Palladium-Catalyzed Coupling of (η⁶-Chlorobenzene)-
(η⁵-cyclopentadienyl)iron(II) Hexafluorophosphate with
Organostannanes

Nina Jevnaker, Tore Benneche and Kjell Undheim

Department of Chemistry, University of Oslo, N-0315 Oslo 3, Norway

of (η⁶-Chlorobenzene)(η⁵-cyclopentadienyl)iron(II) Hexafluorophosphate with

The chlorine substituent in (η⁶-chlorobenzene)(η⁵-cyclopentadienyl)iron(II)
hexafluorophosphate is activated for Pd(0)-catalyzed coupling reactions with
aryl-(heteroaryl)-, alkylnyl-, 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
which can be formed by an aluminium chloride-mediated ligand exchange reaction between chlorobenzene and ferrocene.⁴ Activation of bromo-arenes by the corresponding reaction with ferrocene was less satisfactory because of partial demethylation.⁵ The substituted benzene product can be regenerated from its
metal complex by pyrolysis or by oxidation.⁶,⁷

The chlorine in (η⁶-chlorobenzene)(η⁵-cyclopenta
dienyl)iron(II) salts is exchanged by simple heteroatom
nucleophiles,⁸,⁹ and with stabilized carbanions such as enolates.⁹,¹⁰ Depending on the substituents in the aren 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 (η⁶-chlorobenzene)(η⁵-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(triphenylphos
phine)palladium(II) dichloride, tetrakis(triisopropyl
phosphite)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 tributy(styryl)stannane. The reaction is slower with tributy(phenyl)stannane, and tetrabuty(stannane was
unreactive. It appears that the activation in the iron-complexed chlorobenzene is less marked than in corre-
sponding chromium tricarbonyl complexes since teta-
butylstannane 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 corre-
sponding chromium complex.¹²

Pd-catalyzed coupling reactions between aryl halides and organostannanes are believed to involve σ-bonded
aryl(palladium(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.¹³ We set out to isolate the postulated intermediate in the Pd-catalyzed coupling
reactions and found that (η⁶-chlorobenzene)(η⁵-cyclopenta
dienyl)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-
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-phenylthiényl 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.

**General procedure for palladium-catalyzed coupling with organostannanes.** The organostannane (1.13 mmol) in anhydrous DMF (2 ml) was added to a solution of \((\eta^6\text{-chlorobenzene})(\eta^6\text{-cyclopentadienyl})\)iron(II) hexafluorophosphate (378 mg, 1.00 mmol) and tetrakis(triphenylphosphine)palladium(0) (67 mg, 0.358 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.

\((\eta^6\text{-Biphenyl})(\eta^6\text{-cyclopentadienyl})\)iron(II) hexafluorophosphate (2a). Compound 2a was obtained in 72% yield from tributyl(phenyl)stannane after 20 h. MS (FD): 275 (100, M).

\((\eta^6\text{-Cyclopentadienyl})[\eta^6\text{- (2-thienyl) benzene} ]\)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. C₃₅H₂₆Fe₂S found: C 41.57; H 3.69. Caled. C 42.28; H 3.07. ¹H NMR (acetone-d₄): δ 5.14 (C₃H₃, 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), 7.81 (H-3', dd, J 3.8, < 1 Hz). ¹³C NMR (acetone-d₄): δ 78.5 (C₃H₃), 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).

---

**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.**

\((\eta^6\text{-Chlorobenzene})(\eta^6\text{-cyclopentadienyl})\)iron(II) hexafluorophosphate.⁵ trityl(phenyl)stannane,¹³ benzyl-(tributyl)stannane,¹⁴ trityl(2-thienyl)stannane,¹⁵ tri-

\[(\eta^6\text{-Cyclopentadienyl})[\eta^6\text{- (2-thienyl) benzene} ]\]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. C₃₅H₂₆Fe₂S found: C 41.57; H 3.69. Caled. C 42.28; H 3.07. ¹H NMR (acetone-d₄): δ 5.14 (C₃H₃, 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), 7.81 (H-3', dd, J 3.8, < 1 Hz). ¹³C NMR (acetone-d₄): δ 78.5 (C₃H₃), 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).

---

407
(η⁶-Benzylbenzene)(η⁶-cyclopentadienyl)iron(II) hexafluorophosphate (2e). Compound 2e was obtained in 77% yield from benzyl(trityl)stannane after 22 h; m.p. 135–144°C (decomp). Anal. C₁₉H₁₇Fe₂F₆P found: C 49.52; H 4.42. Calcd. C 49.80; H 4.35. ¹H NMR (acetone-d₆): δ 4.24 (CH₃), 5.21 (s, C₅H₅N), 6.4–6.5 (m, 5 H, Ph), 7.3–7.4 (PhCH₃). ¹³C NMR (acetone-d₆): δ 41.3 (CH₃), 78.2 (C₅H₅N), 88.1, 89.14, 89.5 and 108.4 (η⁶-Ph), 128.4, 130.0, 130.02, 140.1 (PhCH₃). MS (FD): 289 (100, M).

(η⁶-Cyclopentadienyl)(η⁶-β-styrylbenzene)iron(II) hexafluorophosphate (2d). Compound 2d was obtained in 89% yield from trityl(β-styryl)stannane after 31/2 h; m.p. 172–178°C. Anal. C₁₉H₁₇Fa₂FeP found: C 50.97; H 4.43. Calcd. C 51.15; H 3.84. ¹H NMR (acetone-d₆): δ 5.18 (s, C₅H₅N), 6.4–6.8 (m, 5 H, Ph), 7.3–7.7 (styril). ¹³C NMR (acetone-d₆): δ 78.6 (C₅H₅N), 86.4, 88.1, 89.4 and 102.7 (Ph), 125.1, 128.7, 130.1, 130.5, 136.9, 137.1 (styril). MS (FD): 301 (100, M).

(η⁶-Cyclopentadienyl)(η⁶-phenylethynylbenzene)iron(II) hexafluorophosphate (2e). Compound 2e was obtained in 82% yield from trityl(phenylethynyl)stannane after 31/2 h; m.p. 150–157°C. Anal. C₁₉H₁₇Fe₂FaP found: C 51.01; H 3.86. Calcd. C 51.38; H 3.40. ¹H NMR (acetone-d₆): δ 5.34 (s, C₅H₅N), 6.5–6.8 (m, 5 H, Ph), 7.4–7.7 (m, 5 H, Ph). ¹³C NMR (acetone-d₆): δ 79.7 (C₅H₅N), 85.5 and 88.0 (acycetene), 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).

(η⁶-Cyclopentadienyl)(η⁶-vinylbenzene)iron(II) hexafluorophosphate (2f). Compound 2f was obtained in 91% yield from trityl(vinyl)stannane after 10/2 h; m.p. 105–115°C. Anal. C₁₉H₁₇Fe₂FaP found: C 42.30; H 4.01. Calcd. C 42.19; H 3.54. ¹H NMR (acetone-d₆): δ 5.16 (s, C₅H₅N), 6.4–6.7 (m, 5 H, Ph), 5.75, 6.24 and 6.90 (vinyl). ¹³C NMR (acetone-d₆): δ 78.7 (C₅H₅N), 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 (η⁶-chlorobenzene)(η⁶-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).

(η⁶-Cyclopentadienyl)(η⁶-phenylethynylhexadienyl)iron (3a). MS (EI): 276 (0.1, M), 275 (0.2), 154 (100), 128 (5), 121 (8), 115 (5), 77 (7).

(η⁶-Cyclopentadienyl)η⁶-(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, C₅H₅N), 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 ('H NMR) as the (arenecyclopentadienyl)iron(II) complexes 2a and 2b with the hydrosquinone as the anion. The compounds were purified by dissolution in acetonitrile and were recrystallized by addition of diethyl ether, yield 40%. NMR spectroscopy showed the (arenecyclopentadienyl)iron(II) complex.

Generation of the Pd-complex (4). A mixture of (η⁶-chlorobenzene)(η⁶-cyclopentadienyl)iron(II) hexafluorophosphate (0.093 g, 0.25 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.29 g, 0.25 mmol) in DMF (2 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%. ¹¹B NMR (acetone-d₆): δ 5.09 (s, C₅H₅N), 5.6–5.7 and 6.1–6.2 (m, 5 H, Ph), 7.2–8.0 (m, PPh₃). ¹³C NMR (DMF-d₇): δ 76.7 (C₅H₅N), 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. The compounds 5a–5f were isolated in >90% yield.

References

Received June 25, 1992.