Specific Cleavage of a Carbon–Carbon Bond in the Complexation of C_6Et_6 by $Fe(C_5Me_5)^+$. Crystal Structure of $[Fe(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6Et_5H)]^+$ PF_6^-

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The reaction between $[Fe(C_5Me_5)(CO)_2Br]$ and C_6Et_6 in the presence of $AlCl_3$ does not give $[Fe(C_5Me_5)(C_6Et_6)]^+$ but, in the presence of protic impurities, $[Fe(C_5Me_5)(C_6Et_5H)]^+$ is the only cation formed; the *X*-ray crystal structure of its PF_6^- salt shows that all Et substituents are distal and a σ intermediate is proposed for the complexation.

The Fischer–Haffner type of synthesis[1] has provided a powerful route to transition metal sandwich complexes.[2] Since a Lewis acid such as $AlCl_3$ is used, retro-Friedel–Crafts processes[3] leading to the loss or transformation of alkyl substituents of aromatic ligands can compete with complexation, at least in principle.[4] This phenomenon has indeed been noted on rare occasions and circumvented to some extent by the metal-vapour technique.[5]

During our search of electron-reservoir complexes,[6] we wished to protect the 19-electron form by using bulky ligands. For instance, the reaction between ferrocene and C_6R_6 (R = Me or Et) or between $[Fe(C_5Me_5)(CO)_2Br]$ and C_6Me_6 did not lead to any loss of alkyl group in the $[Fe(C_5R'_5)(C_6R_6)]^+$ when syntheses were carried out below 110 °C.[6a] In contrast, the reaction of $[Fe(C_5Me_5)(CO)_2Br]$ with C_6Et_6 does not give the expected complex $[Fe(C_5Me_5)(C_6Et_6)]^+$ even when it is carried out at the lowest possible temperature (50 °C). In the rigorous absence of traces of protic substances (flamed Schlenk tube, triply sublimed $AlCl_3$, starting complexes dried *in vacuo*) no complex is obtained. On the other hand, when none of these special precautions is taken, a 25% yield of $[Fe(C_5Me_5)(C_6Et_5H)]^+$ PF_6^- (**1**) is obtained (neat, 80 °C, 72 h) after metathesis with aqueous $H^+PF_6^-$ and recrystallization from hot ethanol. The purity of (**1**) is clearly indicated by its ^1H and ^{13}C NMR spectra [^1H NMR (CD_3COCD_3): δ 5.84 (s, 1H, C_6Et_5H), 2.90 (10H, CH_2Me), 2.163 (s, 15H, C_5Me_5), 1.38 (m, 15H, CH_2Me); ^{13}C NMR (CD_3CN): δ 106.2, 103.3, 89.7 (ArCEt), 103.4 (ArCH), 88.8 (C_5Me_5), 24.6, 22.4, 21.8 (CH_2), 16.7, 16.0, 15.7 (CH_2Me), 9.1 (C_5Me_5)] and satisfactory elemental analyses. The Na/Hg reduction of (**1**) in 1,2-dimethoxyethane (DME) (0 °C; 1 h) followed by work-up and recrystallization from pentane gives a 25% yield of the 19-electron complex $[Fe^I(C_5Me_5)(C_6Et_5H)]$ (**2**) as confirmed by satisfactory elemental analyses and mass spectrometry (calc. 409.2257, found *m/z* 409.2526). Complex (**2**) is extremely air sensitive but thermally stable despite the incomplete arene substitution.

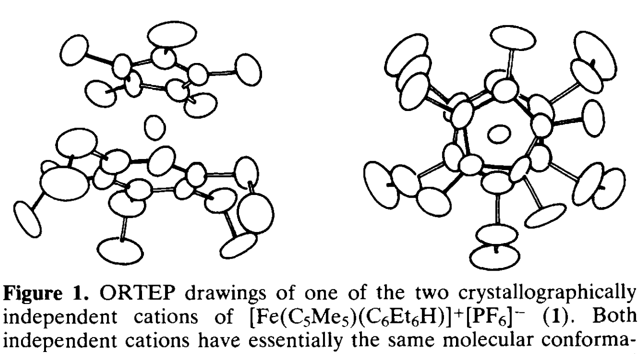

Figure 1. ORTEP drawings of one of the two crystallographically independent cations of $[Fe(C_5Me_5)(C_6Et_6H)]^+[PF_6]^-$ (**1**). Both independent cations have essentially the same molecular conformation: distal ethyl groups and eclipsed position of the unsubstituted aromatic carbon atom. Selected averaged bond distances (Å): Fe–(C_5Me_5) 1.681, Fe–(C_6Et_6) 1.555, Fe–C(C_5Me_5) 2.062 [range: 2.042(10)—2.081(10)], Fe–C(C_6Et_6) 2.097 [range: 2.074(9)—2.097(10)], C–C 1.405 (C_5 ring), 1.406 (C_6 ring) [range: 1.379(14)—1.427(15) (C_5 ring), 1.364(15)—1.472(15) (C_6 ring)].

The *X*-ray crystal structure† of the first example of a pentaethylbenzene transition metal complex (**1**) (Figure 1) shows that all the ethyl substituents have a distal conformation, in contrast to $[Fe(C_5H_5)(C_6Et_6)]^+$ PF_6^- (Figure 2) for which the *X*-ray crystal structure showed four distal Et groups and two proximal ones.[6b]

Labelling experiments in the synthesis of (**1**) using $[Fe\{C_5(CD_3)_5\}(CO)_2Br]$, $C_6(CD_2CH_3)_6$, or $C_6(CH_2CD_3)_6$[7] did not show the formation of $[Fe(C_5Me_5)(C_6Et_5D)]^+$, which could only be observed when 1 equiv. D_2O was added to the reaction mixture. This confirms the retro-Friedel–Crafts

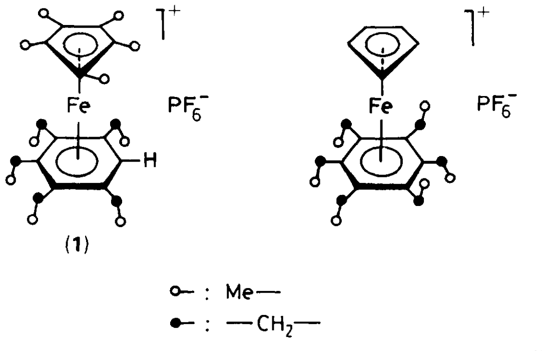

Figure 2. Comparison between the structures of the pentaethylbenzene (**1**) and hexaethylbenzene[6b] complexes.

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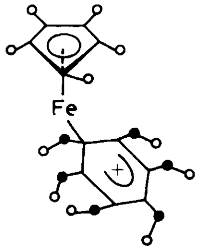
† *Crystal data:* $C_{26}F_6FeH_{41}P$, yellow crystal, monoclinic, space group $P2_1/c$, a = 20.15(3), b = 16.553(5), c = 17.94(2) Å, β = 114.2(1)°, U = 5456(1) Å^3, Z = 8, $F(000)$ = 2336, λ(Mo-K_α) = 0.71073 Å, μ = 6.61 cm^{-1}, D_c = 1.35 g cm^{-1}. Data were collected at room temperature, with a Nonius-CAD4 four-circle diffractometer using the θ–2θ scan mode. 9214 Reflections were collected in the range $1 < \theta < 25°$ and 3654 unique reflections with $I > \sigma(I)$ were used in the refinement (R_{int} = 0.023). The structure was solved using Patterson and difference Fourier synthesis. The two independent molecules appear related by a pseudo-symmetry element in the (a, c) plane. Full-matrix least-square refinement converged with R = 0.095 and R_w = 0.082 (refinement of x, y, z, β_{ij}'s for Fe, P, C, and F; H fixed). The hydrogen atoms were inserted at calculated positions. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



(A)

mechanism for the cleavage of the ethyl group during the complexation reaction (1).

$$C_6R_6 + H^+AlCl_4 \rightleftharpoons C_6R_6H^+AlCl_4^- \rightleftharpoons C_6R_5H + R^+AlCl_4^- \quad (1)$$

This process appears to be usually much slower than the complexation but, in the present case , it produces C_6Et_5H which can be complexed whereas C_6Et_6 cannot. Although the conformation of the C_5Me_5 ligand influences that of the aromatic ligand in (**1**) (a C_5Me_5 carbon eclipses the aromatic carbon bearing the hydrogen), a direct π complexation of C_6Et_6 with all-distal Et groups by the $(C_5Me_5)Fe^+$ moiety should not be much more difficult than that of C_6Et_5H. Thus a mechanistic conclusion can be drawn from these synthetic features. The inhibition of sandwich synthesis by the combined bulk of C_5Me_5 and C_6Et_6 compared to the removal of this inhibition by prior cleavage of one Et substituent of C_6Et_6 strongly suggests that complexation proceeds *via* the σ intermediate (**A**).

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