

Mechanism of Arene Exchange by Phosphines and Phosphites in the 19 Electron Complexes $[\text{Fe}^{\text{I}}\text{Cp}(\text{arene})]$, $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$, $\text{Arene} = \text{C}_6\text{H}_{6-n}\text{Me}_n$ ($n = 0, 1$)

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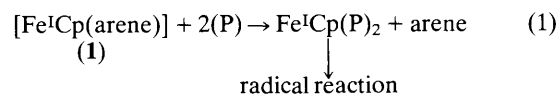
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A low temperature spectroscopic study of the facile arene exchange by phosphines and phosphites in the air-sensitive 19 electron complexes $[\text{Fe}^{\text{I}}\text{Cp}(\eta^6\text{-arene})]$, ($\text{Cp} = \text{cyclopentadienyl}, \eta^5\text{-C}_5\text{H}_5$), shows an associative pathway in the rate limiting step, which suggests a fast pre-equilibrium generating a 17 electron species.

The associative mechanism of ligand substitution is well recognized as being responsible for the marked substitution lability of 17 electron (17 e) complexes.¹⁻³ However, due to their instability, 19 e complexes are much less studied^{3a} and although their substitution lability is recognised,^{2c,3a} precise mechanisms are unknown. Sandwich complexes are sometimes considered as a special group in this respect and efforts have so far concentrated on metal carbonyls.^{1,2} Indeed the stabilisation of the 19 e state by the sandwich structure offers a unique opportunity to study the substitution mechanism. We report here the first kinetic studies of 19 e complexes showing that the rate limiting step is also associative in the latter. This leads us to propose a fast pre-dissociation equilibrium between the 17 e and 19 e states. There are qualitative reports⁴ showing the substitution lability of the 19 e sandwich complexes $[\text{Fe}^{\text{I}}\text{Cp}(\text{arene})]$ ⁵ (**1**), but their instability and sensitivity to air has presumably discouraged mechanistic investigations.

The complexes (**1**) (arene = C_6H_6 or PhMe)^{4a,5} react in tetrahydrofuran (THF) with phosphines (P) ($\text{P} = \text{PMe}_3, \text{PPh}_3$), to give $\text{FeCp}(\text{P})_2(\text{H})$ and with $\text{P}(\text{OMe})_3$ to give $\{\text{FeCp}[\text{P}(\text{OMe})_3]_2[\text{P}(\text{O})\text{Me}_2]\}$ and $\{\text{FeCp}[\text{P}(\text{OMe})_3]_2(\text{Me})\}$ each in 50% yield.^{4d} These products arise by radical reaction (H atom abstraction or Arbuzov-type) of the transient 17 e

species $\text{FeCp}(\text{P})_2$, (equation 1). The reactions can be conveniently monitored by observing the disappearance of the visible spectrum of (**1**) as a function of time.[†] The rate of disappearance of (**1**) varies with the concentration of $\text{P}(\text{OMe})_3$ and the temperature as in Figure 1. Substitution proceeds by a second-order process ($k = 5 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ at -10°C) according to the rate law given in equation 2.



$$-d[\text{FeCp}(\text{toluene})]/dt = k[\text{FeCp}(\text{toluene})][\text{P}(\text{OMe})_3] \quad (2)$$

The better nucleophile PMe_3 substitutes the toluene ligand approximately 3 times faster than $\text{P}(\text{OMe})_3$ and 4.5 times faster than $\text{P}(\text{OPh})_3$. The reaction rate also varies with the nature of the leaving arene ligand; displacement of toluene proceeds about 400 times faster than that of hexamethylbenzene. The bimolecular mechanism is confirmed by the observed activation parameters: $\Delta H^\ddagger = 13.3 \pm 1.0 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -22 \pm 3 \text{ cal mol}^{-1} \text{ K}^{-1}$ ($\text{cal} = 4.184 \text{ J}$) for $\text{P}(\text{OMe})_3$. The relatively large, negative entropy of activation indicates a transition state of higher co-ordination number.

The substitution lability of the arene in (**1**) contrasts with the reported behaviour of the 18 e cation (**1**⁺) which reacts with P donors only at high temperatures.⁶ Thus the complex (**1**) (arene = toluene) reacts about 10⁷ times faster with $\text{P}(\text{OMe})_3$ than its 18 e analogue (**1**⁺).

We believe a direct mechanism involving (**1**) providing a 21 e transition state is highly unlikely because such species have never been proposed^{7-9‡} and would be of too high

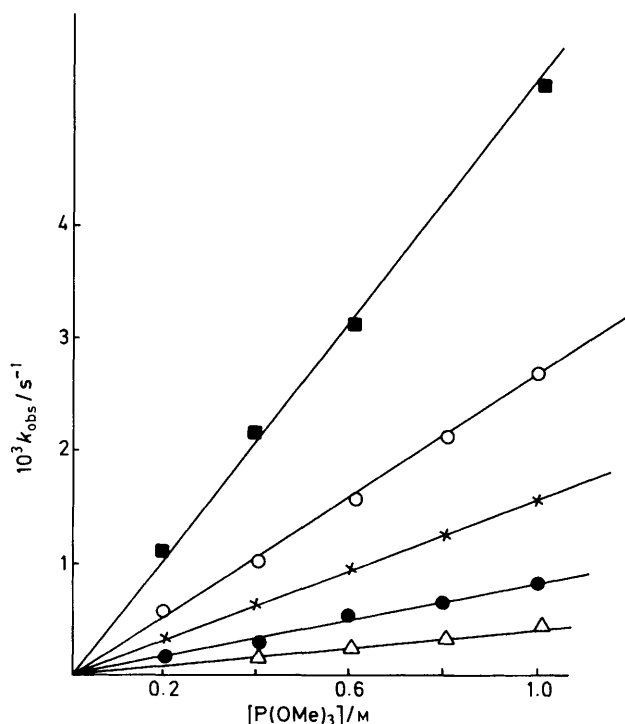
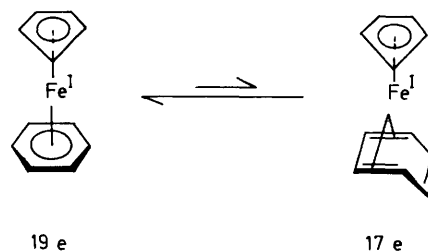


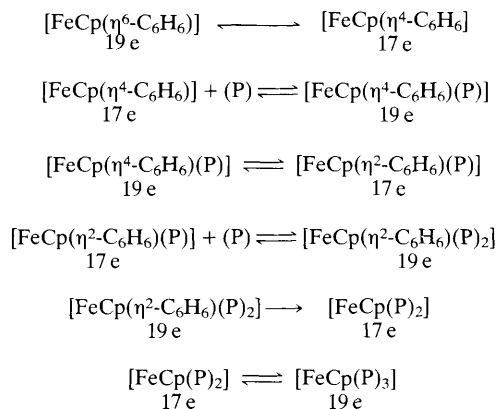
Figure 1. Plot of k_{obs} versus $\text{P}(\text{OMe})_3$ concentration for the substitution of $[\text{Fe}^{\text{I}}\text{Cp}(\text{toluene})]$ in THF solution at various temperatures: Δ , 239.5 K; \bullet , 245.5 K; \times , 251.5 K; \circ , 257.5 K; \blacksquare , 263.5 K.



Scheme 1

[†] Kinetic runs were conducted under pseudo-first-order conditions (with $[\text{P}(\text{OMe})_3] > 10 [\text{Fe}^{\text{I}}\text{Cp}(\text{toluene})]$) by observing the change in optical density at 710 nm. Since $[\text{Fe}^{\text{I}}\text{Cp}(\text{toluene})]$ is very air sensitive, all manipulations were carried out under an atmosphere of Ar. THF was dried (Na/benzophenone) and rigorously degassed prior to use. Reactions were carried out in 1.00 cm quartz cells in the thermostated cell compartment of a Varian Cary 219 spectrophotometer. Plots of $\ln(A_t - A_\infty)$ versus time were linear for more than three half-lives, and k_{obs} was determined from the slope of this line by least-squares analysis.

[‡] Note that the complexes $[\text{Fe}(\text{arene})_2]$ have a 20 electron state in $[\text{Fe}(\eta^6\text{-C}_6\text{Me}_6)_2]$ ^{8a,b} and a 18 electron state in $[\text{Fe}(\eta^6\text{-toluene})(\eta^4\text{-toluene})]$.^{8c-e}



Scheme 2

energy. In contrast, the reaction takes place very readily and a reasonable possibility is a pre-equilibrium with an η^4 -benzene species (17 e) (Scheme 1).^{8,9‡}

Close (but less likely) 17 e alternatives to this species are (i) a slipping of the benzene ligand without bending and (ii) a reduction of hapticity of the Cp ligand in $[\text{Fe}(\eta^3\text{-Cp})(\eta^6\text{-arene})]$.

Extended Hückel calculations¹⁰ have led to estimate that the 19 e species $[\text{Fe}^{\text{I}}\text{Cp}(\eta^6\text{-C}_6\text{H}_6)]$ and the 17 e species $[\text{Fe}^{\text{I}}\text{Cp}(\eta^4\text{-C}_6\text{H}_6)]$ have comparable energies, although solid state Mössbauer studies¹¹ are in favour of the 19 e form. However, in solution, the formation of small amounts of the 17 e form in fast equilibrium with the 19 e form is consequently probable. Furthermore, it explains the reactivity towards ligand exchange with P donors. The reactions of P donors with this 17 e form give 19 e transition states and the mechanism should probably best be formulated as a series of exchanges between 17 e and 19 e states as in Scheme 2. The fast interconversion between 17 e and 19 e appears to be a key feature of the reactivity of organo-transition metal radicals.^{2,12}

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