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Oxidative Addition of Chlorobenzene on an Iron-Cyclopentadienyl Cation to a Low-Valent Palladium Complex

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The oxidative addition of the coordinated chlorobenzene in $[CpFe(C_6H_5Cl)][PF_6]$ to $Pd(PPh_3)_4$ proceeds under THF-reflux conditions to give $[CpFe\{\eta^6-[PdCl(PPh_3)_2]C_6H_5\}][PF_6]$. X-Ray analysis of this complex revealed that the phenyl ring is σ-bound to Pd and π-bound to Fe, and that the palladium center takes the *cis*-configuration. This complex reacts with CO / MeOH, CO / $HNEt_2$, styrene, and methyl acrylate to give methyl benzoate, N,N-diethylbenzamide, stilbene, and methyl cinnamate, respectively,, after photolysis.

It has been well documented that an arene coordinated to an electron-deficient transition metal center is activated toward nucleophilic reactions.1) Recently much attention has been focused on the reactions of the coordinated chlorobenzene with low-valent metal complexes from a viewpoint of catalytic2) and stoichiometric3) transformation of chlorobenzene. However such studies have been limited to those of chlorobenzene-chromium tricarbonyl. With a view to developing a more effective bimetallic system for the activation and chemical transformation of unreactive aryl-heteroatom bonds, we have started the investigation on the reaction between low-valent metal complexes and chlorobenzene coordinated to an iron-cyclopentadienyl cation. Here we wish to report the oxidative addition of $[CpFe(C_6H_5Cl)]^+$ to a Pd(0) complex.

Complex $[CpFe(C_6H_5Cl)][PF_6]$ (1.74 mmol) reacts with $Pd(PPh_3)_4$ (0.87 mmol) in refluxing THF (40 ml) to form a yellow-white precipitate (**1**) in 70% (Eq. 1).4) The ^1H NMR spectrum of this material shows two sets of signals attributable to $[CpFe(C_6H_5Cl)]^+$ and a newly formed complex $[CpFe\{\eta^6-[PdCl(PPh_3)_2]C_6H_5\}]^+$ in 1:1 ratio (vide infra). The $^{31}P\{^1H\}$ NMR spectrum and elemental anaysis were also consistent with the composition $[CpFe(C_6H_5Cl)][CpFe\{\eta^6-[PdCl(PPh_3)_2]C_6H_5\}][PF_6]_2$. A platinum analogue $Pt(PPh_3)_4$ failed to react under similar reaction conditions.

Recrystallization of **1** from hot acetone gave orange crystals (**2**) in 47% based on palladium.

$$[\mathrm{CpFe}(\eta^6\text{-}\mathrm{C_6H_5Cl})][\mathrm{PF_6}] + \mathrm{Pd(PPh_3)_4}$$

$$\xrightarrow{\text{THF reflux}} \underset{\mathbf{1}}{[\mathrm{CpFe}(\eta^6\text{-}\mathrm{C_6H_5Cl})][\mathrm{CpFe}\{\eta^6\text{-}[\mathrm{PdCl(PPh_3)_2}]\mathrm{C_6H_5}\}][\mathrm{PF_6}]_2}$$

$$\xrightarrow{\text{recryst. from acetone}} \underset{\mathbf{2}}{[\mathrm{CpFe}\{\eta^6\text{-}[\mathrm{PdCl(PPh_3)_2}]\mathrm{C_6H_5}\}][\mathrm{PF_6}]} \qquad (1)$$

The NMR and IR spectra, and elemental analysis indicated that this complex is formulated as $[\mathrm{CpFe}\{\eta^6\text{-}[\mathrm{PdCl(PPh_3)_2}]\mathrm{C_6H_5}\}][\mathrm{PF_6}]$,5) in which the phenyl group derived from the coordinated chlorobenzene acts as a $\mu(\eta^6, \eta^1)$-ligand. An iron-cyclopentadienyl cation is known to activate an arene toward nucleophilic attack by coordination.6) In the present reaction, the coordinated chlorobenzene is sufficiently activated to bring about the oxidative addition of the Ph–Cl bond to Pd(0) species. The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR data suggested that the two $\mathrm{PPh_3}$ ligands are mutually *cis*. Oxidative addition of an aryl or alkyl halide to a Pd(0)-monophosphine complex usually produces the *trans*-isomer, and the formation of the *cis*-isomer has rarely been reported.7)

The detailed structure of **2** has been determined by X-ray diffraction.8) Single crystals suitable for X-ray analysis were obtained by slow diffusion of ether in a $\mathrm{CH_2Cl_2}$ solution of **2**. The perspective view shown in Fig. 1 confirms the $\mu(\eta^6, \eta^1)$-coordination of the phenyl group and the square-planar *cis*-configuration around the palladium atom. The steric effect of the $\mathrm{CpFe}(\eta^6\text{-}\mathrm{C_6H_5})$ ligand probably accounts for the *cis*-structure of **2**. In fact, the axis of the Cp–Fe–(η^6–$\mathrm{C_6H_5}$) linkage is almost parallel to the Pd–Cl bond, and this location diminishes the steric congestion between the $\mathrm{CpFe}(\eta^6\text{-}\mathrm{C_6H_5})$ ligand and the $\mathrm{PPh_3}$ ligands. The Pd–C(21) bond length falls in the normal range of that for a Pd(II)–C(sp^2) bond.9) Although the structure of Cp–Fe–(η^6–$\mathrm{C_6H_5}$) moiety is similar to those of related $[\mathrm{CpFe}(\eta^6\text{-arene})]^+$ complexes,10) the Fe–C(21) bond (2.16(1) Å) is longer than the other Fe–C bonds of $\mathrm{Fe}(\eta^6\text{-}\mathrm{C_6H_5})$ (2.00-2.10 Å). The Pd–P(2) bond is rather longer than the Pd–P(1) bond, which may be due to the stronger trans influence of the $\mathrm{CpFe}(\eta^6\text{-}\mathrm{C_6H_5})$ ligand in comparison with Cl anion. The large P(1)–Pd–P(2) angle is attributable to the steric repulsion between the two phosphines.

Further chemical transformation of **2** was also investigated. A reaction of the complex **2** (0.1 mmol) with CO (30 atm) in MeOH-$\mathrm{NEt_3}$ (10 ml / 0.1 ml) at 80 °C for 22 h followed by photolysis of the resulting complex using a super high pressure mercury lamp gave methyl benzoate in 54% yield. Similarly, when **2** was allowed to react with CO (30 atm)-$\mathrm{HNEt_2}$ (0.1 ml), methyl acrylate (2 ml), and styrene (1 ml) in DMF , N,N–diethylbenzamide (88%), methyl cinnamate (40%), and stilbene (64%) were produced, respectively, after photolysis (Eq. 2). These processes accomplish the carbonylation and

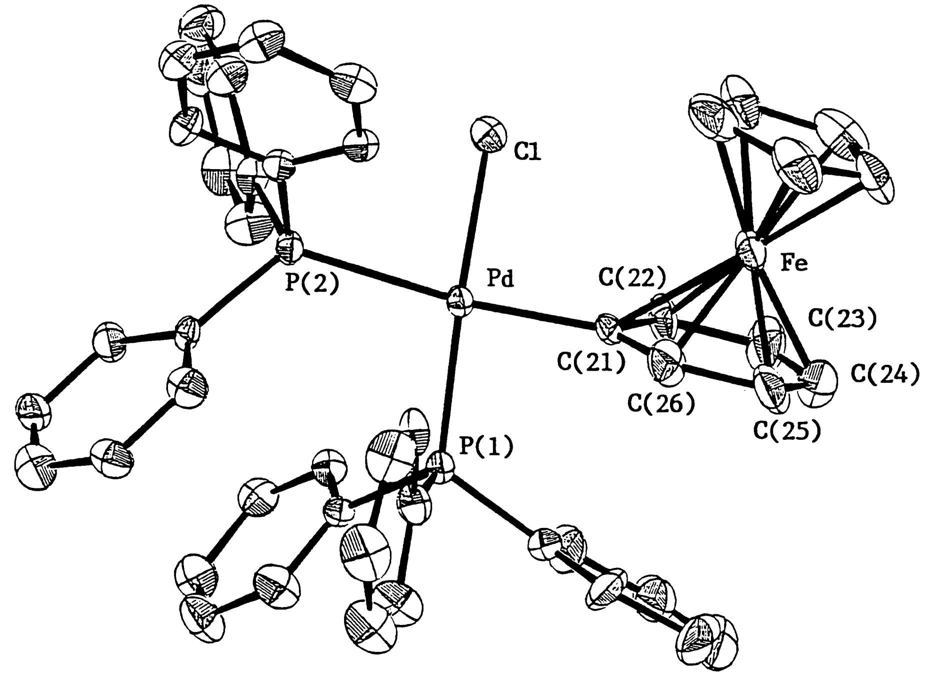
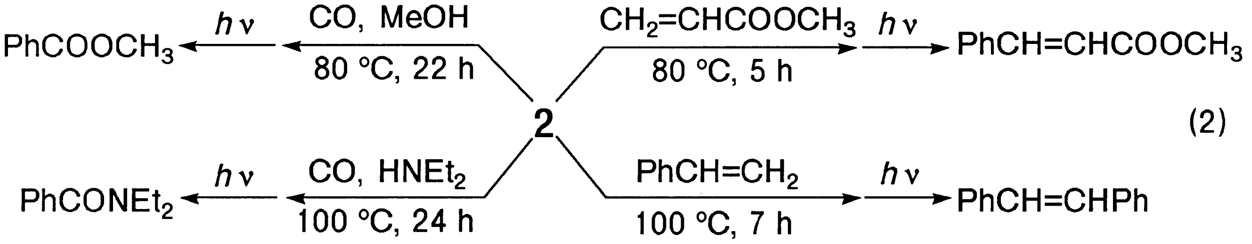


Fig. 1. An ORTEP drawing of molecule *cis*-[CpFe{η^6-[PdCl(PPh_3)$_2$]C_6H_5}]$^+$ (**2**).
Selected bond lengths and angles: Pd–Cl = 2.335(4), Pd–P(1) = 2.272(4), Pd–P(2) = 2.403(3), Pd–C(21) = 2.03(1), Fe–C(21) = 2.16(1), Fe–C(22) = 2.10(1), Fe–C(23) = 2.05(2), Fe–C(24) = 2.04(2), Fe–C(25) = 2.00(2), Fe–C(26) = 2.06(2) Å, Cl–Pd–P(2) = 83.7(1), P(1)–Pd–P(2) = 99.9(1), P(1)–Pd–C(21) = 86.6(4), Cl–Pd–C(21) = 90.4(4)°.



(2)

olefination of chlorobenzene.

However, attempts to effect the reaction with a catalytic amount of Pd(PPh_3)$_4$ has not been successful. Further studies with the aim of developing a more effective bimetallic system for the activation of unreactive aromatic compounds are in progress.

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4) Similar reaction in refluxing acetone for 4 h did not give complexes **1** or **2** in moderate yields.

5) $[CpFe\{\eta^6\text{-}[PdCl(PPh_3)_2]C_6H_5\}][PF_6]$: Found: C, 55.62; H, 4.12%. Calcd for $C_{47}H_{40}F_6ClP_3FePd$: C, 55.92; H, 3.99%. ^1H NMR(CD_2Cl_2 solution, ppm) 4.97(s, 5H, Cp); 5.39(m, 3H, η^6-Ph); 5.97(m, 2H, η^6-Ph); 7.14-7.35(m, 30H, PPh_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2 solution, ppm) 20.09(d, J = 33.1 Hz); 36.88(d, J = 33.1 Hz).

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8) Crystal data for complex **2**; M = 1009.46, monoclinic, space group $P2_1/c$, $a = 10.458(2)$ Å, $b = 32.379(6)$ Å, $c = 13.170(2)$ Å, $\beta = 107.14(1)°$, $V = 4261.4(13)$ Å^3, $Z = 4$, $D_{calcd} = 1.573$ g·cm^{-3}, $D_{measd} = 1.57$ g·cm^{-3} (at 27 °C), μ(Mo K_α) = 9.89 cm^{-1}, $R = 0.070$, $Rw = 0.077$ for 4546 reflections ($|F_0| > 5\sigma(|F_0|)$).

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