

Palladium-Catalyzed Coupling of (η^6 -Chlorobenzene)-(η^5 -cyclopentadienyl)iron(II) Hexafluorophosphate with Organostannanes

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The chlorine substituent in (η^6 -chlorobenzene)(η^5 -cyclopentadienyl)iron(II) hexafluorophosphate is activated for Pd(0)-catalyzed coupling reactions with aryl-(heteroaryl-), alkynyl-, alkenyl- and benzyl-stannanes. An intermediate CpFeAr⁺-Pd complex has been isolated and shown to undergo the coupling reaction with stannanes.

Carbon-carbon bond formation in aryl iodides and bromides by substitution of the halogen atom can be effected by Pd-catalyzed cross-coupling reactions with various organometallic reactants.¹ Aryl chlorides usually do not readily participate in this reaction, because oxidative addition of unactivated aryl chlorides to the Pd(0) species is slow, and the catalyst may largely decompose.² When the chlorine is situated on a strongly electrophilic carbon, however, cross-coupling by Pd-catalysis may readily proceed as we have demonstrated for chlorines in electrophilic positions in π -electron-deficient heterocycles.³ The electrophilic nature of arenes can be increased by metal complexation which leads to withdrawal of electron density from the aromatic ring. Such a molecule would be a cyclopentadienyliron complex of chlorobenzene which can be formed by an aluminium chloride-mediated ligand exchange reaction between chlorobenzene and ferrocene.^{4,5} Activation of bromoarenes by the corresponding reaction with ferrocene was less satisfactory because of partial debromination.⁵ The substituted benzene product can be regenerated from its metal complex by pyrolysis or by oxidation.^{6,7}

The chlorine in (η^6 -chlorobenzene)(η^5 -cyclopentadienyl)iron(II) salts is exchanged by simple heteroatom nucleophiles,^{6,8} and with stabilized carbanions such as enolates.^{6,9} Depending on the substituents in the arene of the CpFeAr⁺ complex, adduct formation with a stabilized carbanion gives a neutral complex which has a new carbon-carbon bond.¹⁰

We herein report on a general method for the formation of carbon-carbon bonds by Pd-catalyzed coupling reactions of (η^6 -chlorobenzene)(η^5 -cyclopentadienyl)iron(II) hexafluorophosphate with organostannanes.

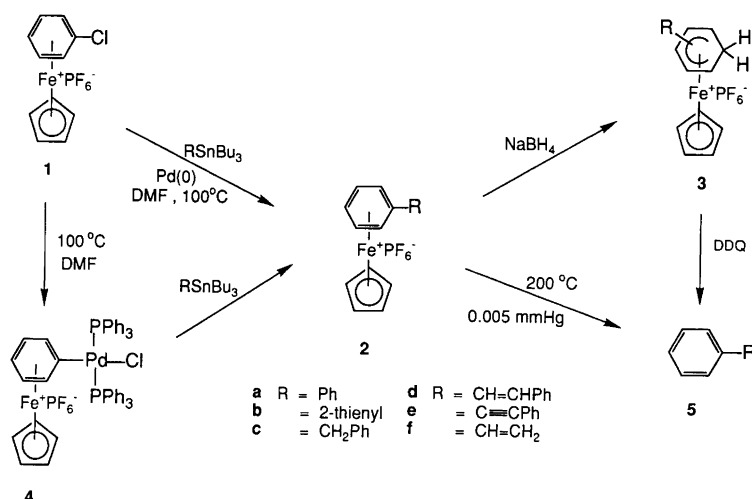
Tetrakis(triphenylphosphine)palladium(0) was our best catalyst in the coupling reactions which were run in DMF at 100°C. Other Pd-catalysts such as bis(triphenylphosphine)palladium(II) dichloride, tetrakis(triisopropylphosphite)palladium(0) and solvents like THF, 1,2-di-

chloroethane gave lower yields, or resulted in longer reaction times.

The coupling reactions proceed well with reactive organostannanes like tributyl(phenylethynyl)stannane and tributyl(styryl)stannane. The reaction is slower with tributyl(phenyl)stannane, and tetrabutylstannane was unreactive. It appears that the activation in the iron-complexed chlorobenzene is less marked than in corresponding chromium tricarbonyl complexes since tetrabutylstannane transfers a butyl group to the chromium arene complex on reflux in THF using the same Pd-catalyst.¹¹ In nucleophilic substitution reactions in complexed haloarenes, however, the reactivity in the iron complex was significantly higher than in the corresponding chromium complex.⁸

Pd-catalyzed coupling reactions between aryl halides and organostannanes are believed to involve σ -bonded arylpalladium(II) complexes.¹ Such complexes have been prepared and characterized. To our knowledge no such complexes have been prepared from metal-complexed aryl chlorides, although palladium(II) complexes of some ferrocenes are known.¹² We set out to isolate the postulated intermediate in the Pd-catalyzed coupling reactions and found that (η^6 -chlorobenzene)(η^5 -cyclopentadienyl)iron(II) hexafluorophosphate (**1**) reacts with tetrakis(triphenylphosphine)palladium(0) in DMF at 100°C to give the Pd(II) complex **4**. Reaction of compound **4** in stoichiometric amount with tributyl-(2-thienyl)stannane, gave the corresponding cross-coupled product **2b** in 56% yield. The Pd-complex **4** can also be used as a catalyst in the cross-coupling reactions of **1** with organostannanes in DMF. The former, however, was inferior to tetrakis(triphenylphosphine)palladium(0), probably because the small amount of phosphine ligand in **4** relative to tetrakis(triphenylphosphine)palladium(0) reduces the stability of the intermediate organopalladium species.

The coupling products obtained are isolated by dissolu-



Scheme 1.

tion in acetone and reprecipitation with diethyl ether. In this respect their properties are similar to those of the starting material. We have found, however, that the products can be purified by either reversed-phase column chromatography on silica (RP-8, LOBAR 40–63 μm) using acetone–water containing some NaCl, or by recrystallisation from water when possible. As salts the products are not volatile in the mass spectrometer by ordinary evaporation. The salt-complexes, however, can be brought into the gas phase by field desorption, and the spectra are characterized by a strong molecular ion and little fragmentation.

The complexes **2** can be demetallated by pyrolysis under vacuum when the substituted benzene **5** is sublimed off as formed. When the complexes are treated with sodium borohydride, the reduced complexes **3** are formed. Two regioisomers in the complexed phenyl ring are formed from the biphenyl **2a** and the 2-phenylthienyl **2b** derivatives. The isomers can be separated by chromatography. Attempts to demetallate the cyclohexadienyl complexes **3a** and **3b** by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), gave biphenyl and 2-phenylthiophene as minor products (ca. 10%). The main products (40%) were the complexes **2a** and **2b** with 2,3-dichloro-5,6-dicyano-4-hydroxyphenoxide as the anion, arising from reoxidation of **3a** and **3b** respectively.

Experimental

The ¹H NMR spectra were recorded at 200 or 300 MHz (specified) and ¹³C NMR spectra at 50.3 MHz. The mass spectra were recorded at 70 eV, or at 10 kV ionising voltage when using field desorption (FD).

Starting materials prepared by literature methods. (η^6 -Chlorobenzene)(η^5 -cyclopentadienyl)iron(II) hexafluorophosphate,⁵ tributyl(phenyl)stannane,¹³ benzyl(tributyl)stannane,¹⁴ tributyl(2-thienyl)stannane,¹⁵ tri-

butyl(β -styryl)stannane,¹⁶ and tributyl(phenylethynyl)stannane.¹⁷

General procedure for palladium-catalyzed coupling with organostannanes. The organostannane (1.13 mmol) in anhydrous DMF (2 ml) was added to a solution of (η^6 -chlorobenzene)(η^5 -cyclopentadienyl)iron(II) hexafluorophosphate (378 mg, 1.00 mmol) and tetrakis(triphenylphosphine)palladium(0) (67 mg, 0.058 mmol) in DMF (2 ml), and the mixture was heated at 100°C with stirring in a dry N₂ atmosphere. The progress of the reactions was monitored by TLC (reversed-phase). When the reaction was stopped, the solvent was distilled off at reduced pressure and the residue triturated with light petroleum. The product was purified by dissolution in acetone and reprecipitation with diethyl ether. The crude product thus obtained, contained 5–10% of the starting material which was removed by either reversed-phase chromatography on silica (RP-8, LOBAR 40–63 μm) using acetone–water containing 0.7% NaCl, or by recrystallisation from water when possible.

(η^6 -Biphenyl)(η^5 -cyclopentadienyl)iron(II) hexafluorophosphate (**2a**).¹⁸ Compound **2a** was obtained in 72% yield from tributyl(phenyl)stannane after 20 h. MS (FD): 275 (100, *M*).

(η^5 -Cyclopentadienyl)[η^6 -(2-thienyl)benzene]iron(II) hexafluorophosphate (**2b**). Compound **2b** was obtained in 88% yield from tributyl(2-thienyl)stannane after 31/2 h; m.p. 149–155°C (decomp.). Anal. C₁₅H₁₃F₆FePS found: C 41.57; H 3.69. Calcd. C 42.28; H 3.07. ¹H NMR (acetone-*d*₆): δ 5.14 (C₅H₅, s), 6.6–6.7 (m, 3 H, Ph), 6.9–7.0 (m, 2 H, Ph), 7.28 (H-4', dd, *J* 5.0, 3.8 Hz), 7.81 (H-5', dd, *J* 5.0, <1 Hz), 7.89 (H-3', dd, *J* 3.8, <1 Hz). ¹³C NMR (acetone-*d*₆): δ 78.5 (C₅H₅), 85.1, 87.4, 88.6 and 98.7 (Ph), 128.6, 129.3, 129.9 and 138.1 (thienyl). MS (FD): 281 (100, *M*).

(η^6 -Benzylbenzene)(η^5 -cyclopentadienyl)iron(II) hexafluorophosphate (**2c**). Compound **2c** was obtained in 77% yield from benzyl(tributyl)stannane after 22 h; m.p. 135–144°C (decomp). Anal. C₁₈H₁₇F₆FeP found: C 49.52; H 4.42. Calcd. C 49.80; H 3.95. ¹H NMR (acetone-*d*₆): δ 4.24 (CH₂, s), 5.21 (s, C₅H₅), 6.4–6.5 (m, 5 H, Ph), 7.3–7.4 (PhCH₂). ¹³C NMR (acetone-*d*₆): δ 41.3 (CH₂), 78.2 (C₅H₅), 88.1, 89.14, 89.5 and 108.4 (η^6 -Ph), 128.4, 130.0, 130.02, 140.1 (PhCH₂). MS (FD): 289 (100, *M*).

(η^5 -Cyclopentadienyl)(η^6 - β -styrylbenzene)iron(II) hexafluorophosphate (**2d**). Compound **2d** was obtained in 89% yield from tributyl(β -styryl)stannane after 31/2 h; m.p. 172–178°C. Anal. C₁₉H₁₇F₆FeP found: C 50.97; H 4.43. Calcd. C 51.15; H 3.84. ¹H NMR (acetone-*d*₆): δ 5.18 (s, C₅H₅), 6.4–6.8 (m, 5 H, Ph), 7.3–7.7 (styryl). ¹³C NMR (acetone-*d*₆): δ 78.6 (C₅H₅), 86.4, 88.1, 89.4 and 102.7 (Ph), 125.1, 128.7, 130.1, 130.5, 136.9, 137.1 (styryl). MS (FD): 301 (100, *M*).

(η^5 -Cyclopentadienyl)(η^6 -phenylethynylbenzene)iron(II) hexafluorophosphate (**2e**). Compound **2e** was obtained in 82% yield from tributyl(phenylethynyl)stannane after 31/2 h; m.p. 150–157°C. Anal. C₁₉H₁₅F₆FeP found: C 51.01; H 3.86. Calcd. C 51.38; H 3.40. ¹H NMR (acetone-*d*₆): δ 5.34 (s, C₅H₅), 6.5–6.8 (m, 5 H, Ph), 7.4–7.7 (m, 5 H, Ph). ¹³C NMR (acetone-*d*₆): δ 79.7 (C₅H₅), 85.5 and 88.0 (acetylene), 88.7, 89.6, 91.1 and 93.3 (Ph), 122.3, 130.1, 131.3 and 133.4 (Ph). MS (FD): 299 (100, *M*).

(η^5 -Cyclopentadienyl)(η^6 -vinylbenzene)iron(II) hexafluorophosphate (**2f**). Compound **2f** was obtained in 91% yield from tributyl(vinyl)stannane after 101/2 h; m.p. 105–115°C. Anal. C₁₃H₁₃F₆FeP found: C 42.30; H 4.01. Calcd. C 42.19; H 3.54. ¹H NMR (acetone-*d*₆): δ 5.16 (s, C₅H₅), 6.4–6.7 (m, 5 H, Ph), 5.75, 6.24 and 6.90 (vinyl). ¹³C NMR (acetone-*d*₆): δ 78.7 (C₅H₅), 86.8, 88.6, 89.4, 101.5 (Ph), 122.3, 134.4 (vinyl). MS (FD): 225 (100, *M*).

Hydride-addition reactions. Sodium borohydride (60 mg, 1.59 mmol) was added in portions over 20 min to (η^6 -chlorobenzene)(η^5 -cyclopentadienyl)iron(II) hexafluorophosphate (1.28 g, 3.0 mmol) in 1,2 dimethoxyethane (25 ml). The solution was stirred for 3 h, and water (25 ml) was added. The solution was extracted thoroughly with pentane, and the extract was washed with water, dried over CaCl₂ and evaporated; yield ca. 30%. The regioisomers can be separated by chromatography on silica gel (hexane).

(η^5 -Cyclopentadienyl)(η^5 -phenylcyclohexadienyl)iron (**3a**).¹⁹ MS (EI): 276 (0.1, *M*), 275 (0.2), 154 (100), 128 (5), 121 (8), 115 (5), 77 (7).

(η^5 -Cyclopentadienyl)[η^5 -(2-thienyl)cyclohexadienyl]iron (**3b**). ¹H NMR (CDCl₃): δ 1.82 (H-6a, d, *J* 12.4 Hz), 2.96 (H-6b, dd, *J* 12.4, 6.9 Hz), 2.58 (H-5, dd, *J* 6.9, 6.6 Hz),

4.14 (s, C₅H₅), 4.47 (H-4, dd, *J* 6.6, 5.6 Hz), 4.74 (H-2, d, *J* 5.6 Hz), 6.19 (H-3, t, *J* 5.6 Hz), 6.76 (H-5', dd, *J* 3.6, 1.1 Hz), 6.90 (H-4', dd, *J* 5.1, 3.6 Hz), 7.13 (H-3', dd, *J* 5.1, 1.1 Hz). MS (EI): 282 (2, *M*), 281 (1), 216 (1), 160 (100), 128 (9), 121 (8), 115 (38), 77 (8).

DDQ oxidation of the cyclohexadienyl derivatives 3a and 3b. DDQ (0.221 g, 1.0 mmol) was added to a solution of **3a** or **3b** (1.0 mmol) in acetonitrile (10 ml), the mixture was stirred at ambient temperature for 30 min and the solution was filtered through sintered glass and evaporated. The residue was triturated with diethyl ether and the mixture was filtered. Evaporation of the filtrate left biphenyl, respectively, 2-phenylthiophene in ca. 10% yield. The remaining solid was identified (¹H NMR) as the (arenecyclopentadienyl)iron(II) complexes **2a** and **2b** with the hydroquinone as the anion. The compounds were purified by dissolution in acetone and were reprecipitated by addition of diethyl ether, yield 40%. NMR spectroscopy showed the (arenecyclopentadienyl)iron(II) complex.

Generation of the Pd-complex (4). A mixture of (η^6 -chlorobenzene)(η^5 -cyclopentadienyl)iron(II) hexafluorophosphate (0.093 g, 0.25 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.29 g, 0.25 mmol) in DMF (2.5 ml) was heated at 100°C for 20 h with stirring (N₂). The progress of the reaction was monitored by TLC (reversed-phase). On completion of the reaction, the solvent was removed at reduced pressure, the residue was dissolved in acetone and the product precipitated by addition of diethyl ether; yield 65%. ¹N NMR (acetone-*d*₆): δ 5.09 (s, C₅H₅), 5.6–5.7 and 6.1–6.2 (m, 5 H, Ph), 7.2–8.0 (m, PPh₃). ¹³C NMR (DMF-*d*₇): δ 76.7 (C₅H₅), 84.8, 86.6, 85.8, 94.6 and 118.4, 119.6 (Ph), 128.8–136.1 (PPh₃). MS (FD): 865 (72, *M*).

Generation of 5 by pyrolytic sublimation. The compounds **2** were pyrolytically sublimed as described in the literature.⁶ The compounds **5a–5f** were isolated in >90% yield.

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