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# Communications

## Synthesis of Aryliron Complexes by Palladium-Catalyzed Transmetalation between [CpFe(CO)$_2$I] and Aryl Grignard Reagents and Their Chemistry Directed toward Organic Synthesis

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*Summary: Palladium-catalyzed transmetalation between [CpFe(CO)$_2$I] and aryl Grignard reagents emerges as a new method for the synthesis of [CpFe(CO)$_2$Ar]. The aryliron complexes thus formed are useful arylmetal reagents that become active upon oxidation or UV irradiation.*

Thanks to the ubiquity of iron, organoiron compounds represent rare organic transition-metal compounds that we can use stoichiometrically in organic synthesis. However, the potential of organoiron compounds have not been fully developed.[1]

Among organoiron compounds, the coordinatively saturated aryldicarbonylcyclopentadienyliron complexes [CpFe(CO)$_2$Ar] are easy to handle and hence can be useful as arylmetal reagents in organic synthesis. However, little is known about the concise synthesis of [CpFe(CO)$_2$Ar].[2] Here we report a new efficient method for the synthesis of [CpFe(CO)$_2$Ar] under palladium catalysis. Several transformations of [CpFe(CO)$_2$Ar] are also disclosed, which will be useful in organic synthesis.[3,4]

As reported previously,[2a] our attempt at a substitution reaction of [CpFe(CO)$_2$I] (**1**) with phenylmagnesium bromide in the absence of a catalyst resulted in failure, affording a poor yield of [CpFe(CO)$_2$Ph] (**2a**), a significant amount of [CpFe(CO)$_2$]$_2$ (**3**), and recovered **1** (Table 1, entry 1). After extensive screening of the reaction conditions, we found that a combination of palladium acetate and diamine **4** efficiently catalyzes the phe-

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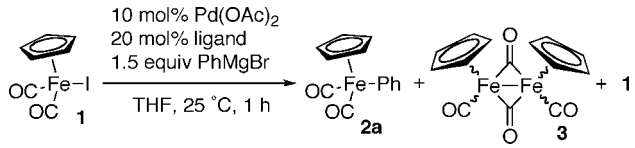
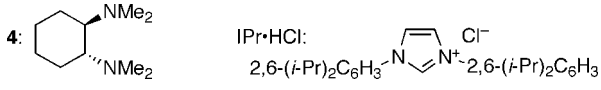
**Table 1. Ligand Effect on Palladium-Catalyzed Arylation of 1**




| entry | ligand | yield/% 2a | 3 | 1 |
|---|---|---|---|---|
| 1[a] | | 5 | 51 | 5 |
| 2 | none | 73 | 9 | 6 |
| 3 | $PPh_3$ | 32 | 38 | 4 |
| 4 | $P(c\text{-}C_6H_{11})_3$ | 15 | 37 | 5 |
| 5 | DPPE[b] | 45 | 31 | 4 |
| 6 | TMEDA[c] | 73 | <1 | 8 |
| 7 | **4** | 87 | 7 | 2 |
| 8 | 2,2′-bipyridyl | 81 | 3 | 5 |
| 9[d] | IPr·HCl[e] | 28 | <1 | 59 |
| 10[f] | **4** | 87 | <6 | <1 |

[a] In the absence of $Pd(OAc)_2$. PhMgBr (2.0 equiv) was used. [b] 1,2-Bis(diphenylphosphino)ethane (10 mol %). [c] *N,N,N′,N′*-Tetramethylethylenediamine. [d] PhMgBr (1.6 equiv) was used. [e] 12 mol %. [f] 5 mol % of $Pd(OAc)_2$, 6 mol % of **4**, 0 °C, 15 min.




nylation reaction (entry 7).[5] The phenylation is regarded as palladium-catalyzed transmetalation between $[CpFe(CO)_2I]$ and phenylmagnesium bromide.

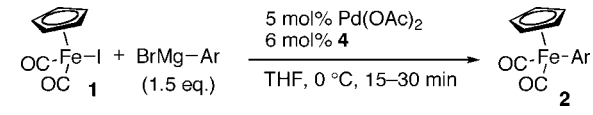
The choice of the ligand is important. The use of phosphine ligands favored the formation of **3** (entries 3−5). The N-heterocyclic carbene ligand IPr·HCl[6] did not work well (entry 9). Palladium acetate by itself had high catalytic activity (entry 2). TMEDA and 2,2′-bipyridyl showed slightly lower activity than diamine **4** (entries 6−8). Diamine **4** was so efficient that the reaction went to completion at 0 °C within 15 min with 5 mol % of the palladium catalyst (entry 10).

The reaction would proceed via a mechanism similar to the conventional cross-coupling reaction,[5c] which consists of oxidative addition of **1** to palladium that generates $[Cp(CO)_2Fe-Pd-I]$, transmetalation with phenylmagnesium bromide, and reductive elimination that forms the phenyl−iron bond.

$[CpFe(CO)_2I]$ is the best starting material for the preparation of **2a**. The corresponding bromide and chloride were arylated with lower efficiency. The palladium-catalyzed reactions of $[CpFe(CO)_2Br]$ and $[CpFe(CO)_2Cl]$ afforded **2a** in 53% and 66% yields along with **3** in 24% and 12% yields, respectively. Advantageously, $[CpFe(CO)_2I]$ was more stable in air than $[CpFe(CO)_2Br]$ and $[CpFe(CO)_2Cl]$.

The scope of aryl Grignard reagents is summarized in Table 2. Substituents at the 4-positions of aryl Grignard reagents had little effect on the arylation reaction. An electron-rich $[CpFe(CO)_2(4\text{-}MeOC_6H_4)]$ (**2d**) was somewhat sensitive to oxygen, which led to a moderate yield of **2d** after silica gel column purification under air. Unfortunately, the reaction of **1** with (2-methylphenyl)magnesium bromide failed to afford **2g** in reasonable yield, probably for steric reasons.

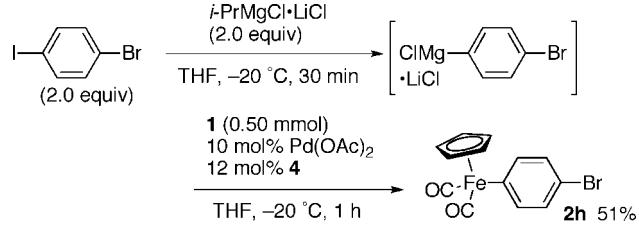
**Table 2. Palladium-Catalyzed Arylation of 1 with ArMgBr**



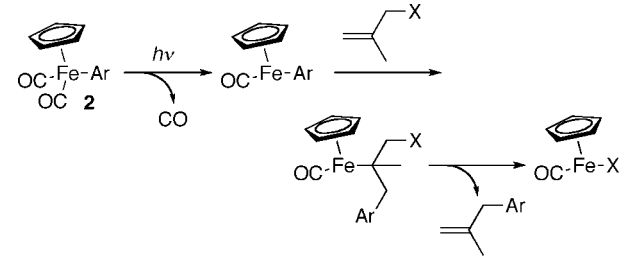

| entry | Ar | 2 | yield/% |
|---|---|---|---|
| 1 | $4\text{-}MeC_6H_4$ | **2b** | 80 |
| 2 | $4\text{-}PhC_6H_4$ | **2c** | 87 |
| 3[a] | $4\text{-}MeOC_6H_4$ | **2d** | 62 (90[b]) |
| 4 | $4\text{-}ClC_6H_4$ | **2e** | 74 |
| 5 | $4\text{-}FC_6H_4$ | **2f** | 87 |
| 6 | $2\text{-}MeC_6H_4$ | **2g** | 21 |

[a] Performed at −20 °C for 2 h. [b] Yield determined by $^1H$ NMR analysis of the crude product.

**Scheme 1. Synthesis of Aryliron Complex from ArMgCl·LiCl**




**Scheme 2**




Although rich coordination chemistry has been reported for $[CpFe(CO)_2Ar]$,[4] the application of $[CpFe(CO)_2Ar]$ to organic synthesis has been almost unknown.[3] Hence, we examined several transformations of $[CpFe(CO)_2Ar]$ which will be useful in organic synthesis.

Many oxidative alkoxycarbonylations of $[CpFe(CO)_2R]$ with ceric ammonium nitrate to form RCOOR′ were reported,[8] although there have been no reports on the reaction of $[CpFe(CO)_2Ar]$. We thus optimized conditions for the reaction of $[CpFe(CO)_2Ar]$ to find the conditions in eq 1. Treatment of **2c** with ceric ammonium nitrate in a methanol−toluene mixed solvent at −78 °C for 30 min provided methyl 4-biphenylcarboxylate (**5**) in 89% yield.

The carbon−iron bond of **2** was robust enough to be compatible under transition-metal-catalyzed conditions. For

(5) Palladium-catalyzed alkynylation reactions of $[CpFe(CO)_2I]$ 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.

(6) (a) Arduengo, A. J., III; Krafczyk, R.; Schmutzler, R.; Craig, H. A.; Goerlich, J. R.; Marshall, W. J.; Unverzagt, M. *Tetrahedron* **1999**, *55*, 14523–14534. (b) Jafarpour, L.; Stevens, E. D.; Nolan, S. P. *J. Organomet. Chem.* **2000**, *606*, 49–54.

(7) Krasovskiy, A.; Knochel, P. *Angew. Chem., Int. Ed.* **2004**, *43*, 3333–3336.

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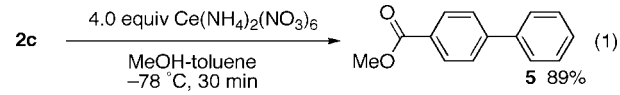
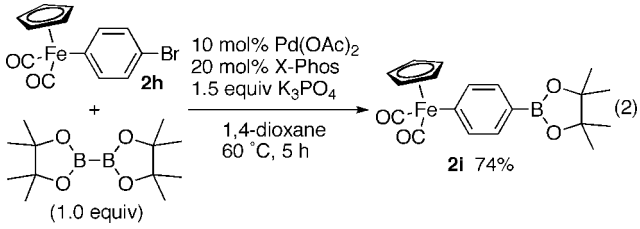


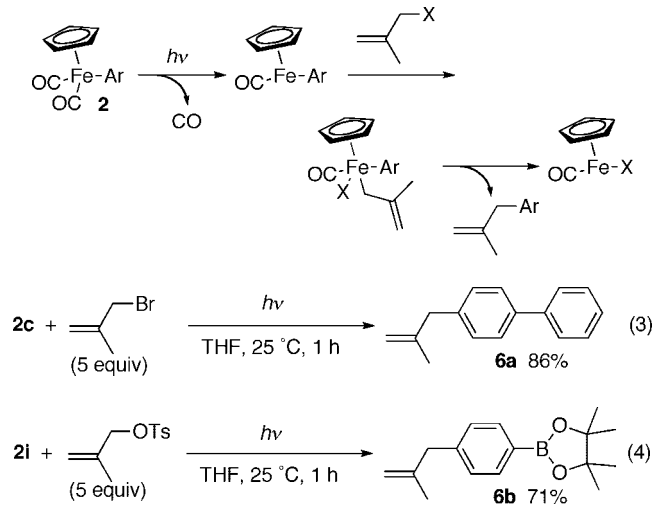

instance, the palladium-catalyzed borylation[9] of **2h** proceeded smoothly to afford the (borylphenyl)iron complex **2i** (eq 2).




Iron complexes **2** reacted with allylic electrophiles under irradiation with a high-pressure mercury lamp to afford allylarenes **6** (eqs 3 and 4). The reaction would proceed as follows (Scheme 2): (1) photoinduced dissociation of a carbonyl ligand,[10–12] (2) coordination of an allylic electrophile followed by migratory insertion,[13] and (3) $\beta$-halide elimination.[14] It is worth noting that the reaction of **2i** with methallyl tosylate occurred selectively at the iron−carbon bond without affecting the boron−carbon bond. This photoinduced additive-free metal-selective carbon−carbon bond formation opens up a new possibility of organoiron-based organic synthesis that takes advantage of the most ubiquitous transition metal.

In summary, we have devised an efficient method for the synthesis of the series of iron complexes [$CpFe(CO)_2Ar$]: that is, palladium-catalyzed transmetalation between [$CpFe(CO)_2I$] and aryl Grignard reagents. The iron complexes thus synthesized are a useful class of arylmetals of significant stability and become reactive upon oxidation or irradiation. As notably demonstrated in the reaction of **2i** and methallyl tosylate, the organoiron complexes [$CpFe(CO)_2Ar$] play unique roles as reagents in organic synthesis.

**Scheme 3**

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

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(11) It was reported that UV irradiation of [$CpFe(CO)_2$(alkyl)] leads to homolytic cleavage of the iron−alkyl bond: (a) Giese, B.; Thoma, G. *Helv. Chim. Acta* **1991**, *74*, 1143–1155. (b) Tawarah, K. M.; Jibril, I.; Bani-Fwaz, M. Z. *Transition Met. Chem.* **2000**, *25*, 659–663.

(12) Boryliron complexes are reagents for the borylation of hydrocarbon upon irradiation: (a) Waltz, K. M.; He, X.; Muhoro, C.; Hartwig, J. F. *J. Am. Chem. Soc.* **1995**, *117*, 11357–11358. (b) Waltz, K. M.; Hartwig, J. F. *Science* **1997**, *277*, 211–213. (c) Waltz, K. M.; Muhoro, C. N.; Hartwig, J. F. *Organometallics* **1999**, *18*, 3383–3393.

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(14) Oxidative addition followed by reductive elimination via an unusual Fe(IV) oxidation state is an alternative process for the allylation (Scheme 3).