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Note

Arylation of Styrenes with Aryliron Complexes [CpFe(CO)$_2$Ar]

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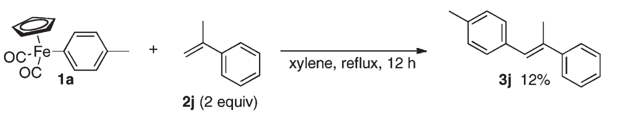
Summary: Treatment of aryliron complexes [CpFe(CO)$_2$Ar] with styrenes in boiling xylene affords the corresponding stilbenes. The aryliron complexes, which become active upon heating, serve as arylating agents in the reaction.

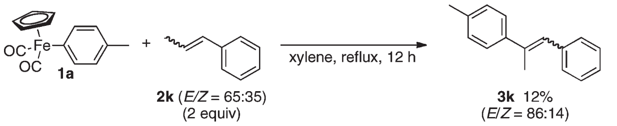
Organoiron complexes bearing a dicarbonylcyclopentadienyliron moiety [CpFe(CO)$_2$R] are utilized as useful organometallic reagents in organic synthesis.[1] Among them, the reactions of the corresponding aryliron complexes [CpFe(CO)$_2$Ar] are still unexplored.[2−8] Studies on chemical reactivity of [CpFe(CO)$_2$Ar] provide useful organic reactions because they are expected to show different reactivity from other arylmetal reagents. Recently, we have developed the efficient synthesis of [CpFe(CO)$_2$Ar] and have been pursuing their synthetic utility as useful arylmetal reagents.[9,10] In the course of these studies, we now report that [CpFe(CO)$_2$Ar] react with styrenes to yield the corresponding stilbenes.[11,12] The reaction begins with insertion of the C=C bond of styrene into the aryl−iron bond. Insertion of unsaturated bonds into aryl−iron bonds of [CpFe(CO)$_2$Ar] is well known.[2,3] However, there has been only one report on application of such insertion to useful organic transformation.[2]

Treatment of [CpFe(CO)$_2$(4-tolyl)] (**1a**) with 2 equiv of styrene in refluxing xylene afforded 4-methylstilbene (**3a**) in 79% yield (Table 1, entry 1). The high temperature is essential. The yield of **3a** was much lower when a similar reaction was performed at a lower temperature (entry 2). Electron-rich styrene **2b** and electron-deficient ones **2c** and **2d** reacted with **1a**, although the yields of the corresponding products were modest (entries 3−5). The reactions with styrenes having a bromo and acetoxy group proceeded to afford **3e** and **3g** in modest yields, leaving the functional groups untouched (entries 6 and 8). The reaction with 4-iodostyrene (**2f**) afforded the corresponding stilbene **3f**, having an iodo group, although the yield of **3f** was low (entry 7). Unfortunately, alkenes other than styrenes were much less reactive in the reactions. For example, the reactions with ethyl acrylate (**2h**) and vinyl boronate **2i** were sluggish (entries 9 and 10). In all cases, some amount of hydridoiron complex [CpFe(CO)$_2$H] was formed as a byproduct.

This arylation reaction with [CpFe(CO)$_2$Ar] was much affected by steric effects. Unfortunately, the reactions of **1a** with sterically demanding α-methylstyrene (**2j**) and *β*-methylstyrene (**2k**) failed to afford the corresponding stilbene derivatives **3j** and **3k** in reasonable yields (eqs 1 and 2).



(1)



(2)

The reactions of various aryliron complexes with styrene were investigated (Table 2). The reaction of 2-naphthyliron **1c** afforded **3l** in slightly lower yield than the case of **1a**

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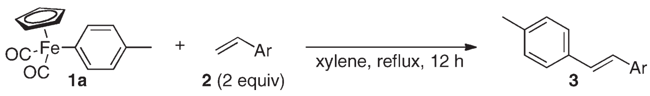
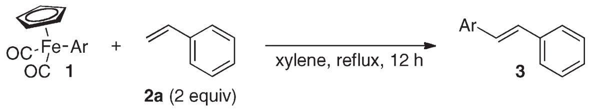
Table 1. Reactions of [CpFe(CO)$_2$(4-tolyl)] with Various Styrenes



entry	Ar	2	3	yield/%
1	Ph	**2a**	**3a**	79
2[a]	Ph	**2a**	**3a**	23
3	4-MeOC$_6$H$_4$	**2b**	**3b**	59
4	4-FC$_6$H$_4$	**2c**	**3c**	71
5	4-ClC$_6$H$_4$	**2d**	**3d**	58
6	4-BrC$_6$H$_4$	**2e**	**3e**	53
7[b]	4-IC$_6$H$_4$	**2f**	**3f**	23
8	4-AcOC$_6$H$_4$	**2g**	**3g**	50
9	(CO$_2$Et)	**2h**	**3h**	15
10	(B(pin))	**2i**	**3i**	10

[a] Performed in refluxing toluene. [b] [CpFe(CO)$_2$Ph] (**1b**) was used instead of **1a**.

Table 2. Scope of Aryliron Complexes



entry	Ar	1	3	yield/%
1	2-naphthyl	**1c**	**3l**	69
2	2-MeC$_6$H$_4$	**1d**	**3m**	32
3[a]	4-MeOC$_6$H$_4$	**1e**	**3n**	53
4	4-FC$_6$H$_4$	**1f**	**3o**	57
5	4-ClC$_6$H$_4$	**1g**	**3p**	58
6	4-BrC$_6$H$_4$	**1h**	**3q**	58
7[a]	3-CF$_3$C$_6$H$_4$	**1i**	**3r**	58
8	4-EtOC(=O)C$_6$H$_4$	**1j**	**3s**	70
9[a]	4-(pin)BC$_6$H$_4$	**1k**	**3t**	84

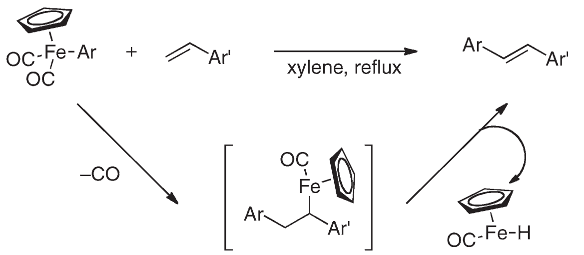
[a] Performed for 24 h.

(entry 1). The reaction of sterically demanding aryliron **1d** was sluggish (entry 2). Electron-rich aryliron **1e**, halophenylirons **1f**−**1h**, and electron-deficient aryliron **1i** underwent the reaction to afford the corresponding stilbene derivatives in modest yields (entries 3−7). The reaction of arylirons having an ester (**1j**) and a boron (**1k**) moiety occurred selectively at the iron−carbon bond without affecting the functional groups (entries 8 and 9).

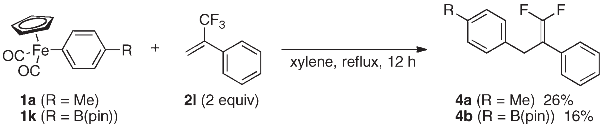
The reaction would proceed as shown in Scheme 1. Dissociation of a carbonyl ligand by heating and subsequent insertion of the C=C bond of styrene into the aryl−iron bond generates the corresponding benzylic iron complex. Subsequent β-hydride elimination affords the stilbene derivative.[13]

We could assume another mechanism where the Ar radical generated in situ would participate in the reaction. Therefore, we carried out the reaction of **1a** with **2a** in the presence of a radical inhibitor, TEMPO. The reaction proceeded to afford **3a** in 45% yield, although the yield was lower than that in the absence of TEMPO (vs Table 1, entry 1). This result rules out the mechanism in which an Ar radical addition to styrene is involved.

Scheme 1



In the reactions with α-trifluoromethylstyrene (**2l**), we obtained an outcome different from the case with **2a**. The reactions of **1a** with **2l** and **1k** with **2l** afforded *gem*-difluoroalkenes **4a** and **4b**, respectively, although the yields were low (eq 3).[14] In the reactions, the stilbene derivatives were not obtained. We assume that β-fluoride elimination, not β-hydride elimination, occurred selectively from the benzylic iron complex generated in situ.



(3)

Aryliron complexes [CpFe(CO)$_2$Ar] have emerged as arylating agents in the reaction with styrenes. This reaction utilizes insertion of the C=C bond of styrene into the aryl−iron bond, representing a new chemical reactivity of [CpFe(CO)$_2$Ar] toward carbon−carbon multiple bonds.

Experimental Section

General Procedures. ^{1}H NMR (500 and 300 MHz) and ^{13}C NMR (125.7 and 75.3 MHz) spectra were taken on a Varian UNITY INOVA 500 spectrometer and a Varian GEMINI 300 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were obtained in CDCl$_3$ with tetramethylsilane as an internal standard. Chemical shifts (δ) are in parts per million relative to tetramethylsilane at 0.00 ppm for ^{1}H and relative to CDCl$_3$ at 77.2 ppm for ^{13}C unless otherwise noted. IR spectra were determined on a JASCO IR-810 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. [CpFe(CO)$_2$Ar] were synthesized by palladium-catalyzed transmetalation between [CpFe(CO)$_2$I] and arylmetal reagents according to the methods reported previously.[9a−c,e] Xylene was purchased from Nacalai Tesque and stored over slices of sodium. Silica gel (Wakogel 200 mesh) was used for column chromatography.

Experimental Procedure. Typical Procedure for Reactions of [CpFe(CO)$_2$Ar] with Styrenes (Table 1, entry 1). Dicarbonylcyclopentadienyl(4-methylphenyl)iron (**1a**, 80 mg, 0.30 mmol), styrene (**2a**, 62 mg, 0.60 mmol), and xylene (1.5 mL) were sequentially added in a 30 mL reaction flask under argon. The mixture was heated at reflux for 12 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: hexane) of the crude product provided 4-methylstilbene (**3a**, 46 mg, 0.24 mmol, 79% yield).

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Characterization Data. The spectral data of the products **3a**,[15] **3b**,[16] **3d**,[15] **3e**,[17] **3f**,[18] **3h**,[19] **3i**,[20] **3j**,[21] **3k**,[22] **3l**,[23] **3m**,[15] **3n**,[18] **3p**,[15] **3q**,[18] **3r**,[24] **3s**,[25] **3t**,[26] and **4a**[14] can be found in the literature.

(*E*)-4-Fluoro-4′-methylstilbene (3c). IR (Nujol): 1507, 1233, 1210, 972, 829, 719 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 2.36 (s, 3H), 7.00 (d, J = 4.0 Hz, 2H), 7.02−7.05 (m, 2H), 7.16 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.44−7.47 (m, 2H). ^{13}C NMR (CDCl$_3$): δ 21.46, 115.78 (d, J_{C-F} = 21.5 Hz), 126.57, 126.71, 128.04 (d, J_{C-F} = 8.1 Hz), 128.64 (d, J_{C-F} = 2.4 Hz), 129.63, 133.92 (d, J_{C-F} = 3.4 Hz), 134.61, 137.79, 162.43 (d, J_{C-F} = 245.4 Hz). Anal. Calcd for $C_{15}H_{13}F$: C, 84.88; H, 6.17. Found: C, 84.63; H, 6.28. Mp: 125−126 °C.

(*E*)-4-[2-(4-Methylphenyl)ethenyl]phenyl Acetate (3g). IR (Nujol): 1752, 1701, 1685, 1507, 1223, 1196, 1013, 972, 915 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 2.30 (s, 3H), 2.36 (s, 3H), 7.03 (s, 2H), 7.07 (d, J = 9.0 Hz, 2H), 7.16 (d, J = 8.5 Hz, 2H), 7.40 (d, J = 8.5 Hz, 2H), 7.49 (d, J = 9.0 Hz, 2H). ^{13}C NMR (CDCl$_3$): δ 21.35, 21.46, 121.96, 126.63, 126.87, 127.49, 129.09, 129.62, 134.60, 135.57, 137.83, 150.10, 169.67. Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.69; H, 6.46. Mp: 157−159 °C.

(*E*)-4-Fluorostilbene (3o). IR (Nujol): 1030, 964, 824, 690 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 6.99−7.08 (m, 4H), 7.25 (t, J = 7.5 Hz, 1H), 7.35 (dd, J = 7.5, 7.5 Hz, 2H), 7.45−7.50 (m, 4H). ^{13}C NMR (CDCl$_3$): δ 115.82 (d, J_{C-F} = 22.0 Hz), 126.65, 127.70, 127.87, 128.19 (d, J_{C-F} = 7.8 Hz), 128.71 (d, J_{C-F} = 2.4 Hz), 128.92, 133.74 (d, J_{C-F} = 3.4 Hz), 137.39, 162.55 (d, J_{C-F} = 245.8 Hz). Anal. Calcd for $C_{14}H_{11}F$: C, 84.82; H, 5.59. Found: C, 84.82; H, 5.55. Mp: 118−119 °C.

1-(3,3-Difluoro-2-phenyl-2-propen-1-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (4b). IR (neat): 2978, 2932, 1728, 1612, 1366, 1319, 1242, 1150, 1088, 955, 856 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.32 (s, 12H), 3.74 (dd, J = 2.5, 2.0 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 7.18−7.28 (m, 5H), 7.69 (d, J = 8.0 Hz, 2H). ^{13}C NMR (CDCl$_3$): δ 25.07, 34.37, 83.92, 91.74 (dd, J_{C-F} = 21.0, 13.9 Hz), 127.51, 127.96, 128.49 (dd, J_{C-F} = 3.4, 3.3 Hz), 128.57, 133.66 (dd, J_{C-F} = 3.9, 3.8 Hz), 135.22, 141.95 (dd, J_{C-F} = 2.9, 2.4 Hz), 154.64 (dd, J_{C-F} = 290.1, 285.9 Hz). The borylated carbon could not be observed. Anal. Calcd for $C_{21}H_{23}BF_2O_2$: C, 70.81; H, 6.51. Found: C, 70.51; H, 6.39.

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