. J.* **2014**, *20*, 7935–7938; i) R. B. Bedford, P. B. Brenner, E. Carter, J. Clifton, P. M. Cogswell, N. J. Gower, M. F. Haddow, J. N. Harvey, J. A. Kehl, D. M. Murphy, E. C. Neeve, M. L. Neidig, J. Nunn, B. E. R. Snyder, J. Taylor, *Organometallics* **2014**, *33*, 5767–5780; j) M. Jin, L. Adak, M. Nakamura, J. Am. Chem. Soc. **2015**, *137*, 7128–7134; k) T. Iwamoto, C. Okuzono, L. Adak, M. Jin, M. Nakamura, *Chem. Comm.* **2019**, *55*, 1128–1131.

- [9] a) S. K. Ghorai, M. Jin, T. Hatakeyama, M. Nakamura, Org. Lett. 2012, 14, 1066-1069; b) Z. Mo, Q. Zhang, L. Deng, Organometallics 2012, 31, 6518-6521; c) R. Agata, T. Iwamoto, N. Nakagawa, K. Isozaki, T. Hatakeyama, H. Takaya, M. Nakamura, Synthesis, 2015, 47, 1733–1740; d) Y. Liu, J. Xiao, L. Wang, Y. Song, L. Deng, Organometallics, 2015, 34, 599-605; e) L. X. Wang, J. Zhang, L. Wang, Deng. Organometallics, 2015, 34, 2775-2782; f) J. A. Przyojski, K. P. Veggeberg, H. D. Arman, Z. J. Tonzetich, ACS Catal. 2015, 5, 5938-5946; g) S. B. Muñoz, V. E. Fleischauer, W. W. Brennessel, M. L. Neidig, Organometallics, 2018 37, 3093-3101.
- [10] a) T. Hatakeyama, M. Nakamura, J. Am. Chem. Soc. 2007, 129, 9844–99845; b) T. Hatakeyama, S. Hashimoto, K. Ishizuka, M. Nakamura, J. Am. Chem. Soc. 2009, 131, 11949–11963; c) Y.-Y. Chua, H. A. Duong, Chem. Commun. 2014, 50, 8424–8427; d) Y.-Y. Chua, H. A. Duong, Chem. Commun. 2016, 52, 1466–1469.
- [11] a) T. Nagano, T. Hayashi, Org. Lett. 2004, 6, 1297–1299; b) R. B. Bedford, D. W. Bruce, R. M. Frost, J. W. Goodby, M. Hird, Chem. Commun. 2004, 2822–2823; c) R. Martin, A. Fürstner, Angew. Chem. 2004, 116, 4045–4047; Angew. Chem. Int. Ed. 2004, 43, 3955–3949; d) A. Fürstner, R. Martin, H. Krause, G. Seidel, R. Goddard, C. W. Lehmann, J. Am. Chem. Soc. 2008, 130, 8773–8787; e) Y. Yamaguchi, H. Ando, M. Nagaya, H. Hinago, T. Ito, M. Asami, Chem. Lett. 2011, 40, 983–985; f) M, Jin, M. Nakamura, Chem. Lett. 2011, 40, 1012–1014; g) G. Bauer, C. W. Cheung, X. Hu, Synthesis 2015, 47, 1726–1732.
- [12] K. Bica, P. Gaertner, Org. Lett. 2006, 8, 733-735.

- [13] a) H.-H. Gao, C.-H. Yan, X.-P. Tao, Y. Xia, H.-M. Sun. Q. Shen, Y. Zhang, *Organometallics* 2010, 29, 4189–4192; b) C.-H. Yan, L. Wang, H. Gao, H. Sun, S. Qi, *Chin. Sci. Bull.* 2012, 57, 1953–1958; c) H.-N. Deng, T.-L. Xing, C.-L. Xia, H.-M. Sun. Q. Shen, Y. Zhang, *Dalton Trans.* 2012, 41, 11597–11607; d) Y. Xia, C.-H. Yan, Z. Li, H.-H. Gao, H.-M. Sun, Q. Shen, Y. Zhang, *Chin. Sci. Bull.* 2013, 58, 493–499; e) L.-L. Wang, B. Lu, A.-D. Zhu, H.-M. Sun, Q. Shen. *Chin. Sci. Bull.* 2013, 58, 3624–3629; f) C.-L. Xia, C.-F. Xie, Y.-F. Wu, H.-M. Sun, Q. Shen, Y. Zhang, *11*, 8135–8144.
- [14] G. P. Algra, S. Balt, Inorg. Chem. 1981, 20, 1102– 1106.
- [15] For details, see the Supporting Information.
- [16] The crystallographic data can be obtained free of charge from The Cambridge Crystallographic Data Centre under reference number CCSC 1893663.
- [17] In this reaction, decane (20%) and 1-decene (31%) were formed, while iodide **2i** was recovered in 17%.
- [18] For recent mechanistic studies on iron-catalyzed cross-coupling reactions of alkyl halides, see: a) D. Noda, Y. Sunada, T. Hatakeyama, M. Nakamura, H. Nagashima, J. Am. Chem. Soc. 2009, 131, 6078-6079; b) R. B. Bedford, P. B. Brenner, E. Carter, P. M. Cogswell. M. F. Haddow, J. N. Harvey, D. M. Murphy, J. Nunn, C. H. Woodall. Angew. Chem. 2014, 126, 1835-1839; Angew. Chem. Int. Ed. 2014, 53, 1804-1808; c) J. D. Sears, P. G. N. Neate, M. L. Neidig, J Am. Chem. Soc. 2018, 140, 11872-11883; d) S. L. Daifuku, M. H. Al-Afyouni, B. E. R. Snyder, J. I. Kneebone, M. L. Neidig, J. Am. Chem. Soc. 2014, 136, 9132-9143; e) S. L. Daifuku, J. L. Kneebone, B. E. R. Snyder, M. L. Neidig, J. Am. Chem. Soc. 2015, 137, 11432 - 11444; f) H. Takaya, S. Nakajima, N. Nakagawa, K. Isozaki, T. Iwamoto, R. Imayoshi, N. J. Gower, L. Adak, T. Hatakeyama, T. Honma, M. Takagaki, Y. Sunada, H. Nagashima, D. Hashizume, O. Takahashi, M. Nakamura, Bull. Chem. Soc. Jpn. 2015, 88, 410–418, and the references cited therein.

COMMUNICATION

Cross-coupling Reactions of Alkyl Halides with Aryl Grignard Reagents using a Tetrachloroferrate with an Innocent Countercation

Adv. Synth. Catal. Year, Volume, Page - Page

Toru Hashimoto,* Tsubasa Maruyama, Takamichi, Yamaguchi, Yutaka Matsubara, and Yoshitaka Yamaguchi*

