

Supporting Information

Synthesis of Aryliron Complexes by Palladium-Catalyzed Transmetalation between [CpFe(CO)₂I] and Aryl Grignard Reagents and Their Chemistry Directed toward Organic Synthesis

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Contents

Instrumentation and Chemicals	S1
Experimental Procedure	S1
Characterization Data	S3

Instrumentation and Chemicals

¹H NMR (500 and 300 MHz) and ¹³C NMR (125.7 and 75.3 MHz) spectra were taken on a Varian UNITY INOVA 500 spectrometer and a Varian GEMINI 300 spectrometer. ¹H NMR and ¹³C NMR spectra were obtained in CDCl₃ with tetramethylsilane as an internal standard. Chemical shifts (δ) are in parts per million relative to tetramethylsilane at 0.00 ppm for ¹H and relative to CDCl₃ at 77.2 ppm for ¹³C unless otherwise noted. IR spectra were determined on a JASCO IR-810 spectrometer. TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel 60F₂₅₄. Silica gel (Wakogel 200 mesh) was used for column chromatography. Mass spectra (EI unless otherwise noted) were determined on a JEOL Mstation 700 spectrometer. The elemental analyses were carried out at the Elemental Analysis Center of Kyoto University. Photochemical reactions were conducted with a 100-W high-pressure mercury lamp, SEN LIGHTS Corporation HL100CH-4.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Dicarboxylcyclopentadienyliron dimer was purchased from Aldrich. THF was purchased from Kanto Chemical Co., stored under nitrogen, and used as it is.

Experimental Procedure

Procedure for Synthesis of [CpFe(CO)₂I]: Dicarboxylcyclopentadienyliron dimer (10.0 g, 28 mmol), chloroform (150 mL), and iodine (8.6 g, 34 mmol) were sequentially added in a 300-mL round-bottomed flask under air. After the mixture was filled with argon, it was refluxed and stirred for 2 h. Then the resulting mixture was cooled to room temperature and quenched with an aqueous solution of sodium thiosulfate. The products were extracted with chloroform (100 mL × 3) and the combined organic layer was dried over sodium sulfate and concentrated. Silica gel column purification (eluent: CHCl₃) of the

crude product provided dicarbonylcyclopentadienyliodoiron (**1**, 16.4 g, 96% yield). Complex **1** was recrystallized from chloroform/hexane prior to use in the following reactions.

A Typical Procedure for Palladium-Catalyzed Arylation Reactions of [CpFe(CO)₂I] (Tables 1 and 2): Dicarbonylcyclopentadienyliodoiron (**1**, 152 mg, 0.50 mmol), palladium(II) acetate (5.6 mg, 0.025 mmol), diamine **4** (6.0 mg, 0.030 mmol), and THF (1.0 mL) were sequentially added in a 20-mL reaction flask under argon. The mixture was cooled to 0 °C and then phenylmagnesium bromide (1.1 M THF solution, 0.68 mL, 0.75 mmol) was added. After the resulting mixture was stirred for 15 min at 0 °C, a saturated ammonium chloride solution (0.2 mL) was added to the reaction mixture. The mixture was filtered through a pad of Florisil, and the filtrate was concentrated. Silica gel column purification (eluent: CS₂) of the crude product provided dicarbonylcyclopentadienylphenyliron (**2a**, 110 mg, 87% yield).

Procedure for Palladium-Catalyzed Arylation Reactions of [CpFe(CO)₂I] with Grignard Reagent Generated in situ by I/Mg Exchange Reaction (Scheme 1): 1-Bromo-4-iodobenzene (283 mg, 1.0 mmol) and THF (1.0 mL) were added in a 20-mL reaction flask under argon. The mixture was cooled to –20 °C and then isopropylmagnesium chloride/lithium chloride complex (1.0 M THF solution, 1.0 mL, 1.0 mmol) was added. After the mixture was stirred for 30 min at –20 °C, palladium(II) acetate (11 mg, 0.050 mmol), diamine **4** (12 mg, 0.060 mmol), and dicarbonylcyclopentadienyliodoiron (152 mg, 0.50 mmol) were sequentially added to the reaction mixture. After the resulting mixture was stirred for 1 h at –20 °C, a saturated ammonium chloride solution (0.2 mL) was added to the reaction mixture. The mixture was filtered through a pad of Florisil, and the filtrate was concentrated. Silica gel column purification (eluent: CS₂) of the crude product provided (4-bromophenyl)dicarbonylcyclopentadienyliron (**2h**, 85 mg, 51% yield).

Procedure for Oxidation Reactions of [CpFe(CO)₂Ar] with Ce(IV)(NH₄)₂(NO₃)₆ (Eq 1): Diammonium cerium(IV) nitrate (658 mg, 1.2 mmol), and MeOH (6.0 mL) were added in a 50-mL reaction flask under argon. The mixture was cooled to –78 °C and then (4-biphenyl)dicarbonylcyclopentadienyliron (**2c**, 99 mg, 0.30 mmol) in toluene (1.0 mL) was added slowly over 1 min. After being stirred for 30 min at –78 °C, the reaction mixture was quenched with aqueous solution of sodium thiosulfate and sodium bicarbonate. The products were extracted with diethyl ether (20 mL × 3) and the combined organic layer was dried over sodium sulfate and concentrated. Silica gel column purification (eluent: hexane/ethyl acetate = 40:1) of the crude product provided methyl 4-biphenylcarboxylate (**5**, 56 mg, 89% yield).

Procedure for Palladium-Catalyzed Borylation Reactions of [CpFe(CO)₂(4-Br-C₆H₄)] with Bis(pinacolato)diboron (Eq 2): (4-Bromophenyl)dicarbonylcyclopentadienyliron (**2h**, 333 mg, 1.0 mmol), bis(pinacolato)diboron (254 mg, 1.0 mmol), palladium(II) acetate (22 mg, 0.10 mmol),

dicyclohexyl[2-(2,4,6-triisopropylphenyl)phenyl]phosphine (95 mg, 0.20 mmol), tripotassium phosphate (318 mg, 1.5 mmol), and 1,4-dioxane (3.0 mL) were sequentially added in a 30-mL reaction flask under argon. The reaction mixture was heated at 60 °C and stirred for 5 h. Then the reaction mixture was cooled to room temperature and filtered through a pad of Florisil, and the filtrate was concentrated. Silica gel column purification (eluent: CHCl₃) of the crude product provided dicarbonylcyclopentadienyl[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]iron (**2i**, 281 mg, 74% yield).

A Typical Procedure for Photo-Induced Allylation Reactions of [CpFe(CO)₂Ar] with Allylic Electrophiles (Eq 3): (4-Biphenyl)dicarbonylcyclopentadienyliron (**2c**, 99 mg, 0.30 mmol), 3-bromo-2-methylpropene (203 mg, 1.5 mmol), and THF (1.5 mL) were sequentially added in a quartz tube under argon. The reaction mixture was irradiated by a UV lamp at 25 °C and stirred for 1 h with irradiation. The distance between the reaction flask and the UV lamp was 2 cm. After irradiation, the mixture was filtered through a pad of Florisil, and the filtrate was concentrated. Silica gel column purification (eluent: hexane) of the crude product provided 4-(2-methyl-2-propenyl)biphenyl (**6a**, 54 mg, 86% yield).

Characterization Data

Dicarbonylcyclopentadienylphenyliron (2a): IR (neat) 3052, 2011, 1953, 1564, 1470, 1421, 1054, 1010, 995, 832, 732, 698, 633 cm⁻¹; ¹H NMR (CDCl₃) δ = 4.87 (s, 5H), 6.91–6.94 (m, 1H), 6.97–6.99 (m, 2H), 7.46 (d, *J* = 7.0 Hz, 2H); ¹³C NMR (CDCl₃) δ = 85.77, 122.87, 127.51, 145.07, 145.51, 216.04; Found: C, 61.46; H, 4.08%. Calcd for C₁₃H₁₀FeO₂: C, 61.46; H, 3.97%. Known Compound: Li, H.-J.; Turnbull, M. M. *J. Organomet. Chem.* **1991**, 419, 245–249.

Dicarbonylcyclopentadienyl(4-methylphenyl)iron (2b): IR (nujol) 2019, 1998, 1968, 1939, 1915, 1480, 1431, 1009, 793, 635, 596 cm⁻¹; ¹H NMR (CDCl₃) δ = 2.24 (s, 3H), 4.86 (s, 5H), 6.84 (d, *J* = 7.5 Hz, 2H), 7.33 (d, *J* = 7.5 Hz, 2H); ¹³C NMR (CDCl₃) δ = 20.51, 85.71, 128.74, 132.23, 139.68, 144.75, 216.14; Found: C, 62.86; H, 4.52%. Calcd for C₁₄H₁₂FeO₂: C, 62.72; H, 4.51%. m.p.: 83–84 °C.

(4-Biphenyl)dicarbonylcyclopentadienyliron (2c): IR (nujol) 2008, 1953, 1938, 1919, 1466, 1443, 1003, 815, 761, 702, 637, 606, 596, 579 cm⁻¹; ¹H NMR (CDCl₃) δ = 4.89 (s, 5H), 7.23–7.29 (m, 3H), 7.38–7.41 (m, 2H), 7.52–7.56 (m, 4H); ¹³C NMR (CDCl₃) δ = 85.82, 126.00, 126.51, 126.72, 128.61, 136.02, 141.49, 145.20, 145.23, 215.99; Found: C, 68.95; H, 4.29%. Calcd for C₁₉H₁₄FeO₂: C, 69.12; H, 4.27%. m.p.: 113–115 °C.

Dicarbonylcyclopentadienyl(4-methoxyphenyl)iron (2d): IR (neat) 2834, 2010, 1953, 1581, 1481, 1463, 1420, 1264, 1232, 1181, 1052, 1026, 1000, 812, 634, 593 cm⁻¹; ¹H NMR (CDCl₃) δ = 3.74 (s, 3H), 4.85 (s, 5H), 6.68 (d, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 7.5 Hz, 2H); ¹³C NMR (CDCl₃) δ = 55.09, 85.71,

114.27, 131.03, 144.70, 157.04, 216.22; Found: C, 58.83; H, 4.26%. Calcd for $C_{14}H_{12}FeO_3$: C, 59.19; H, 4.26%.

Dicarbonyl(4-chlorophenyl)cyclopentadienyliron (2e): IR (neat) 2016, 1959, 1468, 1432, 1420, 1090, 1034, 1003, 909, 845, 835, 803, 734, 631, 592, 572 cm^{-1} ; 1H NMR ($CDCl_3$) δ = 4.86 (s, 5H), 6.96 (d, J = 7.5 Hz, 2H), 7.35 (d, J = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 85.77, 127.25, 129.85, 143.44, 145.51, 215.70; Found: C, 54.33; H, 3.42%. Calcd for $C_{13}H_9ClFeO_2$: C, 54.12; H, 3.14%.

Dicarbonylcyclopentadienyl(4-fluorophenyl)iron (2f): IR (nujol) 2022, 2005, 1971, 1941, 1920, 1477, 1468, 1163, 810, 635, 596, 578 cm^{-1} ; 1H NMR ($CDCl_3$) δ = 4.85 (s, 5H), 6.74–6.77 (m, 2H), 7.31–7.34 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 85.75, 114.60 (d, J = 18.6 Hz), 136.99, 144.76 (d, J = 5.8 Hz), 161.46 (d, J = 239.0 Hz), 215.94; Found: C, 57.29; H, 3.32%. Calcd for $C_{13}H_9FFeO_2$: C, 57.39; H, 3.33%. m.p.: 62–63 °C.

Dicarbonylcyclopentadienyl(2-methylphenyl)iron (2g): IR (nujol) 2016, 1998, 1965, 1941, 1905, 1448, 826, 741, 635, 592 cm^{-1} ; 1H NMR ($CDCl_3$) δ = 2.44 (s, 3H), 4.88 (s, 5H), 6.80–6.83 (m, 1H), 6.88–6.91 (m, 1H), 7.03 (d, J = 7.0 Hz, 1H), 7.59 (d, J = 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 28.15, 86.05, 123.35, 124.59, 129.23, 144.33, 146.80, 148.86, 215.92; Found: C, 62.47; H, 4.42%. Calcd for $C_{14}H_{12}FeO_2$: C, 62.72; H, 4.51%. m.p.: 68–69 °C.

(4-Bromophenyl)dicarbonylcyclopentadienyliron (2h): IR (nujol) 2023, 2003, 1973, 1950, 1917, 1456, 1418, 1359, 998, 850, 801, 631, 594 cm^{-1} ; 1H NMR ($CDCl_3$) δ = 4.88 (s, 5H), 7.11 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 85.77, 117.98, 130.08, 144.51, 146.05, 215.63; Found: C, 47.00; H, 3.10%. Calcd for $C_{13}H_9BrFeO_2$: C, 46.89; H, 2.72%. m.p.: 104–105 °C.

Dicarbonylcyclopentadienyl[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]iron (2i): IR (nujol) 2006, 1959, 1577, 1456, 1357, 1143, 1093, 1008, 813, 734, 659 cm^{-1} ; 1H NMR ($CDCl_3$) δ = 1.33 (s, 12H), 4.87 (s, 5H), 7.40 (d, J = 8.0 Hz, 2H), 7.55 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 24.85, 83.35, 85.83, 133.07, 144.99, 154.28, 215.80. The borylated carbon could not be observed. Found: C, 60.17; H, 5.56%. Calcd for $C_{19}H_{21}BFeO_4$: C, 60.05; H, 5.57%. m.p.: 180 °C (decomposed).

4-(2-Methyl-2-propenyl)biphenyl (6a) showed the identical spectra found in the literature: Iwasaki, M.; Hayashi, S.; Hirano, K.; Yorimitsu, H.; Oshima, K. *J. Am. Chem. Soc.* **2007**, *129*, 4463–4469.

1-(2-Methyl-2-propenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (6b): IR (nujol) 1611, 1456, 1398, 1362, 1321, 1272, 1146, 1090, 1023, 963, 891, 861, 659 cm^{-1} ; 1H NMR ($CDCl_3$) δ = 1.36 (s, 12H), 1.68 (s, 3H), 3.35 (s, 2H), 4.74–4.75 (m, 1H), 4.82–4.83 (m, 1H), 7.22 (d, J = 8.0 Hz, 2H), 7.76 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 22.28, 25.08, 45.05, 83.87, 112.32, 128.60, 135.04, 143.36, 145.04. The borylated carbon could not be observed; Found: C, 74.35; H, 9.11%. Calcd for $C_{16}H_{23}BO_2$: C, 74.44; H, 8.98%. m.p.: 33–34 °C.