6050 *Organometallics* **2008,** *27,* 6050–6052

Synthesis of Functionalized Aryliron Complexes by Palladium-Catalyzed Transmetalation between [CpFe(CO)$_2$I] and Arylzinc or Arylboron Reagents

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Received September 19, 2008

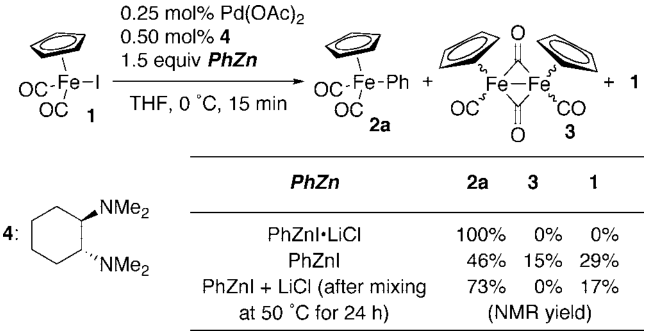
Summary: Transmetalation between [CpFe(CO)$_2$I] and arylzinc reagents or arylboronic acids under palladium catalysis yields the corresponding aryliron complexes [CpFe(CO)$_2$Ar]. The reactions offer easy and reliable accesses to a variety of [CpFe(CO)$_2$Ar] species bearing a functionalized aryl group.

The rich coordination chemistry of dicarbonylcyclopentadienylorganoiron complexes [CpFe(CO)$_2$R] has been attracting significant interest.[1] Among them, the corresponding aryliron complexes [CpFe(CO)$_2$Ar] are interesting not only as fundamental organometallic compounds[2] but also as potentially useful arylmetal reagents in organic synthesis.[3] However, little is known about the concise synthesis of [CpFe(CO)$_2$Ar].[4]

Recently, we have developed an easy and efficient method for the synthesis of [CpFe(CO)$_2$Ar], the palladium-catalyzed transmetalation between [CpFe(CO)$_2$I] and arylmagnesium reagents.[5] However, the functional group compatibility of the reaction is not sufficiently wide because of the high reactivity of arylmagnesium reagents. Moreover, ortho-substituted arylmagnesium reagents reacted sluggishly with [CpFe(CO)$_2$I] under the palladium catalysis. Here we report palladium-catalyzed arylation reactions of [CpFe(CO)$_2$I] with arylzinc or arylboron reagents, the mild reactivities of which should ensure high functional group compatibility.[6]

The arylzinc reagents used were prepared according to the procedure of Knochel:[7] treatment of iodoarenes with zinc powder and lithium chloride afforded the corresponding arylzinc iodide−lithium chloride complexes. Reaction of [CpFe(CO)$_2$I] (**1**) with phenylzinc iodide−lithium chloride proceeded very smoothly under conditions that are similar to those in the previous report (Figure 1).[5] [CpFe(CO)$_2$Ph] (**2a**) was obtained in 100% NMR yield (90% isolated yield) by the action of 0.25 mol % of palladium acetate and 0.50 mol % of diamine **4**.[8] The use of Knochel's arylzinc reagent was essential to attain high yield. It is worth noting that commercially available lithium chloride free phenylzinc iodide was less reactive, and dimer **3** was formed as a byproduct. The reactivity of the commercially supplied phenylzinc iodide could be improved upon mixing with lithium chloride at 50 °C for 24 h prior to the reaction.

The scope of arylzinc reagents is summarized in Table 1. Sterically demanding arylzinc reagents reacted with **1** with reasonable efficiency (entries 2, 3, and 11), which we had failed to attain by the arylation with Grignard reagents.[5] Thanks to



PhZn	2a	3	1
PhZnI•LiCl	100%	0%	0%
PhZnI	46%	15%	29%
PhZnI + LiCl (after mixing at 50 °C for 24 h)	73%	0%	17%

(NMR yield)

Figure 1. Reactions of [CpFe(CO)$_2$I] (**1**) with phenylzinc reagents.

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(3) Butler, I. R.; Cullen, W. R.; Lindsell, W. E.; Preston, P. N.; Rettig, S. J. *J. Chem. Soc., Chem. Commun.* **1987**, 439–441.

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(5) Yasuda, S.; Yorimitsu, H.; Oshima, K. *Organometallics* **2008**, *27*, 4025–4027.

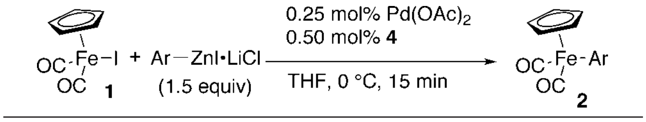
(6) Palladium-catalyzed alkynylation reactions of [CpFe(CO)$_2$I] with 1-alkynylstannanes are known: (a) Lo Sterzo, C. *J. Chem. Soc., Dalton Trans.* **1992**, 1989–1990. (b) Crescenzi, R.; Lo Sterzo, C. *Organometallics* **1992**, *11*, 4301–4305. (c) Ricci, A.; Angelucci, F.; Bassetti, M.; Lo Sterzo, C. *J. Am. Chem. Soc.* **2002**, *124*, 1060–1071, and references cited therein. (d) Long, N. J.; Williams, C. K. *Angew. Chem., Int. Ed.* **2003**, *42*, 2586–2617.

(7) Krasovskiy, A.; Malakhov, V.; Gavryushin, A.; Knochel, P. *Angew. Chem., Int. Ed.* **2006**, *45*, 6040–6044.

(8) Experimental procedure: THF (1.0 mL) was placed in a 20 mL reaction flask under argon. [CpFe(CO)$_2$I] (**1**; 152 mg, 0.50 mmol), palladium acetate (0.050 M THF solution, 0.025 mL, 0.0013 mmol), diamine **4** (0.050 M THF solution, 0.050 mL, 0.0025 mmol), and phenylzinc iodide−lithium chloride complex (0.66 M THF solution, 1.14 mL, 0.75 mmol) were sequentially added at 0 °C. After the mixture was stirred for 15 min, a saturated ammonium chloride solution (1 mL) was added, and the product was extracted with ethyl acetate (10 mL × 3). The combined organic layers were passed through a pad of anhydrous sodium sulfate/Florisil and concentrated. ^{1}H NMR analysis of the crude product by using 1,1,2,2-tetrabromoethane as an internal standard indicated that **2a** was quantitatively formed. The crude oil was purified in air on silica gel by using carbon disulfide as an eluent to yield **2a** (114 mg, 0.45 mmol, 90%) as a brown solid.

10.1021/om800916r CCC: $40.75

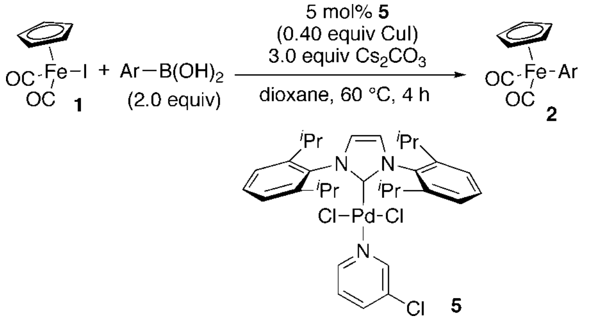
Table 1. Palladium-Catalyzed Arylation of 1 with ArZnI·LiCl



entry	Ar	2	isolated yield /%
1	C_6H_5	**2a**	90 (100[a])
2	1-naphthyl	**2b**	92
3	2-MeC_6H_4	**2c**	73[b]
4	4-MeOC_6H_4	**2d**	94
5	3-$CF_3C_6H_4$	**2e**	94
6	4-BrC_6H_4	**2f**	92
7	4-NCC_6H_4	**2g**	94
8	4-EtOC(=O)C_6H_4	**2h**	82
9	3-EtOC(=O)C_6H_4	**2i**	90
10	2-EtOC(=O)C_6H_4	**2j**	trace[c]
11	2-FC_6H_4	**2k**	74
12	2-thienyl	**2l**	79

[a] Yield determined by ^{1}H NMR analysis of the crude product. [b] With 3.0 equiv of the zinc reagent. [c] 94% of **1** was recovered.

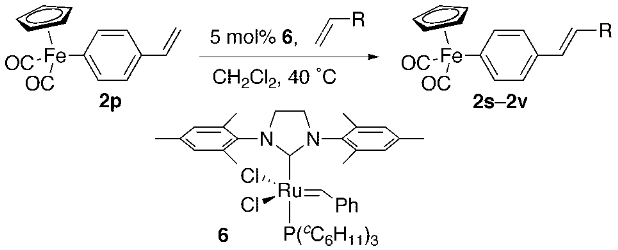
Table 2. Palladium-Catalyzed Arylation of 1 with ArB(OH)$_2$

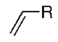
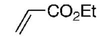
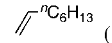
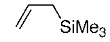


entry	Ar	2	isolated yield /%[a]
1	C_6H_5	**2a**	88
2	1-naphthyl	**2b**	82
3	2-MeC_6H_4	**2c**	76
4	4-MeOC_6H_4	**2d**	68 (82)
5	4-$CF_3C_6H_4$	**2m**	80
6	4-MeC_6H_4	**2n**	79
7	4-MeO$CH_2C_6H_4$	**2o**	73 (86)
8	4-EtOC(=O)C_6H_4	**2h**	67 (87)
9	2-EtOC(=O)C_6H_4	**2j**	(75)
10	4-CH_2=CHC_6H_4	**2p**	72 (83)

[a] Yields obtained in the presence of 0.40 equiv of CuI are given in parentheses.

Table 3. Self- and Cross-Metathesis of 2p under Ruthenium Catalysis



entry		time /h	2	yield /%
1	**2p**	8	**2s**	91
2	 (3 equiv)	6	**2t**	79
3	 (30 equiv)	8	**2u**	76
4	 (10 equiv)	15	**2v**	66[a]

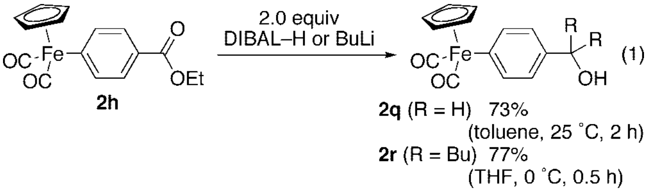
[a] Yield determined by ^{1}H NMR.

the mild reactivity of organozinc reagents, aryliron complexes having a bromo (**2f**), cyano (**2g**), and ethoxycarbonyl (**2h**,**i**) group were readily prepared. However, the reaction of *o*-ethoxycarbonyl-substituted arylzinc reagent resulted in recovery of **1** (entry 10). The heteroaryliron complex **2l** was obtained in high yield (entry 12).

We next turned our attention to transmetalation from organoboron compounds. After extensive screening of the reaction conditions, we found that palladium complex **5**,[9] having a bulky N-heterocyclic carbene ligand, showed the highest catalytic activity for the reaction of phenylboronic acid with the aid of cesium carbonate (Table 2, entry 1).[10] Other arylboronic acids underwent the transmetalation with high efficiency (entries 2, 3, 5, and 6). When the yields of the products were unsatisfactory, the addition of copper(I) iodide improved the efficiency of the reactions (entries 4, 7, and 8).[11,12] It is worth noting that transmetalation from 2-(ethoxycarbonyl)phenylboronic acid to **1** proceeded smoothly by the action of **5** and copper(I) iodide (entry 9). Iron complex **2j** could not be prepared from the corresponding arylzinc reagent (Table 1, entry 10). Styrene derivative **2p** was prepared from 4-vinylphenylboronic acid in good yield (entry 10). Unfortunately, arylboronic acids having a hydroxy or amino group failed to react with **1**.

Further transformations of the functional groups on the phenyl ring could increase the diversity of [CpFe(CO)$_2$Ar].

Treatment of **2h** with diisobutylaluminum hydride (DIBAL-H) or butyllithium afforded the benzylic alcohol **2q** or **2r**, respectively, in high yield (eq 1). The CpFe(CO)$_2$ moiety remained untouched under these reaction conditions, and selective nucleophilic attacks to the ester moiety took place.



The vinylphenyliron complex **2p** underwent metathesis in the presence of ruthenium catalyst **6** (Table 3).[13] Self-metathesis

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[9] (a) O'Brien, C. J.; Kantchev, E. A. B.; Valente, C.; Hadei, N.; Chass, G. A.; Lough, A.; Hopkinson, A. C.; Organ, M. G. *Chem. Eur. J.* **2006**, *12*, 4743–4748. (b) Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G. *Angew. Chem., Int. Ed.* **2007**, *46*, 2768–2813.

[10] Experimental procedure: [CpFe(CO)$_2$I] (**1**; 152 mg, 0.50 mmol), phenylboronic acid (122 mg, 1.0 mmol), **5** (17 mg, 0.025 mmol), and cesium carbonate (489 mg, 1.50 mmol) were placed in a 20 mL reaction flask under an atmosphere of argon. 1,4-Dioxane was then added, and the resulting mixture was stirred for 2 h at 60 °C. The reaction was quenched with a saturated ammonium chloride solution (1 mL). Extractive workup followed by silica gel column purification (eluent: carbon disulfide) afforded **2a** (104 mg, 0.41 mmol) in 82% yield.

[11] (a) Hodgson, P. B.; Salingue, F. H. *Tetrahedron Lett.* **2004**, *45*, 685–687. (b) Yamamoto, Y.; Takizawa, M.; Yu, X.-Q.; Miyaura, N. *Angew. Chem., Int. Ed.* **2008**, *47*, 929–931. (c) Liu, X.-X.; Deng, M.-Z. *Chem. Commun.* **2002**, 622–623. (d) Boland, G. M.; Donnelly, D. M. X.; Finet, J.-P.; Rea, M. D. *J. Chem. Soc., Perkin Trans. 1* **1996**, 2591–2597.

[12] We assume that arylcopper species generated from CuI and arylboronic acids would undergo the more efficient transmetalation with the iodopalladium intermediate: (a) Liebeskind, L. S.; Fengl, R. W. *J. Org. Chem.* **1990**, *55*, 5359–5364. (b) Kang, S.-K.; Yamaguchi, T.; Kim, T.-H.; Ho, P.-S. *J. Org. Chem.* **1996**, *61*, 9082–9083.

of **2p** proceeded smoothly to yield the stilbene derivative **2s** in 91% yield (entry 1). A cross-metathesis reaction with ethyl acrylate provided the (*E*)-cinnamoyl ester **2t** in good yield (entry 2). A cross-metathesis reaction of **2p** with 1-octene required a large excess of 1-octene to obtain a satisfactory amount of desired product **2u**, due to the much lower reactivity of 1-octene in the metathesis reaction (entry 3). Allyltrimethylsilane also participated in cross-metathesis[14] to furnish the bimetallic styrene **2v**, which can undergo a number of further transformations (entry 4). Notably, all the reactions proceeded with exclusive *E* selectivity. Again, the $CpFe(CO)_2$ moiety of the aryliron complex **2p** has thus proved to be compatible under typical conditions for metathesis.

In summary, the palladium-catalyzed transmetalation between $[CpFe(CO)_2I]$ and arylzinc or arylboron reagents has emerged as an efficient method for the synthesis of various functionalized iron complexes. The sufficient stability of the carbon−iron bonds of $[CpFe(CO)_2Ar]$ allows for selective transformations of the functional groups on the phenyl ring to prepare a wider variety of functionalized aryliron complexes. The iron complexes thus synthesized could find applications in organic synthesis as well as in materials chemistry.

Acknowledgment. This work was supported by Grants-in-Aid for Scientific Research and for GCOE Research from the MEXT and JSPS.

Supporting Information Available: Text and figures giving characterization data for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) (a) Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953–956. (b) Grubbs, R. H.; Chang, S. *Tetrahedron* **1998**, *54*, 4413–4450. (c) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18–29.

(14) (a) Crowe, W. E.; Goldberg, D. R.; Zhang, Z. J. *Tetrahedron Lett.* **1996**, *37*, 2117–2120. (b) BouzBouz, S.; De Lemos, E.; Cossy, J. *Adv. Synth. Catal.* **2002**, *344*, 627–630. (c) Huber, J. D.; Perl, N. R.; Leighton, J. L. *Angew. Chem., Int. Ed.* **2008**, *47*, 3037–3039.