Aspects of aromatic iron sandwiches: application to organic and organometallic synthesis

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Abstract – Reaction of nucleophiles with $[Fe^{II}(\eta^5\text{-cyclohexadienyl})(\eta^6\text{-}C_6H_6)]^+$ give substituted cyclohexadiene Fe^0 complexes which, on treatment with Ph_3C^+ produce substituted cyclohexadienyl complexes which can then undergo reaction with a second nucleophile. Reaction of $[FeCp(C_6(CH_3)_6)]^+$ with t-BuOK and alkyl halides RX gives $[FeCp(C_6(CH_2R)_6)]^+$.
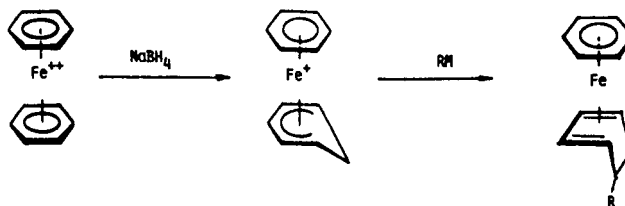
INTRODUCTION

Among the many kinds of transition metal-aromatic complexes known (including various types of hapticities), π–aromatic iron sandwiches represent especially rich series of 18 electron complexes. Their robustness is conferred by the rare gas rule and the sandwich structure (ref. 1). In these compounds, the activation by the iron moiety is of the cationic type, thus larger than in neutral π–aromatic transition metal complexes. The two common types of complexes are FeCp(arene)$^+$ (Cp = cyclopentadienyl) (ref. 2) and Fe(arene)$_2$$^{++}$ (ref. 3).
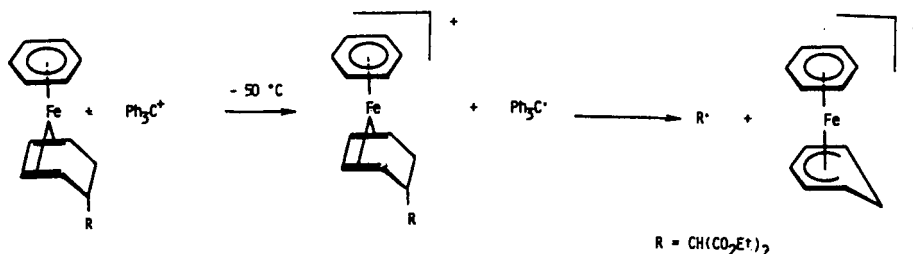
SUBSTITUTED CYCLOHEXADIENYL COMPLEXES

Prior to our work, Helling had reacted a series of hard carbanions with $[Fe(mesitylene)_2]^{++}$-$(PF_6^-)_2$ to obtain an attack on each ring giving the bis(cyclohexadienyl)Fe^{II} complexes (ref. 4). Stabilized carbanions reacted only once (ref. 4).

We found that a large variety of nucleophiles cleanly react on $[Fe^{II}(\eta^5\text{-cyclohexadienyl})\text{-}(\eta^6\text{-}C_6H_6)]^+$ to give exclusively substituted cyclohexadiene Fe^0 complexes in high yields (ref. 5). Extended Hückel calculations by Saillard and Hoffmann (ref. 5b) showed that orbital control is in agreement with the observed regiospecificity, as opposed to the explanation involving charge control (ref. 6).
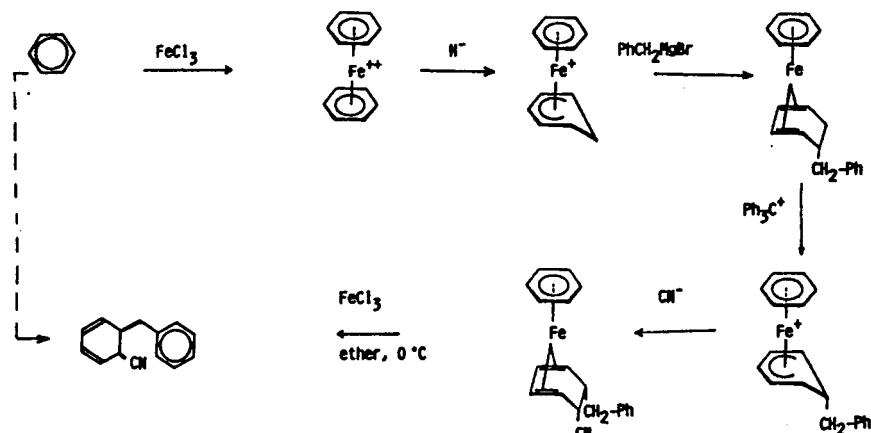

We attempted to remove the hydride from the substituted cyclohexadiene complexes with Ph_3C^+. When the reaction was effected at -40°C, the ET produced a 17e cation which did not decompose but was characterized by ESR and smoothly transferred a hydrogen atom to $Ph_3C^·$. The reaction
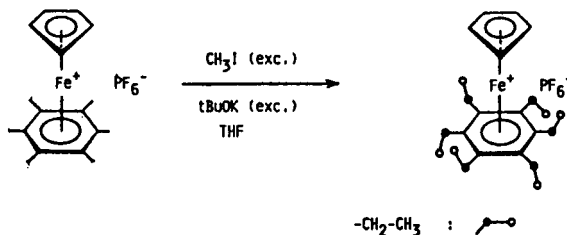

$$R = CH(CO_2Et)_2$$

between the two organic and organometallic radicals (observed by ESR) is much easier than hydride transfer between closed shell compounds and does not suffer from the steric restriction of the latter (ref. 7).

Thus, functional cyclohexadienyl complexes were obtained in this way which allowed a second reaction with a nucleophile. Bifunctionalization could indeed be performed to synthesize exo,exo-1,2-disubstituted cyclohexadiene Fe^0 complexes. These regio- and stereocontrols were confirmed by the X-ray crystal structure of the cyano-benzyl complex. Decomplexation of the Fe^0 complex using Al$_2$O$_3$ + O$_2$ gave the free ligand characterized by its mass spectrum (aromatization occurred at 40°C in the mass spectrum showing the bifunctional arene) (ref. 8).
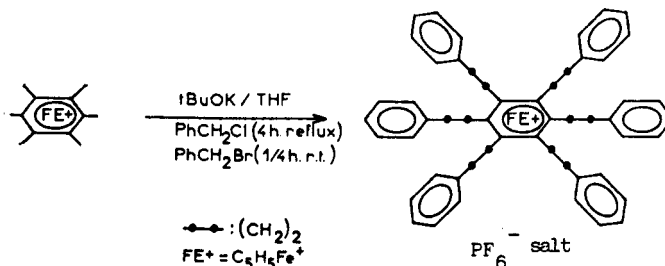

CpFe(ARENE)$^+$ MONOCATIONS: BENZYLIC DEPROTONATION

The first attempted reaction was of [FeCp(C$_6$Me$_6$)]$^+$PF$_6^-$ with t-BuOK and CH$_3$I, both reagents being in excess in THF. After a mild reflux of about 1 minute, a quantitative yield of [FeCp(C$_6$Et$_6$)]$^+$PF$_6^-$ was obtained (ref. 8). The reaction with CD$_3$I gave [FeCp(C$_6$(CH$_2$CD$_3$)$_6$)]$^+$ and the reactions of [FeCp(C$_6$(CD$_3$)$_6$)]$^+$ with CH$_3$I and CD$_3$I respectively gave [FeCp(C$_6$(CD$_2$CH$_3$)$_6$)]$^+$ and [FeCp(C$_6$(CD$_2$CD$_3$)$_6$)]$^+$ respectively.

The reaction was extended to PhCH$_2$X (X = Cl or Br) which gives the hexa(phenyl-ethyl)benzene complex. The new free aromatic ligand is easily disengaged by uv photolysis in acetonitrile (ref. 9).

Similarly, allyl bromide reacts to give the hexabutenyl complex. The latter can be photolyzed. The new hexabutenylbenzene ligand is recovered in this way.

The X-ray crystal structures of the hexaethyl- and hexabutenylbenzene complexes show noteworthy conformational effects. The hexaethylbenzene complex has four distal chains whereas the hexabutenylbenzene complex has five distal chains (ref. 10). (Figs. 1,2).

The hexabutenylbenzene complex reacts with Br$_2$ to give the dodecabromobenzene complex, with bulky silanes and boranes to give regiospecific hydrosilylation and hydroboration. Oxidation of the hexahydroboration product by HO$_2^-$ gives the hexol which can be esterified in neat acyl chloride RCOCl (R = Ph or n-Bu).
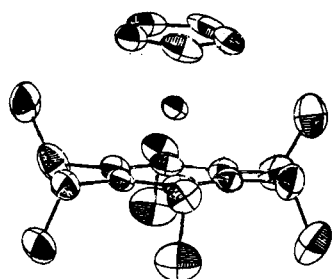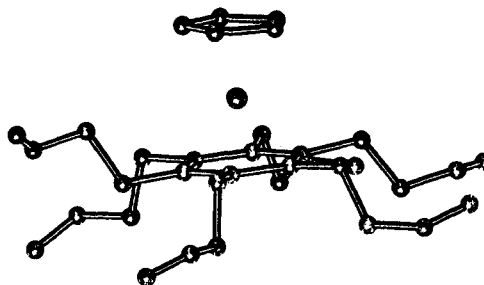
Fig. 1 Ortep view of [FeCp(hexaethylbenzene)]$^+$-PF$_6^-$

Fig. 2 Ortep view of [FeCp(hexabutenylbenzene)]$^+$PF$_6^-$

The free ligands can be obtained by visible photolysis as above and they were characterized by elemental analyses and ^{1}H and ^{13}C NMR spectroscopies. Low-temperature reduction in ESR tubes also provided the green Fe^I 19e complexes which gave the characteristic 3 g values typical of the rhombic distortion of Fe^I (ref. 11).

A major limitation of the hexaalkylation system with t-BuOK was the failure of the reactions with alkyl halides bearing at least one β-hydrogen. Dehydrohalogenation by t-BuOK gave the olefin, the reaction being always faster than the organometallic alkylation. Thus [FeCp(C$_6$Me$_6$)]$^+$PF$_6^-$ remained unchanged:

$$RCH_2-CH_2X \ + \ t\text{-}BuOK \longrightarrow RCH=CH_2 \ + \ t\text{-}BuOH \ + \ K^+X^-$$

(R = H, X = I)
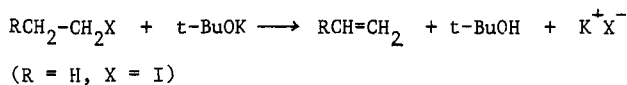
This difficulty could be overcome by using KOH instead of t-BuOK. No reaction between KOH and RX was noted and although the organometallic reaction is somewhat slower, it proceeds smoothly. Thus, this technique opens a general route to the complexes of hexaalkylbenzenes with various chain lengths. So far, the hexapropyl, hexabutyl, and hexahexylbenzene complexes have been made in a pure form. The hexaalkylation reaction tolerates an oxygen atom in the chain (ether group) provided it is remote from the alkylation site (ref. 12). Efforts are continuing along these lines to make polyether derivatives, polyfunctional complexes, hexaligands, and templates.

peralkylation reactions : KOH, RI, DME.
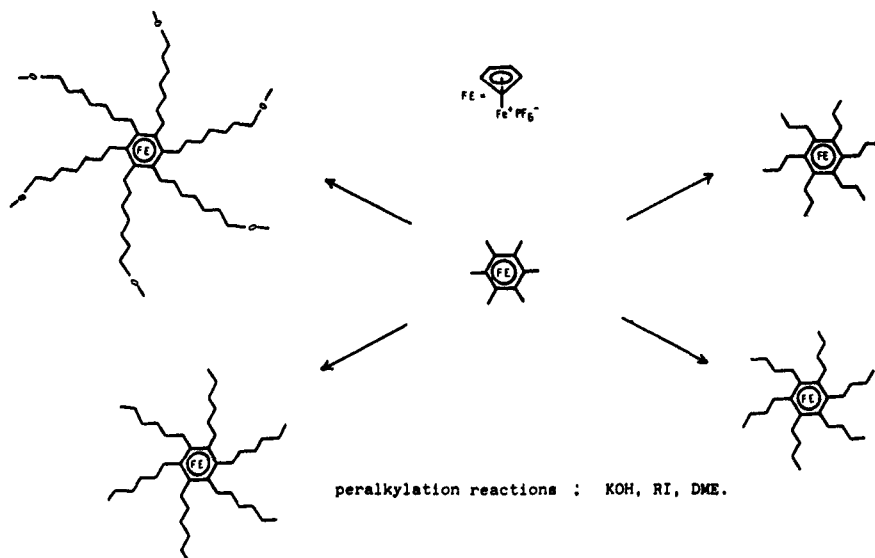
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