

# Synthesis of Functionalized Aryliron Complexes $[\text{CpFe}(\text{CO})_2\text{Ar}]$ by Copper-Mediated Transmetalation between $[\text{CpFe}(\text{CO})_2\text{I}]$ and Aryltin Reagents

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**Summary:** Transmetalation between  $[\text{CpFe}(\text{CO})_2\text{I}]$  and aryltin reagents in the presence of copper salts yields the corresponding aryliron complexes  $[\text{CpFe}(\text{CO})_2\text{Ar}]$ . The high functional group compatibility of this copper-mediated reaction enables us to obtain  $[\text{CpFe}(\text{CO})_2\text{Ar}]$  having an acetyl or formyl group, which cannot be prepared by the previous methods with arylzinc or arylboron reagents under palladium catalysis.

Because of their unique reactivity, organoiron complexes bearing a dicarbonylcyclopentadienyliron moiety  $[\text{CpFe}(\text{CO})_2\text{R}]$  have been attracting much attention as useful reagents and have found numerous applications in organic synthesis.<sup>1</sup> Among them, the reactivity of the corresponding aryliron complexes  $[\text{CpFe}(\text{CO})_2\text{Ar}]$  has not been fully investigated<sup>2</sup> partly because there are few methods for the synthesis of  $[\text{CpFe}(\text{CO})_2\text{Ar}]$ .<sup>3</sup> Therefore, the development of efficient approaches to  $[\text{CpFe}(\text{CO})_2\text{Ar}]$  should lead to the progress of the chemistry of  $[\text{CpFe}(\text{CO})_2\text{Ar}]$ , which have high potential as useful arylmetal reagents.<sup>4</sup>

Recently, we have developed an easy and efficient method for the synthesis of  $[\text{CpFe}(\text{CO})_2\text{Ar}]$ : palladium-catalyzed transmetalation between  $[\text{CpFe}(\text{CO})_2\text{I}]$  and arylmagnesium,<sup>5</sup>

arylzinc, or arylboron reagents.<sup>6</sup> Especially, the reactions with arylzinc or arylboron reagents showed high functional group compatibility and allowed us to prepare a wide range of  $[\text{CpFe}(\text{CO})_2\text{Ar}]$ . However, the functional group compatibility of these methods was not perfect. For example,  $[\text{CpFe}(\text{CO})_2\text{Ar}]$  bearing an acetyl, formyl, or hydroxy group could not be obtained. Therefore, we turned our attention to transmetalation from other organometallic compounds. Herein we report that copper salts can promote arylation reactions of  $[\text{CpFe}(\text{CO})_2\text{I}]$  with aryltin reagents, which show a higher functional group compatibility than the previous methods.<sup>5,6</sup>

After extensive screening of the reaction conditions, we found that copper(I) trifluoromethanesulfonate efficiently promoted a substitution reaction of  $[\text{CpFe}(\text{CO})_2\text{I}]$  (**1**) with tributylphenyltin to afford  $[\text{CpFe}(\text{CO})_2\text{Ph}]$  (**2a**) in excellent yield (Table 1, entry 1). Although dinuclear complex  $[\text{CpFe}(\text{CO})_2]_2$  (**3**) was formed as a byproduct in the reactions with arylmagnesium,<sup>5</sup> arylzinc, or arylboron reagents,<sup>6</sup> no formation of **3** was observed in this copper-mediated reaction. The combination of CuOTf and a catalytic amount of palladium acetate lowered the yield of **2a** (entry 2).<sup>7</sup> The amounts of the copper salt and the tin reagent could be reduced to 1.2 equiv to afford **2a** in slightly lower yield (entry 3). The phenylation reaction did not proceed efficiently in the presence of a catalytic amount of the copper salt (entry 4). Copper(II) trifluoromethanesulfonate and silver(I) trifluoromethanesulfonate showed lower activity (entries 5 and 6). In entries 4–6, the reactions afforded significant amounts of unidentified byproducts other than **1** and **2a**. Copper(I) halide showed no activity (entries 7–9).

We assume that phenylcopper species would be generated from CuOTf and the phenyltin reagents<sup>8</sup> and would undergo transmetalation with **1** to afford **2a**.

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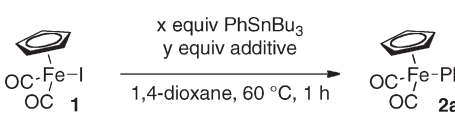
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**Table 1. Optimization of Copper-Mediated Reaction of **1** with PhSnBu<sub>3</sub><sup>a</sup>**

					
entry	x	additive	y	<b>2a</b> /%	<b>1</b> /%
1	2.0	CuOTf	2.0	97	0
2 <sup>b</sup>	2.0	CuOTf	2.0	77	0
3	1.2	CuOTf	1.2	86	0
4	1.2	CuOTf	0.10	4	9
5	1.2	Cu(OTf) <sub>2</sub>	1.2	27	0
6	1.2	AgOTf	1.2	17	1
7	1.2	CuI	1.2	0	82
8	1.2	CuBr	1.2	0	84
9	1.2	CuCl	1.2	0	47

<sup>a</sup> Yields were determined by <sup>1</sup>H NMR analysis of the crude products.<sup>b</sup> With 10 mol % Pd(OAc)<sub>2</sub>.

The scope of aryltin reagents is summarized in Table 2. Basically, 1.3 equiv of the copper salt and 1.3 equiv of an aryltin reagent were used to complete the reactions. The sterically demanding (2-methylphenyl)tin reagent reacted with **1** to afford **2b** in modest yield (entry 2). The electronic nature of aryltin reagents had little effect on the yields of aryliron complexes, and the electron-rich aryliron complex **2c** and electron-deficient ones **2d** and **2e** were obtained in high yields (entries 3–5). Thanks to the mild reactivity of organotin reagents, aryliron complexes having a cyano (**2f**), acetyl (**2g**), and formyl (**2h**) group were readily prepared (entries 6–8). It is worth noting that aryliron complexes **2g** and **2h** could not be prepared from the corresponding arylzinc or arylboron reagents under palladium catalysis.<sup>6</sup> Unfortunately, the reaction of **1** with (4-hydroxyphenyl)tin reagent failed to afford **2i** in reasonable yield (entry 9).

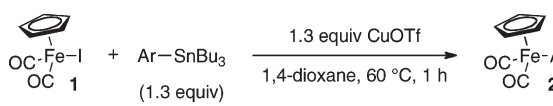
In summary, CuOTf has proven to mediate transmetalation between [CpFe(CO)<sub>2</sub>I] and aryltin reagents, which represents an efficient method for the synthesis of various functionalized aryliron complexes. As notably demonstrated in the synthesis of **2g** and **2h**, this method shows a higher functional group compatibility than the previous reported palladium-catalyzed arylation reaction with arylzinc or arylboron reagents. The iron complexes would be useful in various fields of organic chemistry.

## Experimental Section

**General Procedures.** <sup>1</sup>H NMR (500 and 300 MHz) and <sup>13</sup>C NMR (125.7 and 75.3 MHz) spectra were taken on a Varian Unity Inova 500 spectrometer and a Varian Gemini 300 spectrometer. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were obtained in CDCl<sub>3</sub> [using tetramethylsilane (for <sup>1</sup>H, δ = 0.00 ppm) and CDCl<sub>3</sub> (for <sup>13</sup>C, δ = 77.2 ppm) as internal standards] or C<sub>6</sub>D<sub>6</sub> [using C<sub>6</sub>H<sub>6</sub> (for <sup>1</sup>H, δ = 7.15 ppm) and C<sub>6</sub>D<sub>6</sub> (for <sup>13</sup>C, δ = 128.6 ppm) as internal standards]. IR spectra were determined on a JASCO IR-810 spectrometer. Mass spectra (EI) were determined on a JEOL Mstation 700 spectrometer. The elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. THF was purchased from Kanto Chemical Co., stored under nitrogen, and used as is. 1,4-Dioxane was obtained from Wako Pure Chemicals Co. and stored over slices of sodium. Copper(I)

**Table 2. Copper-Mediated Arylation of **1** with ArSnBu<sub>3</sub>**

			
entry	Ar	<b>2</b>	yield/%
1	C <sub>6</sub> H <sub>5</sub>	<b>2a</b>	86
2	2-MeC <sub>6</sub> H <sub>4</sub>	<b>2b</b>	68
3 <sup>a</sup>	4-MeOC <sub>6</sub> H <sub>4</sub>	<b>2c</b>	80
4	4-FC <sub>6</sub> H <sub>4</sub>	<b>2d</b>	89
5	3-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	<b>2e</b>	92
6	4-NCC <sub>6</sub> H <sub>4</sub>	<b>2f</b>	69
7	4-MeC(=O)C <sub>6</sub> H <sub>4</sub>	<b>2g</b>	91
8	4-HC(=O)C <sub>6</sub> H <sub>4</sub>	<b>2h</b>	84
9 <sup>b</sup>	4-HOC <sub>6</sub> H <sub>4</sub>	<b>2i</b>	14

<sup>a</sup> 4-MeOC<sub>6</sub>H<sub>4</sub>SnMe<sub>3</sub> was used. Performed for 5 min. <sup>b</sup> With 2.0 equiv of tin reagent and 2.0 equiv of Cu salt. Performed for 20 min.

trifluoromethanesulfonate was purchased from Aldrich. Aryltin reagents were prepared according to the literature<sup>9</sup> and stored under argon. [CpFe(CO)<sub>2</sub>I] was prepared according to the literature.<sup>5</sup> Silica gel (Wakogel 200 mesh) was used for column chromatography.

**Typical Procedure for Copper-Mediated Arylation Reactions of [CpFe(CO)<sub>2</sub>I] (Table 2).** Dicarboxylcyclopentadienyliron (**1**, 152 mg, 0.50 mmol), copper(I) trifluoromethanesulfonate/benzene complex (164 mg, 0.65 mmol), tributylphenyltin (239 mg, 0.65 mmol), and 1,4-dioxane (1.7 mL) were sequentially added in a 30 mL reaction flask under argon. The mixture was heated to 60 °C and stirred for 1 h. Then the reaction mixture was cooled to room temperature and filtered through a pad of silica gel. After evaporation, silica gel column purification (eluent: CS<sub>2</sub>) of the crude product provided dicarbonylcyclopentadienylphenyliron (**2a**, 109 mg, 0.43 mmol, 86% yield).

**Characterization Data.** The spectral data of the products **2a–2d**,<sup>5</sup> **2e**, and **2f**<sup>6</sup> can be found in the literature.

**Dicarbonylcyclopentadienyl(4-acetylphenyl)iron (**2g**):** IR (Nujol) 2022, 2007, 1943, 1672, 1356, 1275, 1006, 810 cm<sup>-1</sup>; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 2.24 (s, 3H), 3.98 (s, 5H), 7.51 (d, *J* = 7.5 Hz, 2H), 7.69 (d, *J* = 7.5 Hz, 2H); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>) δ 26.62, 86.33, 127.10, 134.40, 145.74, 159.77, 197.60, 216.66. Anal. Found: C, 60.85; H, 4.46. Calcd for C<sub>15</sub>H<sub>12</sub>FeO<sub>3</sub>: C, 60.84; H, 4.08. Mp: 82–84 °C.

**Dicarbonylcyclopentadienyl(4-formylphenyl)iron (**2h**):** IR (Nujol) 2283, 2014, 1964, 1943, 1685, 1573, 1546, 1179, 1037, 1008, 834, 813 cm<sup>-1</sup>; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 3.94 (s, 5H), 7.42 (d, *J* = 5.5 Hz, 2H), 7.51 (d, *J* = 5.5 Hz, 2H), 9.84 (s, 1H); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>) δ 86.34, 127.89, 134.19, 146.13, 163.74, 192.40, 216.42. Anal. Found: C, 59.62; H, 3.73. Calcd for C<sub>14</sub>H<sub>10</sub>FeO<sub>3</sub>: C, 59.61; H, 3.57. Mp: 98–100 °C.

**Dicarbonylcyclopentadienyl(4-hydroxyphenyl)iron (**2i**):** IR (Nujol) 2013, 1942, 1583, 1534, 1365, 1289, 1236, 1187, 1146, 875, 845, 656 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 4.92 (s, 5H), 6.46 (bs, 1H), 6.85 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 86.44, 114.83, 129.64, 143.84, 158.75, 214.28; HRMS (*m/z*) obsd 269.9977 (Δ = -0.9 ppm), calcd for C<sub>13</sub>H<sub>10</sub>FeO<sub>3</sub> 269.9979. Mp: 75 °C (dec).

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