ORGANOMETALLICS

Volume 27, Number 16, August 25, 2008

Communications

Synthesis of Aryliron Complexes by Palladium-Catalyzed Transmetalation between $[\mathrm{CpFe(CO)_2I}]$ and Aryl Grignard Reagents and Their Chemistry Directed toward Organic Synthesis

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Received June 17, 2008

Summary: Palladium-catalyzed transmetalation between $[\mathrm{CpFe(CO)_2I}]$ *and aryl Grignard reagents emerges as a new method for the synthesis of* $[\mathrm{CpFe(CO)_2Ar}]$. *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 $[\mathrm{CpFe(CO)_2Ar}]$ are easy to handle and hence can be useful as arylmetal reagents in organic synthesis. However, little is known about the concise synthesis of $[\mathrm{CpFe(CO)_2Ar}]$.[2] Here we report a new efficient method for the synthesis of $[\mathrm{CpFe(CO)_2Ar}]$ under palladium catalysis. Several transformations of $[\mathrm{CpFe(CO)_2Ar}]$ are also disclosed, which will be useful in organic synthesis.[3,4]

As reported previously,[2a] our attempt at a substitution reaction of $[\mathrm{CpFe(CO)_2I}]$ (**1**) with phenylmagnesium bromide in the absence of a catalyst resulted in failure, affording a poor yield of $[\mathrm{CpFe(CO)_2Ph}]$ (**2a**), a significant amount of $[\mathrm{CpFe(CO)_2}]_2$ (**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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(1) (a) Pearson, A. J. *Iron Compounds in Organic Synthesis*; Academic Press: London, 1994. (b) Pearson, A. J. *Pure Appl. Chem.* **1983**, *55*, 1767–1779. (c) Knölker, H.-J. *Curr. Org. Synth.* **2004**, *1*, 309–331. (d) Knölker, H.-J. *Chem. Rev.* **2000**, *100*, 2941–2961. (e) Knölker, H.-J. *Chem. Soc. Rev.* **1999**, *28*, 151–157. (f) Rück-Braun, K.; Mikulás, M.; Amrhein, P. *Synthesis* **1999**, 727–744. (g) Li, C.-L.; Liu, R.-S. *Chem. Rev.* **2000**, *100*, 3127–3161. (h) Abd-El-Aziz, A. S.; Bernardin, S. *Coord. Chem. Rev.* **2000**, *203*, 219–267. (i) Donaldson, W. A. *Curr. Org. Chem.* **2000**, *4*, 837–868. (j) Nakazawa, H.; Itazaki, M.; Kamata, K.; Ueda, K. *Chem. Asian J.* **2007**, *2*, 882–888. (k) Anson, C. E.; Malkov, A. V.; Roe, C.; Sandoe, E. J.; Stephenson, G. R. *Eur. J. Org. Chem.* **2008**, 196–213, and references cited therein.

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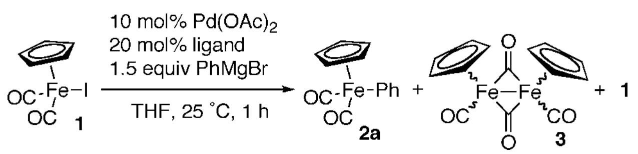
10.1021/om800560m CCC: $40.75

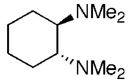
Table 1. Ligand Effect on Palladium-Catalyzed Arylation of 1



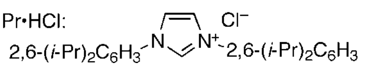
entry	ligand	yield/% 2a	3	1
1[a]		5	51	5
2	none	73	9	6
3	PPh_3	32	38	4
4	$P(c\text{-}C_6H_{11})_3$	15	37	5
5	DPPE[b]	45	31	4
6	TMEDA[c]	73	<1	8
7	**4**	87	7	2
8	2,2′-bipyridyl	81	3	5
9[d]	IPr·HCl[e]	28	<1	59
10[f]	**4**	87	<6	<1

[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.

4:



IPr·HCl:



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

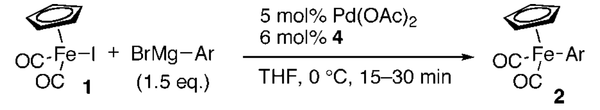
The choice of the ligand is important. The use of phosphine ligands favored the formation of **3** (entries 3−5). The N-heterocyclic carbene ligand IPr·HCl[6] did not work well (entry 9). Palladium acetate by itself had high catalytic activity (entry 2). TMEDA and 2,2′-bipyridyl showed slightly lower 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)$_2$Fe−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.

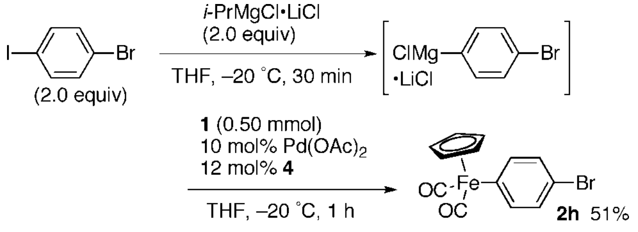
Table 2. Palladium-Catalyzed Arylation of 1 with ArMgBr



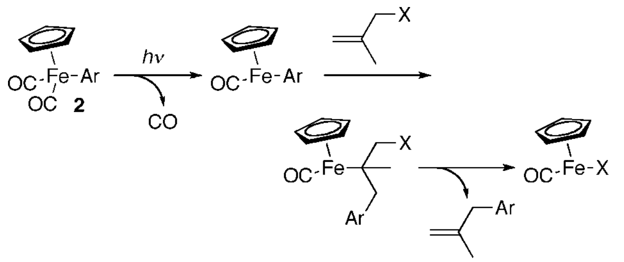
entry	Ar	2	yield/%
1	$4\text{-}MeC_6H_4$	**2b**	80
2	$4\text{-}PhC_6H_4$	**2c**	87
3[a]	$4\text{-}MeOC_6H_4$	**2d**	62 (90[b])
4	$4\text{-}ClC_6H_4$	**2e**	74
5	$4\text{-}FC_6H_4$	**2f**	87
6	$2\text{-}MeC_6H_4$	**2g**	21

[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



(4-Bromophenyl)magnesium reagent, prepared from 4-bromoiodobenzene according to the procedure of Knochel,[7] also underwent the arylation reaction at −20 °C, albeit in modest yield and with a higher catalyst loading (Scheme 1).

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

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(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.

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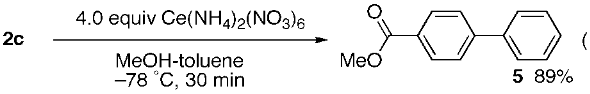
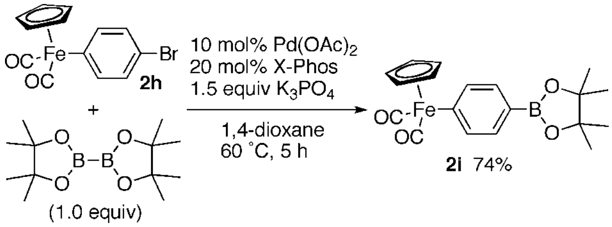


(1)

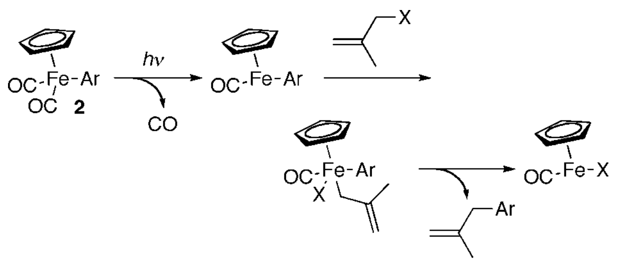
instance, the palladium-catalyzed borylation[9] of **2h** proceeded smoothly to afford the (borylphenyl)iron complex **2i** (eq 2).

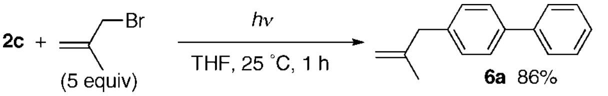


(2)

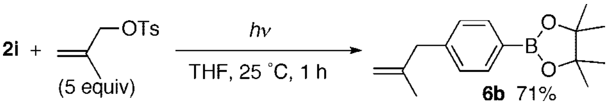
Iron complexes **2** reacted with allylic electrophiles under irradiation with a high-pressure mercury lamp to afford allylarenes **6** (eqs 3 and 4). The reaction would proceed as follows (Scheme 2): (1) photoinduced dissociation of a carbonyl ligand,[10–12] (2) coordination of an allylic electrophile followed by migratory insertion,[13] and (3) *β*-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.

Scheme 3





(3)



(4)

In summary, we have devised an efficient method for the synthesis of the series of iron complexes [CpFe(CO)$_2$Ar]: that is, palladium-catalyzed transmetalation between [CpFe(CO)$_2$I] 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)$_2$Ar] play unique roles as reagents in organic synthesis.

Acknowledgment. This work was supported by Grants-in-Aid for Scientific Research from the MEXT and JSPS. We thank Professor Koichi Ohe and Dr. Koji Miki at Kyoto University for allowing us to use a high-pressure mercury lamp for photochemical reactions.

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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[9] (a) Ishiyama, T.; Itoh, Y.; Kitano, T.; Miyaura, N. *Tetrahedron Lett.* **1997**, *38*, 3447–3450. (b) Ishiyama, T.; Ishida, K.; Miyaura, N. *Tetrahedron* **2001**, *57*, 9813–9816. The use of X-Phos, dicyclohexyl[2-(2,4,6-triisopropylphenyl)phenyl]phosphine, in the palladium-catalyzed borylation: (c) Billingsley, K. L.; Barder, T. E.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2007**, *46*, 5359–5363.

[10] (a) Alt, H. G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 766–782. (b) Olson, A. S.; Seitz, W. J.; Hossain, M. M. *Tetrahedron Lett.* **1991**, *32*, 5299–5302. (c) Kündig, E. P.; Bourdin, B.; Bernardinelli, G. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1856–1858.

[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.

[13] (a) Cavell, K. J. *Coord. Chem. Rev.* **1996**, *155*, 209–243. (b) Zhang, Z.; Lu, X.; Xu, Z.; Zhang, Q.; Han, X. *Organometallics* **2001**, *20*, 3724–3728. (c) Hill, R. H.; Becalska, A.; Chiem, N. *Organometallics* **1991**, *10*, 2104–2109.

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