Tentacled Iron Sandwiches: Peralkylation of $Fe^{II}Cp(C_6Me_6)^+PF_6^-$ (Cp = C_5H_5)

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The title complex reacts with excess KOH and alkyl iodides RI [R = C_2H_5, C_5H_{11}, $(CH_2)_6OMe$] in dimethoxyethane (DME) under mild conditions to give specifically the hexa-alkylated complexes $[FeCpC_6(CH_2R)_6]^+PF_6^-$ (Cp = C_5H_5).

There is an increased interest in organic, inorganic, and organometallic materials which stack segregatively such as liquid crystals[1] and Langmuir–Blodgett films.[2] Along this line, we have developed the research of tentacled iron sandwich complexes. The principle is based on the enhanced acidity of benzylic protons of aromatics co-ordinated in an hexahapto fashion to an electron-withdrawing transition metal moiety. First demonstrated by Trahanovsky and Card with $Cr(CO)_3$,[3,4] it has been used with FeCp$^+$ for a number of mono functionalisations (equation 1).[5]

$$[FeCp(\eta^6\text{-PhMe})]^+ \xrightarrow{\text{t-BuOK}} [FeCp\{\eta^5\text{-Ph}(=CH_2)\}] \xrightarrow{\text{RX}}$$
$$[FeCp(\eta^6\text{-PhCH}_2R)]^+ \quad (1)$$
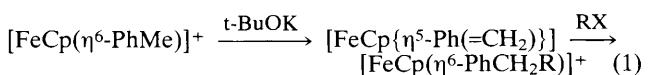
In the case of $[FeCp(C_6Me_6)]^+PF_6^-$, (1),[6] excess of t-BuOK and MeI were shown to give the hexa-alkylation product (equation 2).[7]

$$[FeCp(C_6Me_6)]^+PF_6^- \xrightarrow[\text{MeI}]{\text{t-BuOK}}$$
$$[FeCpC_6(CH_2Me)_6]^+PF_6^- \quad (2)$$
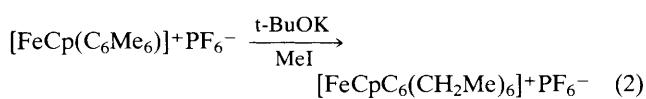
This reaction can be extended to benzyl and allyl bromides[7] but not to ordinary alkyl halides because dehydrohalogenation (equation 3) takes place faster than the organometallic reaction [(1)PF_6^- is recovered unchanged].
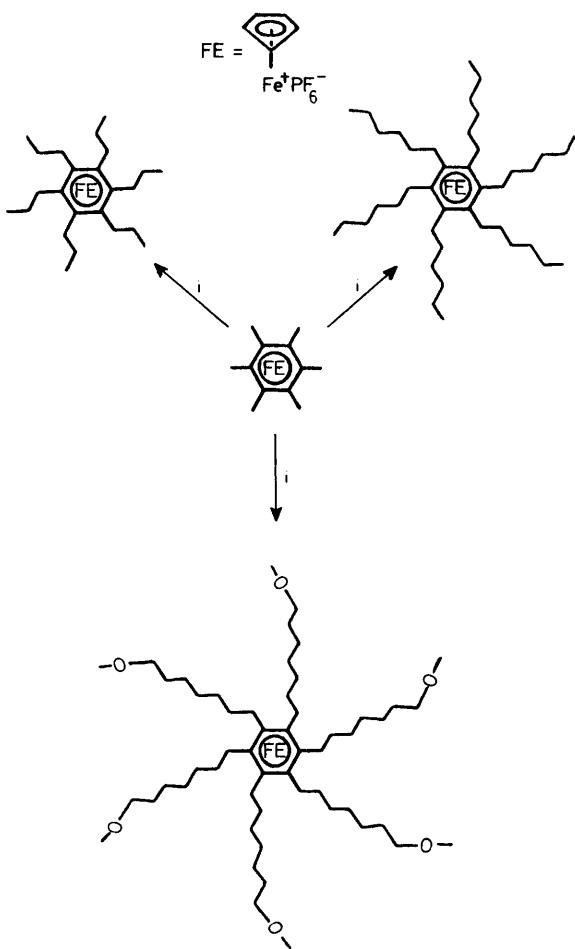
Scheme 1; Peralkylation reactions; i, KOH, RI, DME.

$$RCH_2CH_2X + t\text{-}BuOK \rightarrow t\text{-}BuOH + KX +$$
$$RCH=CH_2 \quad (3)$$
$$(X = Cl, Br, I)$$
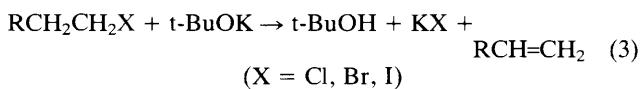
This was a severe limit of the reaction of equation (2) and we have therefore investigated the means to overcome this problem.

We find that using conditions of pseudo phase-transfer catalysis, the organometallic reaction proceeds to completion. Thus (1) PF$_6^-$ was reacted with excess KOH and RI in dimethoxyethane (DME) at 40—80 °C for 1—2 days, which gave pure [FeCpC$_6$(CH$_2$R)$_6$]$^+$PF$_6^-$, R = Et(2), n-C$_5$H$_{11}$(3), (CH$_2$)$_6$OMe(4) (Scheme 1), after chromatography on an alumina column to separate unreacted RI.

The new complexes are soluble in pentane [except (2)]. They were characterised by elemental analysis,† ¹H and ¹³C

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† Satisfactory analytical data have been obtained for all new compounds.

n.m.r. spectroscopy.‡ The 63 MHz ¹³C-{¹H} n.m.r. spectra were found necessary to monitor the reactions and ensure their completion. Since photolysis of (2)—(4) with visible light splits the sandwich complexes, access to the new free aromatics is allowed.[7] Moreover, this method also works well for the hexa-allylation reaction. Reaction of (1)PF$_6^-$ with KOH and allylbromide in DME for 1 day at 40 °C gave the pure known[7c] hexabutenylbenzene complex [FeCpC$_6$(CH$_2$CH$_2$CH=CH$_2$)$_6$]$^+$PF$_6^-$ in 80% yield on a mmol scale after work up and chromatography. Thus a cheap and efficient route to hexa-alkyl and hexafunctional benzene complexes is open. Extensions and physical studies are underway.

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‡ **(2):** yellow crystals, 70% yield; ¹H n.m.r. (CD$_3$COCD$_3$; 200 MHz) AA′BB′C$_3$ Spin system δ 1.06, 1.10, 1.14 (t, 18H, –CH$_2$–CH$_3$), 1.62, 1.66, 1.68, 1.70, 1.74 (m, sym., 12H, –CH$_2$CH$_2$–CH$_3$), 2.85, 2.87, 2.89, 2.91, 2.93 (m, sym., 12H, Aryl–CH$_2$–), 4.84 (s, 5H, C$_5$H$_5$). ¹³C-{¹H} n.m.r. (CD$_3$COCD$_3$; 22.63 MHz) δ 15.04 (–CH$_2$–CH$_3$), 25.83 (–CH$_2$–CH$_3$), 33.48 (Aryl–CH$_2$–), 78.74 (C$_5$H$_5$), 104.42 (C$_6$R$_6$).

(4): yellow resin, 60% yield; ¹H n.m.r. (CD$_3$CN; 250 MHz) 1.59, 1.75 [d, 60H, –(CH$_2$)$_5$–], 3.00 (s, broad, 12H, Aryl–CH$_2$–), 3.44 (s, 18H, –OCH$_3$), 3.53 (12H, –CH$_2$–O–), 4.85 (s, 5H, C$_5$H$_5$). ¹³C-{¹H} n.m.r. (CD$_3$CN; 62.89 MHz) δ 27.02, 29.9, 30.57, 31.20, 31.72, 32.6 [Aryl–(CH$_2$)$_6$–], 58.88 (–O–CH$_3$), 73.46 (–CH$_2$–O–Me), 78.88 (C$_5$H$_5$), 104.49 (C$_6$R$_6$).

(3): yellow resin with arborescence; ¹H n.m.r. (CD$_3$CN; 250 MHz) δ 0.91, 0.94 (18H; –CH$_3$), 1.36, 1.55 [d, broad, 48H, –(CH$_2$)$_4$–], 2.81 (s, broad, 12H, Aryl CH$_2$), 4.61 (s, 5H, C$_5$H$_5$). ¹³C-{¹H}n.m.r. (CD$_3$CN; 62.9 MHz) 14.56 (–CH$_3$), 23.4, 30.78, 31.55, 32.17, 32.51 [(–CH$_2$–)$_5$], 78.66 (C$_5$H$_5$), 104.41 (C$_6$R$_6$).