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ORGANO-IRON COMPLEXES OF AROMATIC COMPOUNDS. APPLICATIONS IN SYNTHESIS†

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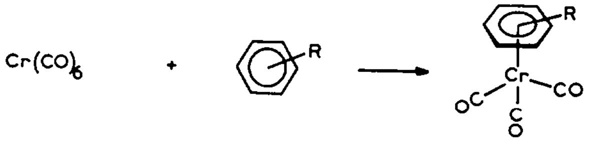
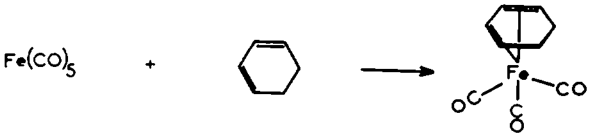
†This article is dedicated to Dr. Bianca Tchoubar.

1. INTRODUCTION

The discovery of the transition metal sandwich structure[1-3] in compounds such as ferrocene[4] and bis benzene chromium[5] thirty years ago was a major advance in organic and organometallic chemistry. However, despite their rich properties, neither of these complexes proved useful in organic synthesis. On the other hand, the use of the longer known metal carbonyls has been fruitful, especially with iron and chromium because of the ability of these transition metals to give stable 18-electron tricarbonyl complexes which are extremely easy to handle (eqn 1, 2).[6-9]

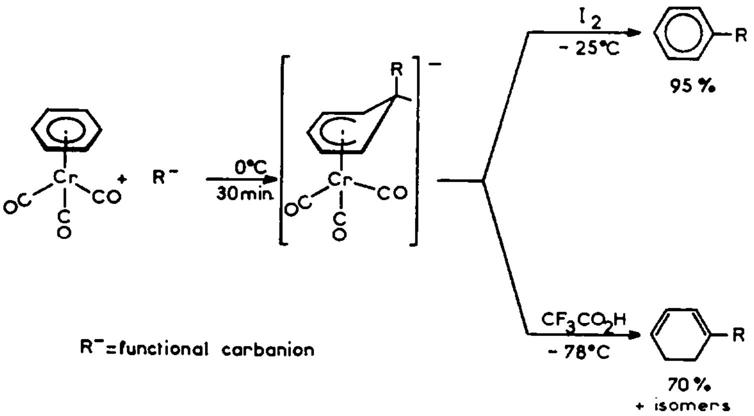


(eq.1)



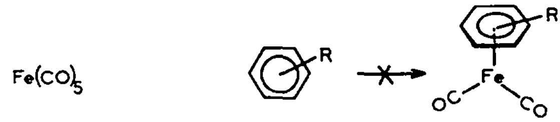
(eq.2)

In these complexes, the metal tricarbonyl group exerts steric, electronic and conformation effects.[9,10] In particular, C–C bond formation by nucleophilic attack of carbanions on arenes temporarily complexed in a hexahapto fashion to $Cr(CO)_3$ has been well developed as a synthetic tool[10a] (Scheme 1). In addition, the stereochemical consequences of the temporary complexation of an arene by $Cr(CO)_3$ have been extensively used to synthesize optically active compounds.[10b]



Scheme 1.

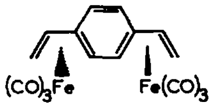
In this context, it is unfortunate that 18-electron hexahapto–arene iron carbonyl complexes could not be obtained by reaction of iron carbonyl with arenes (eqn 3).

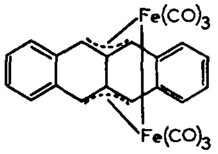


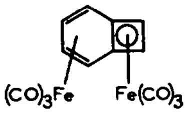
(eq.3)

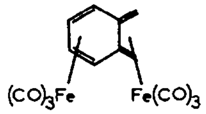
These failures can be accounted for by the fact that the iron tricarbonyl unit is reluctant to lose one CO ligand.

Arene iron tricarbonyl complexes are obtained for arenes bearing an exocyclic unsaturation as in styrenes, polyaromatics, benzocyclobutadiene and orthoxylylenes.[11] In these cases, the reactions of $Fe(CO)_5$ or $Fe_2(CO)_9$ give diene-like complexes. Representatives of this class of "inorganic" complexes are illustrated below.

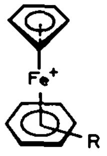




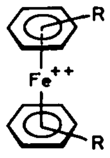




Their syntheses have been extensively reviewed[11] but subsequent reactivity of the coordinated arene is nearly unexplored. We shall concentrate here on "organo–iron" complexes in which the aromatic ring is bound to the iron atom in an hexahapto fashion. Complexes which have proved useful in aromatic synthesis are the readily available cationic sandwiches of the type cyclopentadienyl(arene) iron cations I ($CpFe^+$ arene) and bis(arene) iron dication II.



I



II

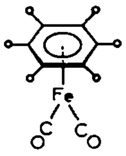
A very large number of complexes I are known whereas the scope of complexes II is so far limited. Our purpose is to review aromatic complexes of iron with special emphasis on organic synthesis. Several authors have reviewed work on aromatic iron complexes up to 1975[11-15] and considerable progress has been achieved since.

We will first describe the structure and bonding, then examine complexation and decomplexation reactions; the most important part of the review will detail the reactivity of coordinated arenes, essentially in cyclopentadienyl(arene) iron complexes.

2. STRUCTURE AND BONDING

2.1 *Neutral complexes*[16]

The main mode of arene complexation to iron in stable compounds is in an hexahapto fashion (with ruthenium, there is one case of a tetrahapto hexamethylbenzene complex).[16a] In neutral diamagnetic complexes, iron needs to complete its coordination with one four-electron or two two-electron ligands and has the oxidation state 0. This is achieved in d^8 complexes of types III–VII by two carbonyls, two phosphines or a closed or open diene.[16-19]



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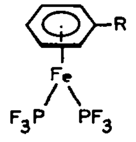
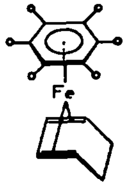
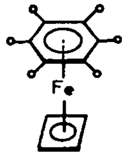


R = H, CH$_3$

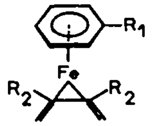
IV



V



VI



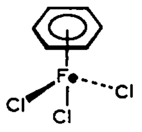
a) $R_1=CH_3, R_2=H$
b) $R_1=PPhEt, R_2=CH_3$

VII

o–: CH_3

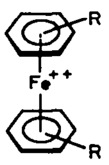
The local symmetry of the arene is apparently always D_{6h}. The equivalence of the ^1H and [^1H] ^{13}C NMR arene signals shows that the complexation is hexahapto. These complexes are electron-rich and air sensitive and their oxidation potentials must be around the −0.7 V/sce value of the system $O_2/O_2^{\cdot -}$ (except III and IV). The electron donation of the arene to metal orbitals is well compensated by the back donation of the metal, so that the arene rings are electron rich and these complexes are nucleophilic as is ferrocene.

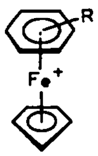
An unstable complex has been reported to form between $FeCl_3$ and benzene at −30° and a C_{3v} symmetry has been proposed.[16c] If so, this may be a d^5 17-electron complex of the following structure:

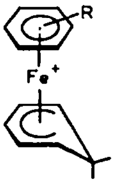


2.2 *Cationic complexes*

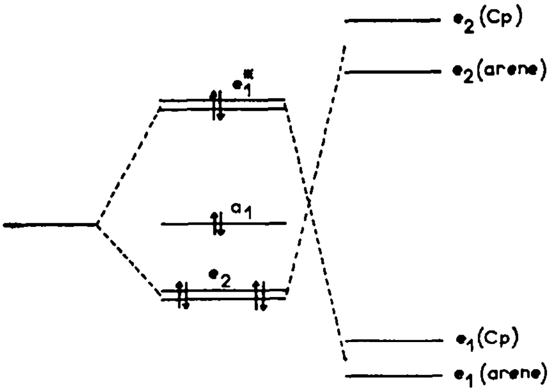
The three related types of cationic iron arene complexes of sandwich structure and 18-electron configuration are stable in air and many other media.



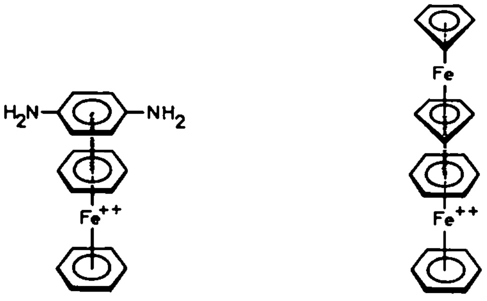




2.2.1 *Bis(arene) iron dications.* The molecular orbital diagram for iron as well as other transition metal sandwiches is well established.[20-22] Bis(arene) iron dications are isoelectronic to

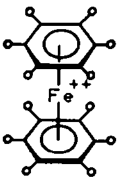


Molecular orbital diagramm for transition metal sandwiches. Maximum occupancy (20-electron) for CpFe$^-$(arene) bis(arene) chromium. The doubly degenerate bonding e_2 level has a high metal character whereas the nonbonding a_1 orbital is a nearly pure d_{z^2} metal orbital. All these levels are fully occupied. Considerable electron density is removed from the arene. Thus, charge–transfer complexes are formed with typical donors such as benzene, polyaromatics, indole, aniline derivatives, hydroquinone, pyridine, furan and ferrocene; their colours range from pink (benzene) to blue (p-phenylenediamine) as the donor ability of the arene is increased.[23]

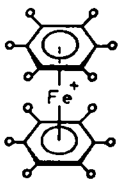


charge transfer complexes

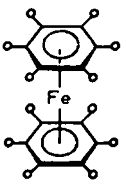
19-electron complexes are formed by addition of one electron to the dication.[24] They are stable only when the arene bears several methyl groups.[25] Addition of a second extra electron gives a nearly stable complex in the case of C_6Me_6.[25] Violation of the 18-electron rule is possible because the antibonding doubly degenerate e_{1g}^* level has a high metal character and is located at relatively low energy.[26] The series of three isostructural complexes $(C_6Me_6)_2Fe^{n+}$, n = 0, 1, 2 has been isolated.



d^6,18e$^-$,Fe^{II}



d^7,19 e$^-$,Fe^I



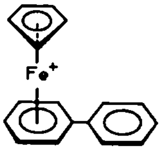
d^8,20 e$^-$,Fe^0

The d^7 19-electron complex is Jahn–Teller active and its EPR spectrum, first erroneously interpretated in terms of population of a ligand e_{eu} orbital[27] was recently better rationalized as being the result of dynamic distortion (at all temperatures).[26] The NMR contact shift of the methyl groups is in accord with limited spin delocalization on the ligands and both σ and π delocalization mechanisms were expected to give downfield shifts.[22] The observation of sharp resonances is also consistent with a Jahn–Teller distortion. Comparison of the Mössbauer parameters for the three compounds[28,29] indicates a high metal character for the antibonding HOMO; the temperature dependence of the quadrupole spitting of the PF_6^- salt of the d^7 complex is consistent with a Jahn–Teller active system. The splitting of the quadrupole doublet (0 Tesla) of the 20-electron complex into a doublet at high energy and a triplet at low energy (6 Tesla) shows that the quadrupole splitting is negative, actually the most negative value known for a neutral organo-iron complex ($-1.35\,\mathrm{mm\ s^{-1}}$).[28,30] This also confirms the very high metal character of e_1^* ($\simeq 90\%$). Magnetic susceptibility measurements confirm that respectively one and two unpaired electrons are found in the 19- and 20-electron complexes.[25]

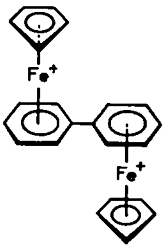
2.2.2 *Cp(arene) iron cations.* The mixed $CpFe^+$(arene) systems display closely related behavior. Since the Cp radical is a 5-electron ligand, the 18-electron configuration of the iron valence shell is attained in monocations. The replacement of an arene ring by a cyclopentadienyl one results in the splitting of the ligand e_1 and e_2 levels, smaller rings having higher energy orbitals.[31] Consequently, the bonding molecular level e_2 is closer to e_2 (arene) than to e_2 (Cp). Thus it has more arene than Cp character[32] and arene substituents have a greater influence on e_2 than Cp substituents. These effects are observed in the electronic[32] and Mössbauer[33,34] spectra and in the values of the reduction potentials recorded by polarography and cyclic voltammetry.[32,35]

Mössbauer parameters are known for a large number of CpFe$^+$(arene) complexes. The isomer shift values are in the range of 0.50–0.62 mm s^{-1}. The quadrupole splitting increases from 1.6 to 2.1 mm s^{-1} upon addition of methyl groups on the arene, which is consistent with increasing covalency of the metal–arene bond.[33,34] The temperature dependent variation of the parameters is small as in other diamagnetic iron complexes. One exception is CpFe$^+$(C$_6$H$_5$X)PF$_6$$^-$ (X = H, F) which, like CpFe$^+$(CO)$_3$PF$_6$$^-$ presents dramatic variations of the spectra as a function of temperature, rationalized by various motions of the cations in the salt lattice[44–46] as is observed with ferrocene in chlathrates.[47]

The ^{1}H NMR chemical shifts (δ) of CpFe$^+$(C$_6$H$_6$) are 5.20 and 6.50 ppm downfield from TMS;[48] thus the Cp hydrogens are 1 ppm downfield from those in ferrocene whereas the benzene hydrogens are 1 ppm upfield from free benzene.[49] Chemical shifts of CpFe$^+$(PhX), CpFe$^+$(p-XC$_6$H$_4$CH$_3$) and C$_5$H$_4$X Fe$^+$ (C$_6$H$_6$) salts containing various substituents have been correlated with Hammet–Taft σ parameters. ^{19}F chemical shifts of p- and m-CpFe(F–C$_6$H$_4$CH$_3$) have been interpretated in terms of the arene ring being a strong acceptor.[50] The ^{13}C chemical shifts of CpFe$^+$ (C$_6$H$_6$) are 89 ppm for benzene and 77 ppm for Cp. The arene carbons are 39 ppm upfield of benzene and the Cp resonance is 9 ppm downfield of ferrocene.[62] A useful consequence of these marked shifts upon complexation of arenes to CpFe$^+$ units is that, in polyaromatic complexes, the ^{1}H and ^{13}C spectra clearly indicate whether the polyaromatic is complexed to one or two CpFe$^+$ units (A or B);[115] complexes bearing two CpFe$^+$ units present much simpler spectra.



A



B

Mössbauer parameters (20°)[44] mm s^{-1} vs Fe	Cp$_2$Fe	CpFe$^+$(C$_6$H$_6$)	CpFe$^+$(C$_6$Me$_6$)
Isomer shifts	0.53	0.41	0.45
Quadrupole splitting	2.37	1.64	2

NMR parameters δ ppm vs TMS, CD$_3$COCD$_3$	Cp$_2$Fe	CpFe$^+$(C$_6$H$_6$)	C$_6$H$_6$	C$_6$Me$_6$	CpFe$^+$(C$_6$Me$_6$)
δ (^{1}H)	4	6.50 (C$_6$H$_6$) 5.20 (Cp)	7.27	2.15	2.56 (Me) 4.76 (Cp)
δ (^{13}C)	68	89 (C$_6$H$_6$) 77.0 (Cp)	128	132 (C$_6$ ring) 17 (CH$_3$)	79.0 (Cp) 99.9 (C$_6$ ring) 17.8 (CH$_3$)

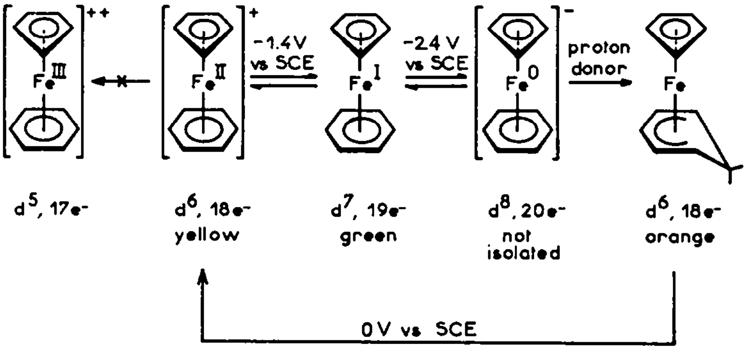
The electronic spectra of CpFe$^+$(arene) complexes have been compared to those of ferrocene and bis(arene) iron dications. Three spin allowed transitions are observed at 22,200, 26,200 and 31,900 cm^{-1} and two bands at 38,200 and 41,800 cm^{-1} are attributed to $\pi \rightarrow \pi^*$ benzene transitions[115b]. Ligand field parameters (cm^{-1}) are $\Delta_1 = 8500$, $\Delta_2 = 21{,}900$, B = 320 (ferrocene $\Delta_1 = 7200$; $\Delta_2 = 22{,}000$, B = 390). The values of the electronic repulsion parameters B indicate large covalency of the metal–ligand bonds.

A careful study[52] of the IR spectra of CpFe$^+$(C$_6$H$_6$) and its perdeuterated analogues indicates that the sandwich is covalent. The vibration of the metal–ligand bond can be treated by local symmetry (C_{5v} for Cp–Fe and C_{6v} for C_6H_6–Fe). The Cp–Fe bond is found to be weaker than in ferrocene and the vibration between the two rings are only weakly coupled. The introduction of substituents on Cp (but not on C_6H_6) removes the bands at 1000 and 1100 cm^{-1}, a rule analogous to the one well known in the ferrocene series.[53]

^{35}Cl NQR spectra for $CpFe^+(C_6H_5Cl)$ ($\nu_{^{35}Cl} = 35.9$ MHz) and $C_5H_4ClFe^+$ (C_6H_6) ($\nu_{^{35}Cl} = 36.98$ MHz) show that the frequencies found are higher than in C_6H_5Cl ($\nu_{^{35}Cl} = 34.62$ MHz) and chloroferrocene ($\nu_{^{35}Cl} = 35.91$ MHz) but lower than in 1-Cl-2,4-$(NO_2)_2C_6H_3$ ($\nu_{^{35}Cl} =$ 37.79 MHZ). The order found correlates with the degree of mobility of the halogen on the rings.[54]

Field desorption techniques afforded the observation of the ions corresponding to $CpFe^+$(arene) cations in the mass spectra of their PF_6^- salts. For $CpFe^+(C_6H_6)$, the dimeric cation was also observed.[55]

Analytical electrochemistry[35,56–61] indicates no oxidation to dicationic Fe(III) species. Two reduction steps are observed by polarography and cyclic voltammetry.[35] The first one is reversible and leads to neutral Fe(I) species, the stability of which is strongly dependent on the medium and ring substituents. $CpFe^+(C_6H_6)$ is reduced on an Hg cathode at −1.4 V/sce in CH_3CN and −1.56 V/sce in aqueous NaOH 0.1 N. The second cathodic save (≃ −2.4 V/sce) is reversible only in the absence of proton donors.[35] For instance, in the presence of phenol as proton source, irreversible reduction gives Cp (cyclohexadienyl) iron complexes (isoelectronic to ferrocene) which are irreversibly oxidized to the $CpFe^+$ (arene) cation at 0 V/sce (Scheme 2).



Scheme 2.

The cathodic reduction of $CpFe^+(C_6H_{6-n}Me_n)$ cations always shows an irreversible second wave, probably because the methyl groups serve as a proton source.[60] The voltammogrammes of $CpFe^+$(halogenoarene) cations also show the formation of $CpFe^+$(arene), dehalogenation occurring in the second reduction step.[60] The effects of ring substituents on the E 1/2 value of the first reduction wave (Fe(II)→Fe(I)) are relatively weak, consistent with an antibonding e_1^* orbital of primarily metal character.[35] Cp substituents have slightly more influence than arene substituents, indicating that e_1^* contains more e_1 (Cp) than e_1 (arene) contribution. The substituent effects are described by the equations:

$$E\ 1/2 = -1.39 + 0.520\ \sigma_p^{\circ},\ r = 0.997\ \text{(Cp substituents)}$$

$$E\ 1/2 = -1.42 + 0.515\ \sigma_p^{\circ},\ r = 0.995\ \text{(arene substituents).}$$

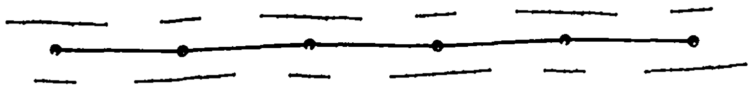
As expected, $CpFe^+$(arene) complexes of polyaromatics are reduced at less negative potentials as follows (CH_3CN, 0.1 N, Bu_4NBF_4, $c = 2.10^{-3}$ mole.l^{-1}, 25°)[35]:

Arene in $CpFe^+$(arene)	Benzene	Fluorene	Biphenyl	Phenanthrene	Naphthalene
1st reduction E 1/2 V vs sce	−1.45	−1.40	−1.30	−1.23	−1.07
2nd reduction E 1/2 V vs sce	−2.39	−2.23	−2.22	−1.80	−1.75

The reduction of dicationic $(CpFe^+)_2$ polyaromatic complexes[51] gives one reduction wave Fe(II)→Fe(I) or two close waves Fe(II)Fe(II)→Fe(II)Fe(I)→Fe(I)Fe(I). The separation between the two waves is only 0.1 V for the dication of diphenyl and 0.15 V for that of pyrene. It can be somewhat larger for dissymetrical arenes (0.37 V for phenylmesitylene). Thus it is theoretically possible to reach mixed Fe(II)–Fe(I) systems.

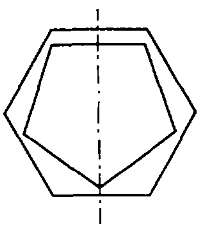
As in the case of the bis (arene) iron series, d^7 19-electron Fe(I) complexes have been isolated and extensively characterized[32,36–38] but, in contrast to the bis(arene) iron series, 20-electron complexes have not been isolated. In general, 19-electron complexes are thermally stable only when the arene ligand is peralkylated;[32,38] steric bulk also stabilizes the complexes of 1,3,5-tris terbutylbenzene[39] and of pentaethylbenzene.[40]

The bis(arene) Fe^+ cations and CpFe(arene) complexes belong to the same d^7, 19-electron Fe(I) series. Their color is attributed to an absorption involving a metal to arene $e_1^* \rightarrow e_2$ transition.[32,41] In the ^1H NMR spectra, the Cp resonance was found to be slightly shifted (30 ppm) whereas the arene methyls gave a signal nearly in the diamagnetic region (−1 ppm).[32,42] These data are in accord with a larger spin delocalization on Cp than on the arene. The Mössbauer parameters indicate a 80% metal character for the e_1^* HOMO and the temperature variation of the quadrupole splitting fits nicely to the thermal population of the Kramers doublet for Fe(I) compounds in which the two rings are comparable in size.[32,38] For Fe(I) compounds having only one permethylated ring, discontinuities are recorded corresponding to phase transitions.[43] For example, $CpFe(I)(C_6Me_6)$ exhibits two doublets at 77 K due to two phases corresponding to alternative sandwich positions in the crystal packing. The two positions must experience differing asymmetry of the external potential. Although the low temperature X-ray crystal structure is not available, X-ray powder pattern indicates a lower symmetry than at 293 K.[43] Sandwich positions at 293 K are represented below. Detailed EPR studies of these Jahn–Teller active Fe(I) sandwiches in frozen solution, in the solid state and in diamagnetic matrixes give evidence for dynamic rhombic distortion, the high degree of covalency, and efficient spin-lattice relaxation.[26]

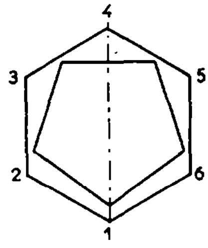


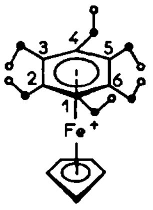
Structure of the 19-electron complex $CpFe^I(C_6Me_6)$: Projection of a chain onto a plane perpendicular to layers of mixed Cp and arene rings.

Fortunately, X-ray crystal structures are known for both the d^6Fe(II) and d^7Fe(I) CpFe (C_6R_6) complexes. The metal–Cp distance is longer in the Fe(I) sandwich by 0.10 Å but the lengthening of the arene–iron distance on addition of the 19th electron is hardly significant (0.04 Å). Conformational problems arise from the interaction of the Cp and arene rings in the sandwiches. The two most stable conformations which could be expected are indeed found, one in CpFe(I) (C_6Me_6), the other in $CpFe^+(C_6Et_6)$.



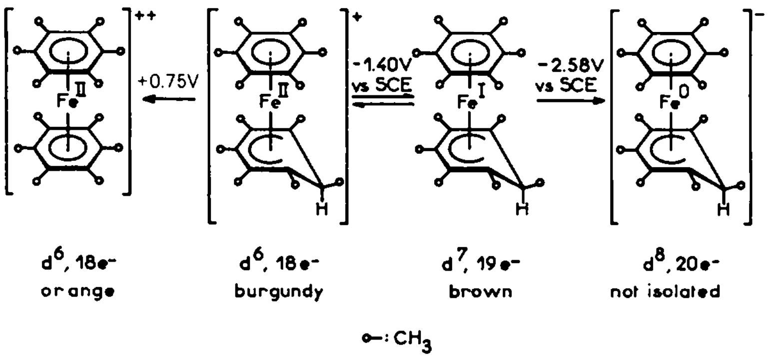
$CpFe^I(C_6Me_6)$





In $CpFe(I)(C_6Me_6)$, the H and Me substituents are slightly bent toward the metal according to the geometric demand of the metal d orbitals. In $CpFe^+(C_6Et_6)PF_6^-$, the orientation of the Me groups is not alternating as in the other complexes of C_6Et_6, but is strongly related to the conformation of the arene ring vs the Cp ring.

2.2.3 *Arene* (*cyclohexadienyl*) *iron cations*. These are isoelectronic to the $CpFe^+$(arene) cations. They are known for benzene,[63,64] mesitylene[65,66] and hexamethylbenzene,[34,67] and for R = H, Ph, allyl, t-butyl, phosphite. Since they are always synthesized from symmetrical bis(arene) iron dications, the arene and cyclohexadienyl rings have the same substituents, except that the cyclohexadienyl ring bears the extra substituent on the sp^3 carbon in exo position. In contrast to neutral bis (cyclohexadienyl) iron systems,[65] they are not fluxional. ^1H and ^{13}C NMR chemical shifts of the arene are as in $CpFe^+$ (arene) cations and cyclohexadienyl complexes; cyclohexadienyl chemical shifts are distributed as in Cp(cyclohexadienyl) complexes, but shifted slightly downfield because of the positive charge. Cyclic voltammetry indicates behavior related to $CpFe^+$(arene) complexes, except that they are easily and irreversibly oxidized, giving the bis(arene) iron dications.[34,67] The first reduction of $(C_6Me_6)(\eta^5\text{-}C_6Me_6H)Fe^+$ is reversible and located at a potential (− 1.4 V/sce) slightly less negative than $CpFe^+(C_6Me_6)$ (− 1.5 V/sce) in DMF (Scheme 3).



Scheme 3.

The d^7 19-electron Fe(I) complex $(C_6Me_6)(\eta^5\text{-}C_6Me_6H)Fe$ has been isolated as stable brown crystals.[34,67] The Mössbauer spectra of both the d^6 and d^7 complexes have been recorded and their comparison indicates that these complexes are related to the bis(arene) iron and Cp(arene) iron series. However the temperature dependence of the quadrupole splitting of the d^7 Fe(I) complex is less marked than for the d^7 complexes of the two other series because of the deviation from the sandwich structure.

Mössbauer parameters of d^6 18-electron Fe(II) cations at 293 K vs Fe ($mm.s^{-1}$)[34]

	$CpFe^+(C_6Me_6)$	$(C_6Me_6H)Fe^+(C_6Me_6)$	$(C_6Me_6)_2Fe^{++}$	$(C_6H_6)_2Fe^{++}$
I.S.	0.45	0.51	0.56	0.41
Q.S.	2.0	1.38	2.06	1.64

Mössbauer parameters of d^7 19-electron Fe(I) complexes vs Fe ($mm.s^{-1}$)[34]

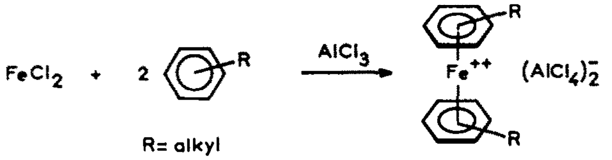
	$CpFe(C_6Me_6)$		$(C_6Me_6H)Fe(C_6Me_6)$		$(C_6Me_6)_2Fe^+$	
	293 K	77 K	293 K	77 K	293 K	77 K
I.S.	0.74	0.85	0.46	0.58	0.74	0.83
Q.S.	0.50	$\begin{cases} 0.56 \\ 1.18 \end{cases}$	0.93	1.04	0.63	0.80

3. COMPLEXATION OF ARENES TO IRON

The two known types of complexation are the extensively studied Fischer–Haffner synthesis[14,70] and the as yet undeveloped metal vapor synthesis.[17,18,51] There are a few examples of photolytic complexation. Complexation of heterocycles will also be considered. In the Fischer–Haffner synthesis, arene structure is sometimes modified upon complexation; these cases will be reviewed in a special section.

3.1 (*Bis(arene) iron dications*)

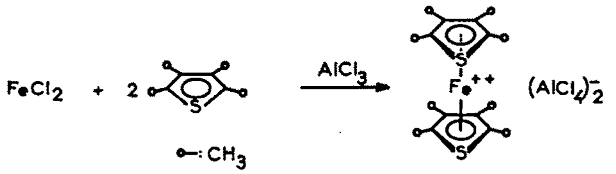
The synthesis of bis(arene) iron dications is typical of the Fischer–Haffner type of synthesis.[24,65] A mixture of the arene, $FeCl_2$ or $FeBr_2$ and $AlCl_3$ is refluxed in the arene as solvent or heated neat or in an alkane such as decalin if the arene is a solid. Yields are good with alkylbenzenes. Reactions conditions can vary in the range 80–190° and 1–20 h without much effect (eqn 4).



(eq.4)

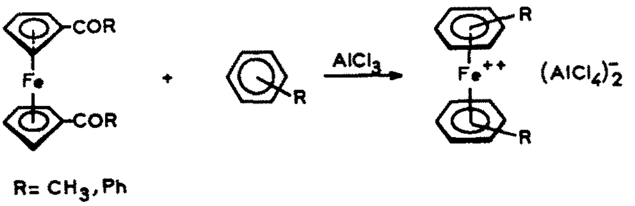
For benzene and toluene, the yields can be much increased by using $FeCl_3$ instead of $FeCl_2$.[71] $FeCl_3$ is reduced *in situ* by the arene and the Fe(II) formed is very reactive. The hydrolysis must be carried out very cautiously in the case of benzene because of the instability to water of $(C_6H_6)_2Fe^{2+}$. The rate of decomplexation of bis(arene) iron dications in water has been measured by titration of free Fe^{2+} by KCN, $K_3Fe(CN)_6$, or $K_4Fe(CN)_6$. It was indeed shown to decrease upon increasing the number of methyl groups on the arene rings.[72]

The synthesis of the bis(tetramethylthiophen) iron dication has been reported as an hydrolytically unstable PF_6^- salt whereas analogues with less than four methyl groups on the thiophene ligand could not be synthesized[73] (eqn 5).



(eq.5)

Bis(arene) salts have been isolated as tetraphenylborates,[24] diaminotetrathiocyanatochromate(III),[24] iodides[24] or hexafluorophosphates. The latter salts are the most convenient to handle; they are soluble in acetone and acetonitrile, nearly insoluble in water and alcohols and totally insoluble in THF and inert solvents; they are readily prepared by addition of HPF_6, $NaPF_6$ or NH_4PF_6 to the aqueous solution obtained after hydrolysis of the reaction mixtures and can be recrystallized from acetone. Alternatively, they can be prepared in good yields by reaction of 1,1′-diacetyl or dibenzoylferrocene- with alkylarenes and $AlCl_3$ at 115–130°,[74–76] followed by a similar work up (eqn 6).



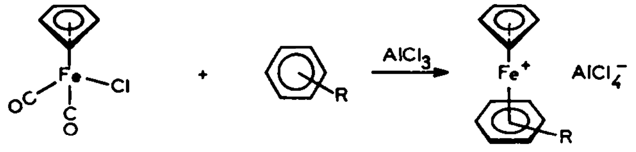
(eq.6)

At more elevated temperatures, partial loss of methyl groups and isomerization occur.[77,78] At lower temperatures such as in refluxing benzene, hardly any reaction takes place.

A patent has reported the synthesis of bis(mesitylene) iron dications using iron pentacarbonyl, mesitylene and aluminium chloride.[79]

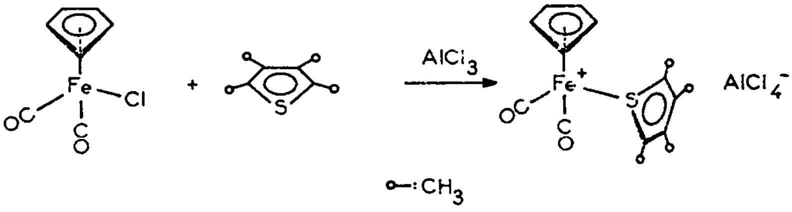
3.2 *Arene (cyclopentadienyl) iron cations*

3.2.1 *Syntheses using* $CpFe(CO)_2Cl$ *and* $C_5Me_5Fe(CO)_2Br$. $CpFe^+$(arene) salts (arene = benzene, toluene, mesitylene) were first synthesized using $CpFe(CO_2Cl$[80–83] according to eqn (7).



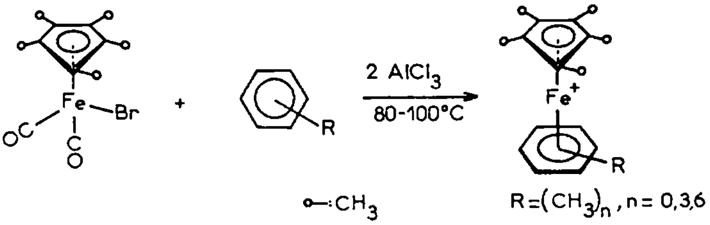
(eq.7)

The salts were isolated as iodides[80,81,83] or tribromides.[82] However this reaction is no longer used (except in the C_5Me_5 series) because ferrocene was found to be a starting material under similar conditions; also, side products were found in the reaction of eqn (7), limiting the yields.[84] With alkylthiophenes as arenes, complexation occurs exclusively in a monohapto fashion via sulfur (eqn 8).[85]



(eq.8)

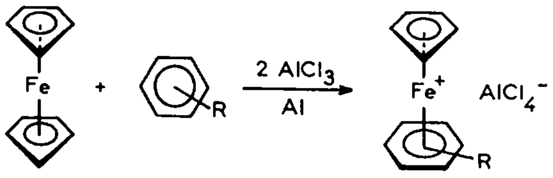
Whereas the synthesis using ferrocene is more convenient than the one using $CpFe(CO)_2Cl$ for the synthesis of $CpFe^+$(arene) complexes, it cannot be applied to that of pentamethylcyclopentadienyl analogues since decamethylferrocene is inert towards ligand exchange by $AlCl_3$.[130] For this series, the route using $C_5Me_5Fe(CO)_2Br$ was found to be clean and convenient[32,38] (eqn 9).



(eq.9)

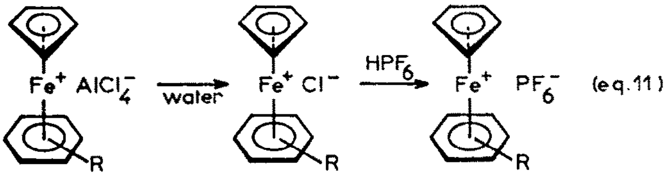
A series of canary-yellow PF_6^- salts have been synthesized in 25–50% yields; thiophene and its methylated derivatives complex only in a monohapto fashion via sulfur as in the parent Cp series. The cation $C_5Ph_5Fe^+(C_6H_6)$ was also synthesized by this route using $C_5Ph_5Fe(CO)_2Br$, $AlCl_3$ and benzene.[83]

3.2.2 *Syntheses using ferrocene.* The ligand exchange reaction between one ring of ferrocene and arenes has attracted a great deal of attention as it is a straightforward way to complex arenes with the $CpFe^+$ unit[89–123] (eqn 10).



(eq.10)

This reaction is carried out at 70–190° during 1–16 h in the arene as solvent; if the arene is a solid the reaction can be carried out neat in a sealed tube or in an inert solvent such as heptane, cyclohexane, methylcyclohexane, octane or decalin. $AlCl_3$ is the most common Lewis acid inducing the reaction and Al powder is added to inhibit oxidation of ferrocene to ferricinium. The stoichiometry of the reactants is ferrocene/arene/$AlCl_3$/Al: 1/1/2/1. However in most cases, the addition of a stoichiometric amount of water increases the yield;[124] then the favorable stoichiometry is ferrocene/arene/$AlCl_3$/Al/H_2O: 1/1/3/1/1. For instance, with benzene, the yield increases from 20 to 90% upon addition of water. It is often best to carry out the reaction at moderate temperatures (70–100°) to avoid any transformation of the arene (*vide infra*, §3.2.5). If the arene is precious, the optimum ferrocene/arene ratio is about 2.5. When complexation of a polyarene by two $CpFe^+$ units is expected, a much larger excess of ferrocene and $AlCl_3$ is necessary (arene/ferrocene/$AlCl_3$: 1/20/100; see also §3.2.5.1). After hydrolysis with ice water, the aqueous phase contains the $CpFe^+$ (arene) cation. Ammonia is added to precipitate $Al(OH)_3$. Aqueous HPF_6 or a PF_6^- salt is added to the filtrate to precipitate the nearly water insoluble PF_6^- salt (eqn 11). Recrystallizations are best effected in ethanol and acetone. BF_4^- salts are sometimes used although they are hygroscopic in many instances.



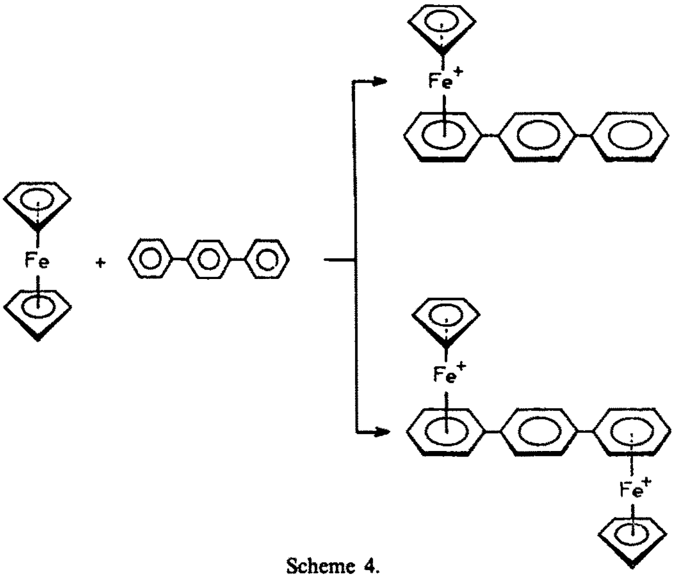
Electron releasing methyl groups on the arene increase the yield.[88,94,95] However inhibiting steric effects predominate when the number of methyl groups is larger than two.[94,95] These effects were shown by competition experiments in which mixtures of two arenes were reacted with ferrocene and the mixtures of $CpFe^+$(arene) salts obtained were determined by ^1H NMR. Electron withdrawing groups inhibit the reaction. For example, the yields decrease dramatically upon increasing the number of fluorine substituents on the arene ring from 0 to 3.[125]

arene	C_6H_6	C_6H_5F	o-$C_6H_4Fe_2$	m-$C_6H_4F_2$	p-$C_6H_4F_2$	$C_6H_3F_3$
yield (%) of $CpFe^+$ (arene)[125]	90	45	6	9	7	0

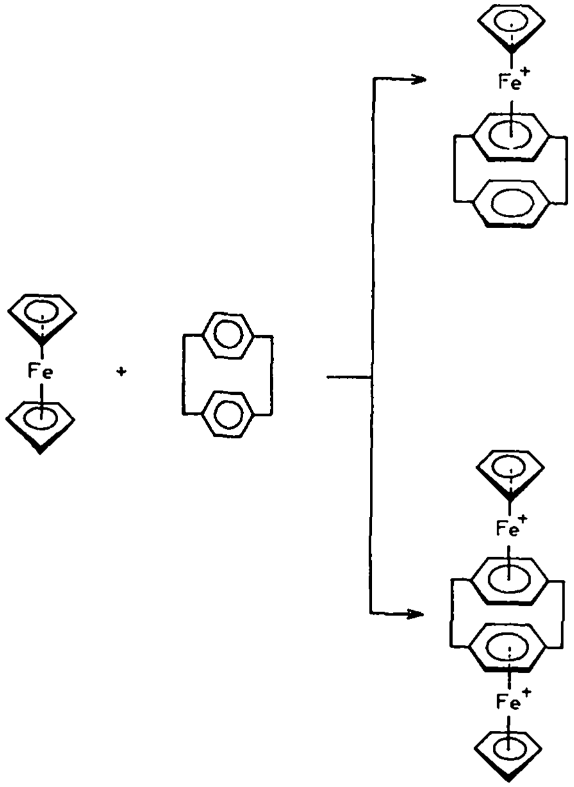
Complexation of halogenoarenes must be carried without Al powder to avoid dehalogenation,[88] a side reaction also disfavored by lower temperatures (with iodobenzene, it is unavoidable).[60]

With arenes bearing an exocyclic heteroatom or an unsaturation (especially CO and CN), exocyclic complexation also removes electron density from the arene ring which, in many instances, inhibits the formation of the $CpFe^+$(arene) complex. However it was possible to complex directly aniline[117] and its derivatives[113,116,118] under drastic conditions (190°). A series of substituted complexes of anisole have also been synthesized.[91] Aromatic heterocycles (carbazole, benzimidazole, acridine, phenazine, xanthenes, 10-methylphenothiazine) have also been complexed.[112,116]

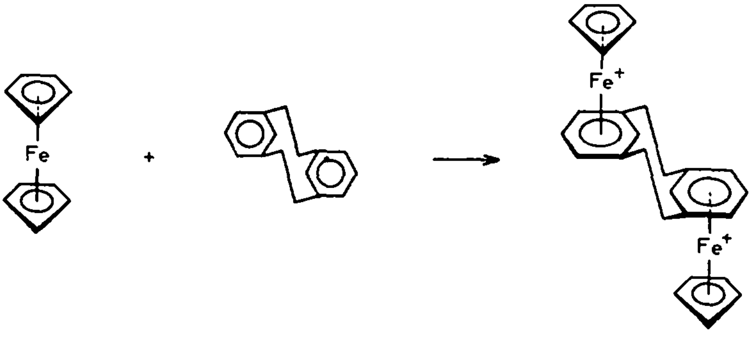
In general, it is possible to complex polyaromatics selectively to one or two $CpFe^+$ units by choosing suitable reaction conditions, as for example with terphenyl (Scheme 4) and para-[119] and metacyclophanes[120] (Scheme 5 and eqn 12).



Scheme 4.

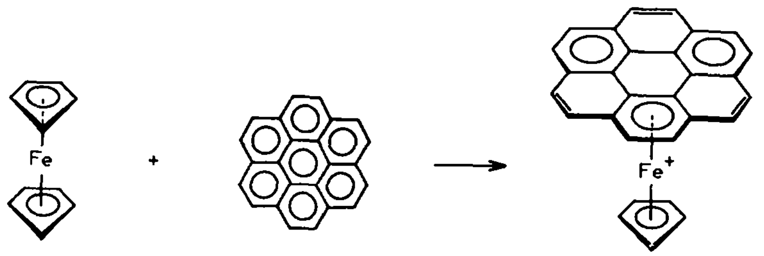


Scheme 5.

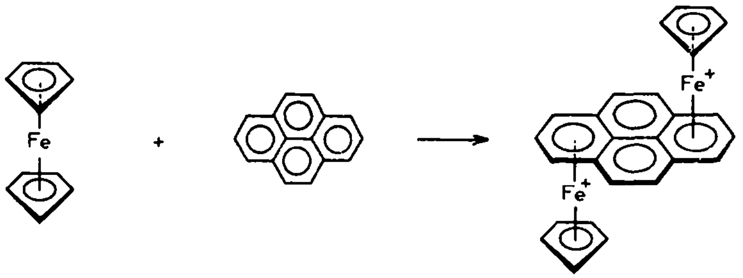


(eq.12)

With condensed polyaromatics, complexation occurs at an outer aromatic ring which is more electron-rich than the inner ones (eqns 13–14); when two rings are complexed, the iron units are *trans* (eqn 14).[115]



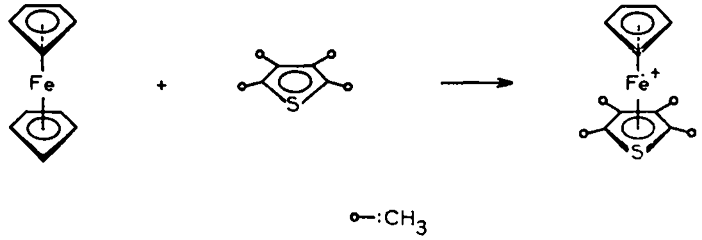
(eq.13)



(eq14)

In a few cases (anthracene and, to some extent, pyrene) hydrogenation of the inner ring cannot be avoided even at 70–80° (see §3.2.5.1) and using minimal amounts of $AlCl_3$.[108]

Failures of complexation were reported with acetophenone, benzonitrile, acetanilide, pyridine, indole, quinoline and isoquinoline. Nor could a complex be obtained with thiophene,[88] but di- and tetramethylthiophene give stable compounds,[8] obtained pure only when mild reaction conditions are used ($T° < 100°$)[125] (eqn 15).



(eq.15)

Whereas the hexamethylbenzene complex is obtained pure even if the reaction is carried out at 190°, the hexaethyl analog must be synthesized at a temperature not exceeding 80° and the yield is lower.[39] Although $AlCl_3$ is almost always used to induce ligand exchange reactions, other efficient Lewis acids are $AlBr_3$, $GaCl_3$, $ZrCl_4$ and $HfCl_4$.[126]

The ligand exchange reaction with ferrocene has been used to remove aromatics from petroleum.

Table 1 lists the arenes which have been complexed by $CpFe^+$ by reaction with ferrocene.

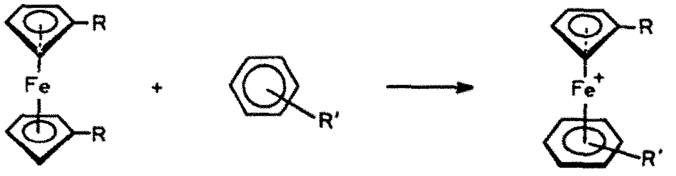
Table 1. Synthese of $CpFe^+$(arene) salts (BF_4^- or PF_6^-) from ferrocene, $AlCl_3$ and Al in excess arene or in a hydrocarbon as solvent

Arene	Reference	Arene	Reference
Benzene	48,80-83,86,87, 94,95,103	2,5 dichloro-p-xylene	60
d^6 benzene	52,97	2,4-dichlorotoluene	60
Toluene	48,80-83,88,94,95		
o-xylene	48,91,94,95	Fluorobenzene	50,93
m-xylene	48,91,94,95	o-difluorobenzene	125
p-xylene	48,91,94,95	m-difluorobenzene	125
Hemimellitene	48	p-difluorobenzene	125
Mesitylene	48,80-83,86	Bromobenzene	49,60,88
Durene	48	o-bromotoluene	49,60
Pentamethylbenzene	48	m-bromotoluene	49,60
Hexamethylbenzene	32,48	p-bromotoluene	49,60
Ethylbenzene	60,93,94,95	m-fluorotoluene	60,93
Hexaethylbenzene	32	p-fluorotoluene	60,93
Propylbenzene	94,95	m-fluorochlorobenzene	93
Isopropylbenzene	94,95		
t-butylbenzene	94,95	p-fluorochlorobenzene	60,93
Biphenyl	60,88,104,115	o-fluorobromobenzene	60
3,3',4,4' tetramethylbiphenyl	115	Anisole	91,197

Table 1. *Contd*

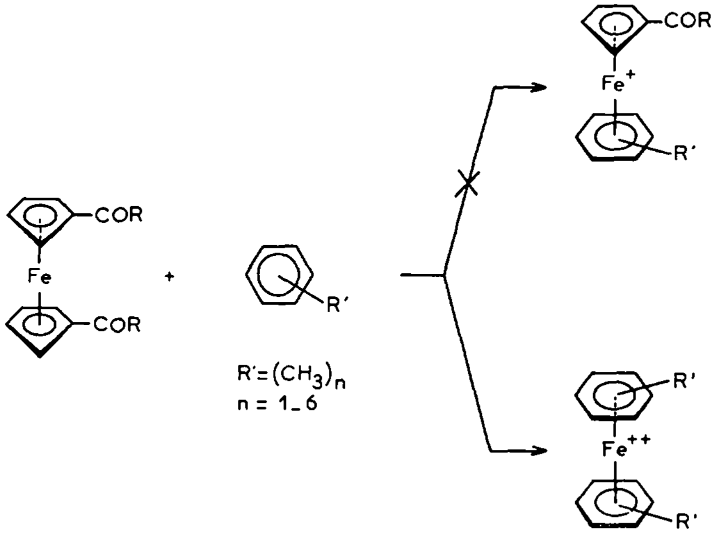
Arene	Reference	Arene	Reference
Tetralin	86,106	o-methoxytoluene	91
p-terphenyl	115	m-methoxytoluene	91
Chlorobenzene	49,60,88	p-methoxytoluene	91
o-chlorotoluene	49,60	2,6 dimethylanisole	91
m-chlorotoluene	49,90	m-chloroanisole	91
p-chlorotoluene	49,90	p-chloroanisole	91
o-dichlorobenzene	49	p-dimethoxybenzene	91
m-dichlorobenzene	49	Phenetole	197
p-dichlorobenzene	49	Diphenylether	60
Diphenylsulfide	60	p-methylaniline	113
Thioanisole	60	N-dimethylaniline	60
p-methylthioanisole	60	Pentamethylaniline	118,196
Naphthalene	88,106	Diphenylaniline	116
β-phenylnaphthalene	115	Acetanilide	88
o-chloronaphthalene	60,106	p-methylacetanilide	197
o-fluoronaphthalene	106	Acridine	112,116
o-bromonaphthalene	106	Carbazole	60,116
p-bromonaphthalene	60	Benzimidazole	116
Acenaphtene	15	Phenazine	112
Tetraphtene	15	Dimethylthiophen	85,102
Fluorene	88,210,211	Tetramethylthiophen	85,102
9,10 dihydroanthracene	107	Xanthene	112
1,2,5,6 dibenzanthracene	115	Thioxanthene	112
9,10-dimethyl, 9,10-dihydroanthracene	107,108	10-methylphenothiazin	112
Phenanthrene	110	Dibenzofuran	112
1,10 dihydrophenanthrene	110	Dibenzothiophene	112
Pyrene	111,115	2,2',3,3',5',6'-hexahydrospiro [1H-indene-1,4'(4H)-pyran 3a]	122
Chrysene	115	β-estradiol	216
1,2:5,6 dibenzanthrene	115	(+) dehydroabiethylamine	60
Corronene	121	(2,2) paracylophane	47,119
1,2:4,5-dibenzocycloheptadiene	115	anti(2,2) metacyclophane	120
Triphenylphosphine	60	anti-4,12-dimethyl-[2,2]metacyclophane	119
Tetraphenylborate	100	5,13 dimethyl[2,2] metacyclophane	119
Tetra-p-tolylborate	100	anti-4,12-dimethyl-7,15-dimethoxy[2,2] metacyclophane	119
Diphenylmethane	104,115	(2,2)(2,5)thiophenophane	119
Triphenylmethane	116		
Aniline	60,117		

3.2.3.1 1,1'-*Disubstituted ferrocenes*. Ligand exchange between arenes and symmetrical 1,1'-disubstituted ferrocenes would be expected to lead to substituted $RCpFe^+$(arene) salts (eqn 16). This was indeed reported with alkyl, acetyl and chloro substituents.[87,93-95] Electron-releasing



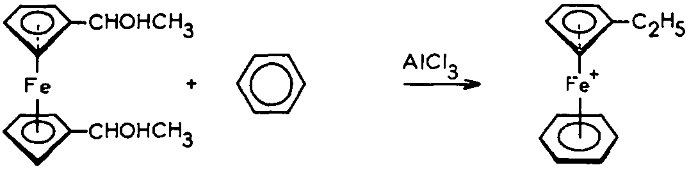
(eq.16)

alkyl substitutents on ferrocene rings increase the reaction yields (water not added). Electron withdrawing acyl groups decrease the reactivity. 1,1′-Diacyl–ferrocene gives almost no reaction at 80°. Although 1,1-diacetyl ferrocene was first reported to give the expected acetylcyclopentadienyl (mesitylene) iron cation in 25% yield at 130°,[12,89] this result was shown later to be in error, the only product formed being the bis(arene) iron dication in high yield, whatever the number of moles of $AlCl_3$ used and the number of methyl groups on the arene[74,75] (Al dust not added, Scheme 6.)



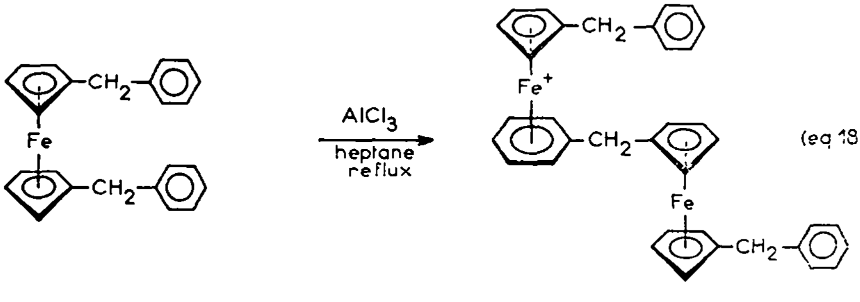
Scheme 6.

Ligand exchange reactions were also examined with functional ferrocenyl substituents[75] such as $CHOHCH_3$, CO_2CH_3 and CO_2H. The $CHOHCH_3$ substituent is reduced to C_2H_5 by the reaction medium in the course of the ligand exchange, giving the EtCpFe$^+$(arene) cation (eqn 17). In the absence of Al dust, CO_2R functions (R = H, Me) are not reduced, but mixtures of $CpCO_2RFe^+$ arene and $(arene)_2Fe^{2+}$ are found.



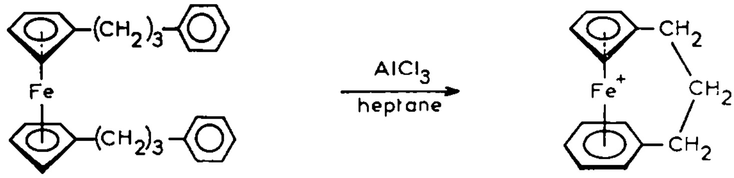
(eq.17)

1,1′-Dibenzylferrocene reacts with $AlCl_3$ in heptane even if no other arene is added; auto-condensation products are formed, this compound providing both the ferrocene and arene sources[96] (eqn 18).



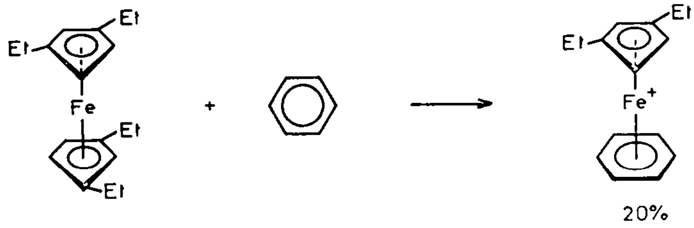
(eq 18)

Under the stoichiometric condition dibenzylferrocene/$AlCl_3$: 1/2, the main product was that resulting from only one exchange, not a polymer. This type of reaction is general for ligand exchange of aryl- and aralkylferrocenes $Ar(CH_2)_nCp_2Fe$ and $Ar(CH_2)_nCpFeCp$. It is probable that the use of more $AlCl_3$ could give further ligand exchange. With a longer aralkyl chain (3 methylene units) it is possible to complex the arene substituent intramolecularly[129] (eqn 19).

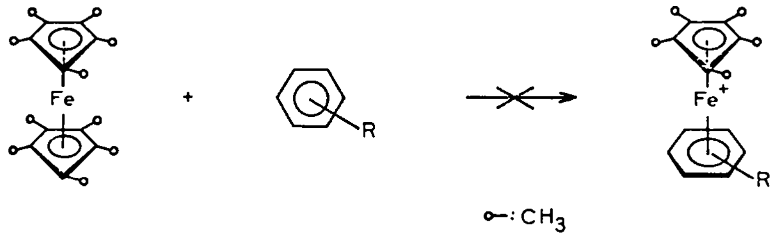


(eq 19)

The steric bulk of the alkyl substituents on the ferrocene ring can counteract the favorable influence of electron release, an effect resembling that cited in the preceding section for arene substituents. For instance, in 1,1′,3,3′-tetraethylferrocene, ligand exchange gives $1,3\text{-}Et_2CpFe^+$(arene) cation with yields not superior to those obtained with ferrocene itself[95] (eqn 20). More dramatically, octa- and decamethylferrocenes do not give any ligand exchange reaction (eqn 21).

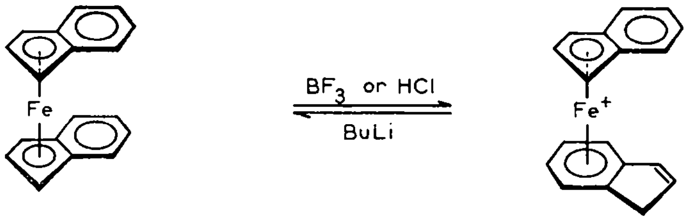


(eq 20)



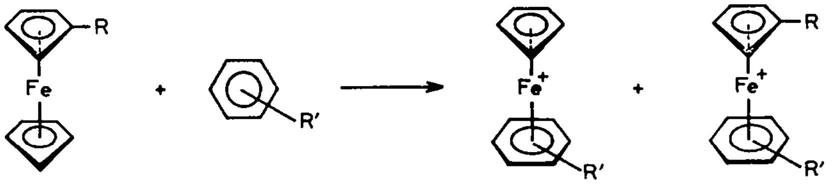
(eq.21)

Both BF_3 and HCl induce an intramolecular ligand shift of bis indenylferrocene[104] to the corresponding η^5-benzocyclopentadienyl (η^6-cyclopentenobenzene)Fe^+ which upon reaction with butyl lithium regenerates bis indenyl ferrocene via deprotonation[127] (eqn 22).



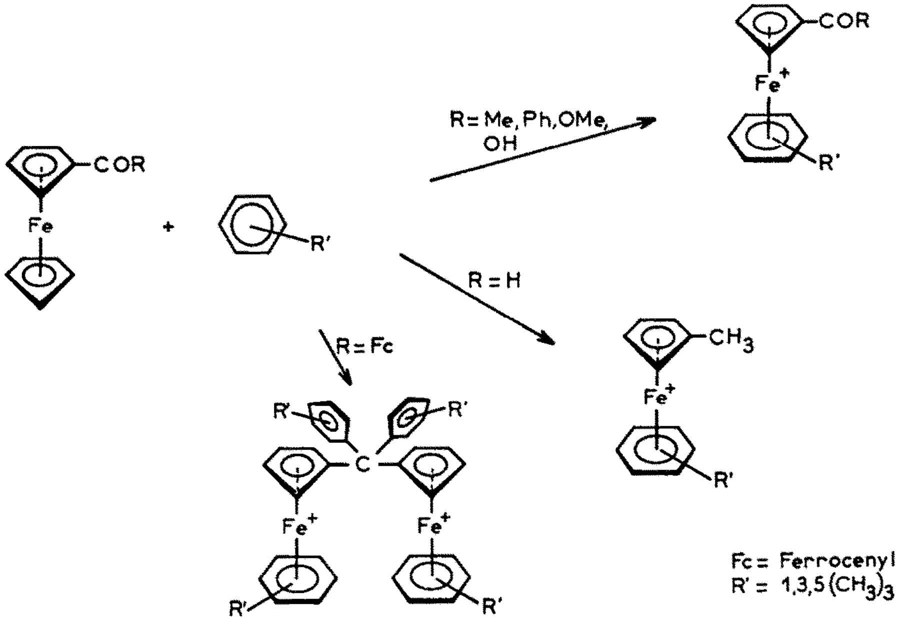
(eq.22)

3.2.3.2 *Monosubstituted ferrocenes.* In principle, monosubstituted ferrocenes give rise to the exchange of either the free or the substituted Cp ring. The ratio of substituted vs non substituted $CpFe^+$(arene) cation formed can be used as an indicator of the influence of the substituent on the ability of the cyclopentadienyl ring to exchange (eqn 23).



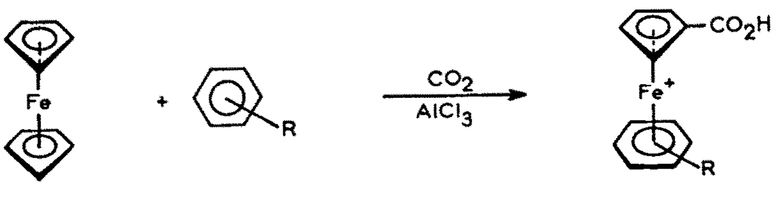
(eq.23)

Alkyl substituents favor cleavage whereas acyl substituents inhibit it,[89,94,95] consistent with what is found for 1,1′-disubstituted ferrocenes. The reaction is of synthetic interest since the ligand exchange of monoacylferrocenes is the only way to synthesize acyl Cp(arene) iron cations.[94,95] However the reaction of formylferrocene gives rise to reduction of the formyl group to methyl in the course of the ligand exchange.[95] Diferrocenylketone gives a dication resulting from the exchange of both unsubstituted rings and condensation of two aryls on the bridging carbonyl[95] (Scheme 7).



Scheme 7.

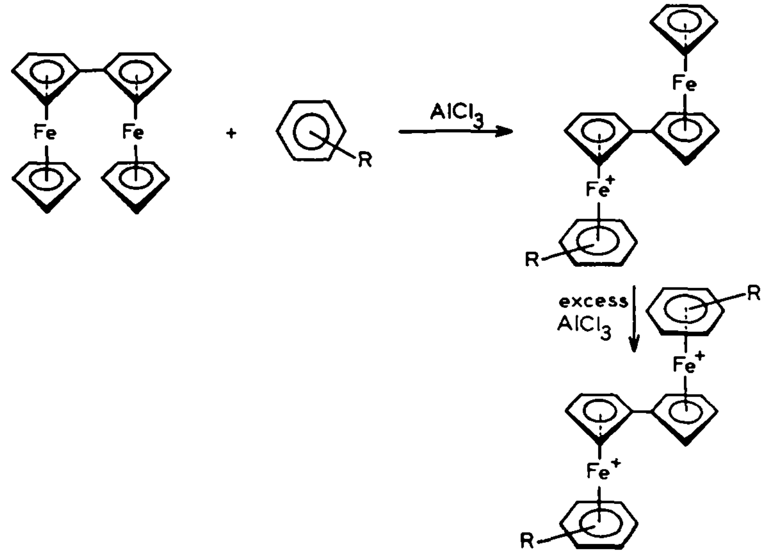
The $CpCO_2H$ (C_6H_6) iron cation can also be synthesized by $KMnO_4$ oxidation of the $CpCH_3(C_6H_6)$ iron cation or of the $(CpCOCH_3)(C_6H_6)$ iron cation (cf. §5.1.1) but a more straightforward one-pot synthesis is the reaction of ferrocene with CO_2, $AlCl_3$ and C_6H_6.[131,132] This method was generalized to other arenes (mesitylene, hexamethylbenzene, naphthalene, eqn 24).



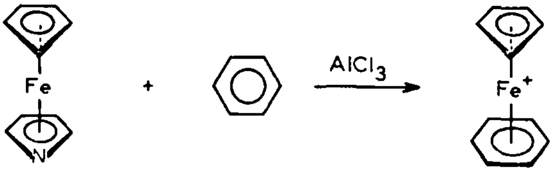
(eq. 24)

Ferrocene carboxylic acid first forms at 50° (1 h), then the reaction mixture is heated to 80–100° to effect ligand exchange of the unsubstituted ring.

Biferrocene gives ligand exchange of either one or two unsubstituted Cp ring(s), depending on the arene stoichiometry and amount of $AlCl_3$ used.[114] Modest yields of mono- or bications were obtained after chromatographic separations for arene = benzene, mesitylene, tetralin, naphthalene[114] and hexamethylbenzene[133] (eqn 25). Azaferrocene gives only $CpFe^+(C_6H_6)$ upon $AlCl_3$ induced ligand exchange with benzene (eqn 26).[123]

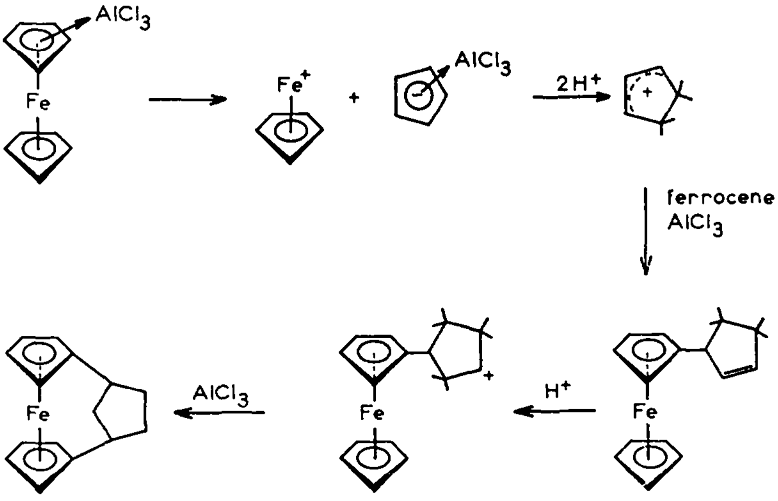


(eq.25)



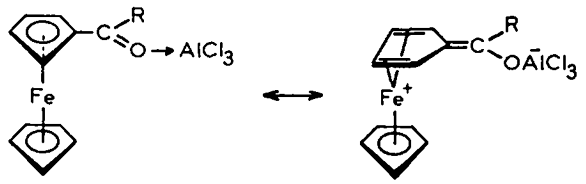
(eq 26)

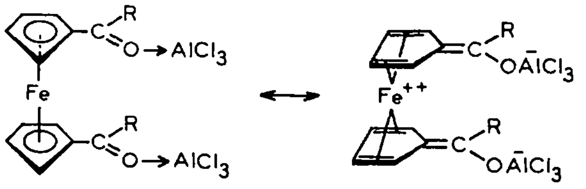
3.2.4 *The mechanism of ligand exchange between ferrocene and arenes.*[97] Although no ferrocene can be detected before hydrolysis of the ligand exchange reaction between ferrocene and benzene, a large amount of ferrocene is recovered after hydrolysis. Indeed the yield of $CpFe^+(C_6H_6)$ salt is only 20%. This indicates that ferrocene is complexed to aluminium chloride before hydrolysis, a complex destroyed by water. The substituent effects described in the preceding section clearly indicates that Cp cleavage is favored by increasing the electron density on the ferrocene ring and disfavored by a decrease. It is particularly striking that, for example 1,1′-diacetylferrocene does not react at 80° whereas monoacetylferrocene rapidly gives a high yield of ligand exchange product. The reactivity sequence is: $(CpCOR)_2Fe \ll Cp_2Fe < CpRFe < (CpR)_2Fe \ll (CpCOR)FeCp$; R = alkyl and is best explained by considering two modes of complexation of $AlCl_3$ with ferrocene (Scheme 7 and 8). One is reversible and involves the Cp ring; it weakens the Cp–Fe bond which



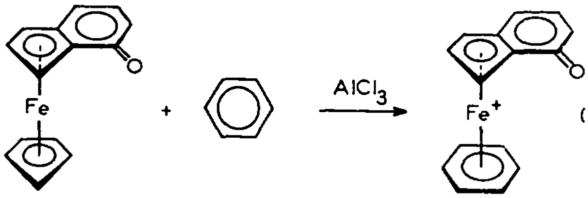
Scheme 8.

is subsequently cleaved thermally and replaced by arene–Fe bond. The other is irreversible, involves the metal and inhibits the cleavage; it is destroyed upon hydrolysis, which regenerates ferrocene and thus considerably decreases the reaction yield. In monoacylferrocenes complexation of the metal by $AlCl_3$ is inhibited because the electron density on the metal is much weaker than in ferrocene, due to the stable carbonium-like structure of the acetylferrocene–$AlCl_3$ complex. Thus the yield is much larger. Complexation of the carbonyl by $AlCl_3$ also inhibits the cleavage of the substituted ring but not that of the unsubstituted one. In 1,1′-diacylferrocene, complexation of $AlCl_3$ to neither iron nor a ring is possible; the complexation of both carbonyls gives a 1,1′-dicarbonium-like structure which is thermally much less stable than in the case of a single acyl substituent because electron density is now pulled away from both sides of the metal. Thus the disubstituted system decomposes above 100°, leaving naked iron(II) which is very reactive towards complexation of two arene molecules.



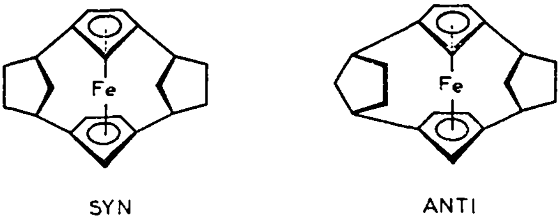


With an optically active monoacylferrocene derivative, ligand exchange of the unsubstituted Cp proceeds with complete retention, which indicates that no σ–π rearrangement of the acyl Cp–Fe unit occurs; this favors the hypothesis of complexation of the arene by a 12-electron $RCpFe^+$ moiety (eqn 27).

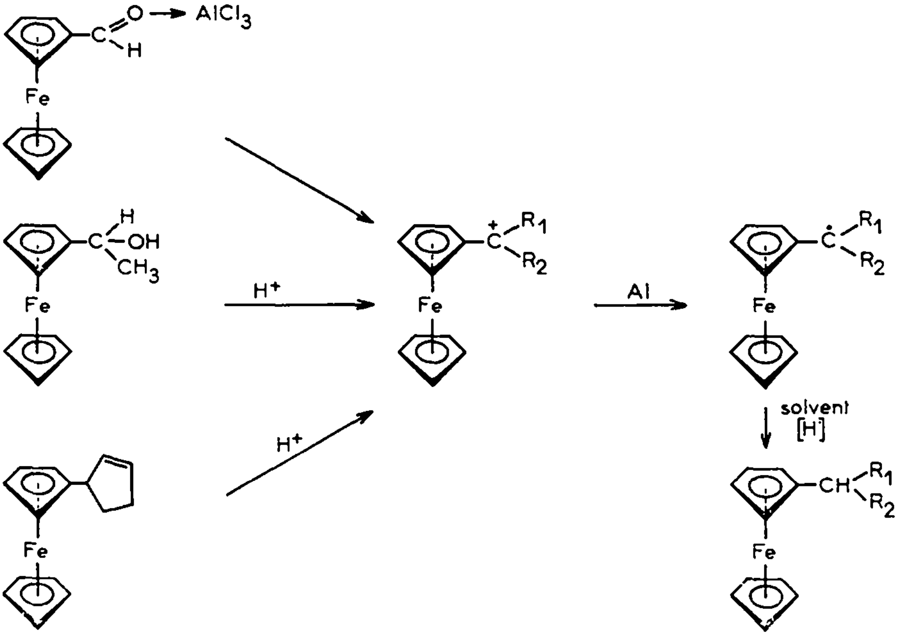


(eq 27)

That the complexation of a Cp ring by $AlCl_3$ induces the cleavage is also consistent with the inertness of decamethylferrocene. The cleaved ferrocene ring is protonated to cyclopentyl cation which reacts with ferrocene according to a Friedel–Crafts mechanism; it gives a ferrocenyl cyclopentene which, after protonation reacts similarly on the unsubstituted ring to form a cyclopentylene bridge (Scheme 8). Two isomers with two cyclopentylene bridges (syn and anti) also form in the reaction and were identified by ^1H and ^{13}C NMR[134,135] and X-ray crystal



structures[134-136,137]. These cyclopentylene bridges bear eight hydrogens whereas only seven are available from Cp and the two ferrocenyl substitutions. Deuterium labelling experiments have shown that the extra hydrogen can come from the solvent, for example benzene.[97] The ability of the ligand exchange media to effect reduction is also illustrated by the reduction of the $-CHOHCH_3$ and $-CHO$ ferrocenyl substituents,[75] of polyaromatics[106-112] and of halogenoarenes.[60,88,106] The reduction of Cp substituents may well occur by H atom abstraction from a ferrocenyl stabilized radical formed by reduction (by Al dust) of a ferrocenyl carbocation (Scheme 9).



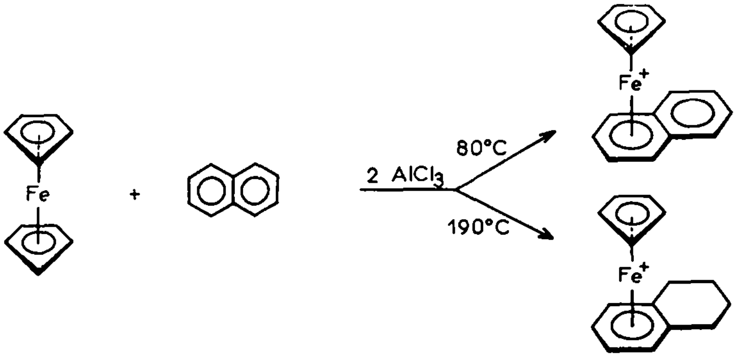
Scheme 9.

Although no studies of the mechanism of the formation of $CpFe^+$(arene) cations from $CpFe(CO)_2X$ have been reported, it is related to the general Fischer–Haffner synthesis using a transition metal halide, AlX_3 and an arene. In the present case, the halide is removed from the metal to form AlX_4^- and an unstable 16-electron intermediate $CpFe(CO)_2^+$ which probably loses the CO ligands prior to complexation to the arene (in the absence of a two-electron ligand such as thiophene). Thus twelve-electron units $CpFe^+$ must be intermediates as in the ferrocene reaction. Note that both $CpFe(CO)_2Cl$ and Cp_2Fe react with $AlCl_3$ under CO pressure to give $CpFe^+(CO)_3$, isolobal with $CpFe^+$(arene).[138,139]

3.2.5 *Transformation of the arene in the course of its complexation by* $CpFe^+$ *or* $C_5Me_5Fe^+$. Three types of transformation of the arene have been found to proceed upon complexation to iron by ligand exchange:

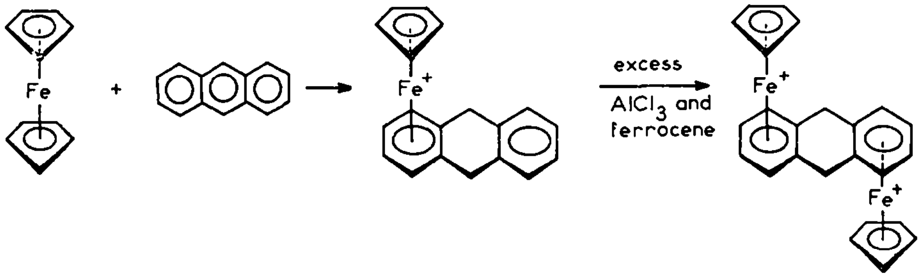
(i) hydrogenation of condensed polyaromatics;
(ii) dehalogenation of halogenoarenes;
(iii) dealkylation of polyalkylarenes.

3.2.5.1 *Hydrogenation of condensed polyaromatics.*[105-112] Hydrogenation of condensed polyaromatics occurs in the course of their complexation by $CpFe^+$ units. Hydrogenation proceeds on carbons bound to the complexed ring(s) and is favored by increasing the amount of $AlCl_3$ and the temperature of reaction. With naphthalene, it is possible to synthesize either the pure $CpFe^+$(naphthalene) salt in refluxing cyclohexane (80°) or the pure hydrogenated complex $CpFe^+$(tetralin) in refluxing decalin (190°) (Scheme 10). The dication with two $CpFe^+$ units cannot be made (in contrast to the case of biphenyl[115]) because naphthalene, as a ten-π electron system, cannot donate twelve electrons.



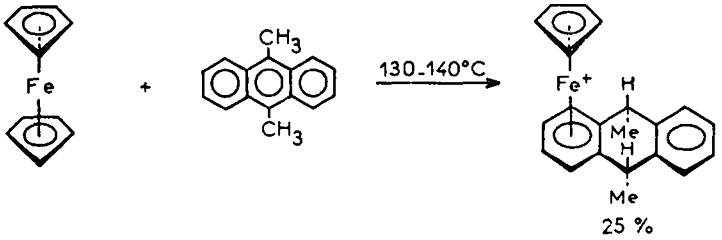
Scheme 10.

It is not possible to synthesize the anthracene complex with either one or two CpFe$^+$ unit(s)[107] even at the lowest temperature compatible with complexation. The CpFe$^+$(anthracene) intermediate is rapidly hydrogenated to the CpFe$^+$ (9,10-dihydroanthracene) complex isolable in 39% yield. If excess AlCl$_3$ and ferrocene are used, a second complexation occurs after hydrogenation and the dication (CpFe$^+$)$_2$ 9,10-dihydroanthracene can be isolated in 28% yield (Scheme 11).



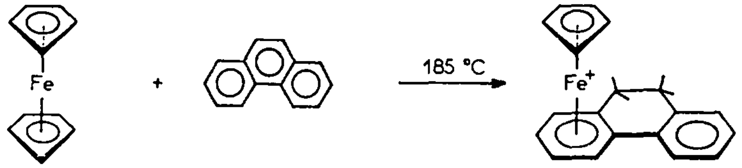
Scheme 11.

This hydrogenation reaction applied to 9,10-dimethylanthracene needs a higher temperature to proceed to completion (130–140°). The monocationic complex CpFe$^+$ (cis 9,10-dihydro, 9-10 dimethylanthracene) was obtained in 25% yield and gave the free arene in 80% yield upon pyrolysis (Scheme 12).



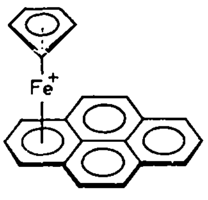
Scheme 12.

Phenanthrene can be complexed[110] in cyclohexane (80°) in 10% yield without hydrogenation whereas the hydrogenation product is obtained selectively at 185° in decalin using a ratio: ferrocene/AlCl$_3$/arene/Al: 1/5/2/1 (eqn 28).

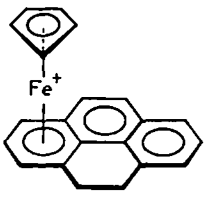


(eq.28)

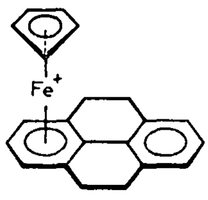
When two $CpFe^+$ units were complexed (*trans*), a mixture of both hydrogenated and non-hydrogenated arenes was found whatever the conditions used. With pyrene,[111] the non-hydrogenated $CpFe^+$ pyrene complex A was contaminated with 25% of dihydrogenated complex B under reaction conditions as mild as refluxing hexane (69°) and a ratio ferrocene/arene/$AlCl_3$/Al: 1/1/2/1, but could be separated by chromatography. Curiously, A was obtained alone in 24% yield in n-decane (174°), B being apparently decomposed. If a ten-fold excess of $AlCl_3$ is used, the tetrahydrogenated monocation C is produced (115° in decalin, 9% yield). The arene ligand was decomplexed upon pyrolytic sublimation under reduced pressure.



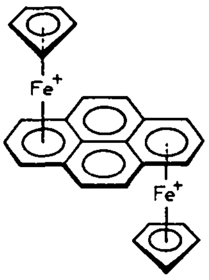
A



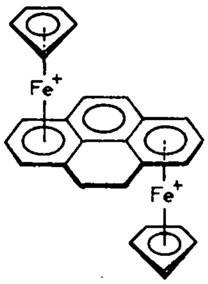
B



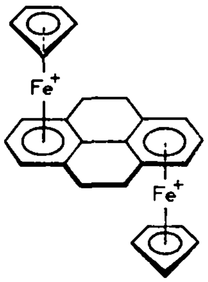
C



D



E



F

With two moles of ferrocene per mole of pyrene, the dicationic complexes D, E, F containing two $CpFe^+$ units *trans* to each other are formed. Decalin is found to be a better hydrogen donor than linear alkanes. Under conditions minimizing the hydrogenation, the dication D is contaminated with E, but is obtained pure in 5% yield after chromatographic separation. Under conditions most favorable for hydrogenation, the tetrahydrogenated dication F is obtained in 35% yield.

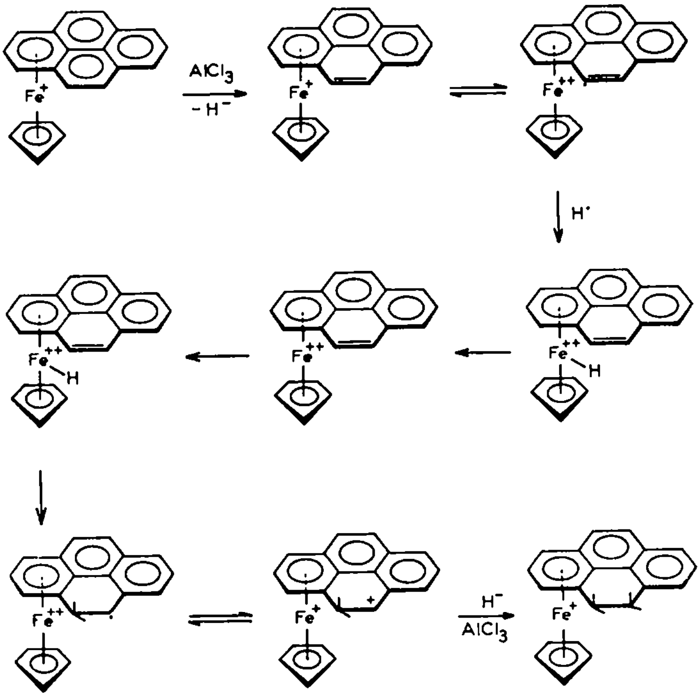
Heterocycles such as acridine (9-azaanthracene) and phenazine (9,10-diazaanthracene) give dihydrogenated mono- or dications upon complexation with one or two $CpFe^+$ units,[112] a behavior which parallels that of anthracene.

All these hydrogenations have been explained in terms of hydride abstraction by $AlCl_3$ from the monocation $CpFe^+$(polyarene) (Scheme 13).[106–111]

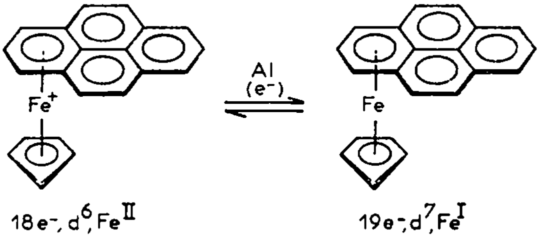
A reasonable alternative is that thermal one-electron reduction of the cation occurs to produce 19-electron d^7 intermediates. These Fe(I) species have been isolated independently and are extremely sensitive to proton sources in alkane solution, being protonated at an exocyclic carbon at −50°.[140] Such protonation presumably proceeds initially at the metal, as does subsequent H atom transfer from the solvent (Scheme 14).

3.2.5.2 *Dehalogenation of halogenoarenes.* The ligand exchange reaction between ferrocene and bromobenzene has long been known to give the dehalogenated $CpFe^+(C_6H_6)$ cation in the presence of Al dust and a mixture of dehalogenated and halogenated cations in the absence of Al[86] (Scheme 15).

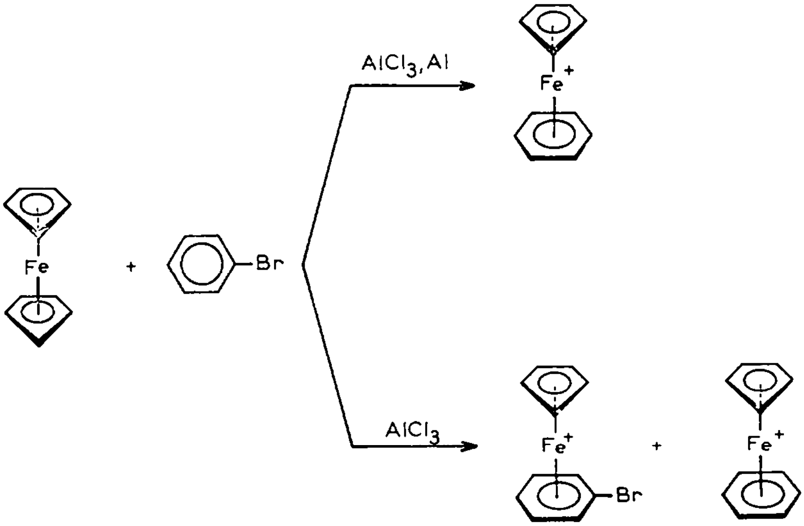
The tendency to lose the halogen in the course of the ligand exchange reaction increases as follows: F < Cl < Br < I. The fluoro- and chloro $CpFe^+$(PhX) complexes can be synthesized pure at moderate temperatures in the absence of Al whereas iodobenzene always gives a major amount of $CpFe^+(C_6H_6)$ salt besides $CpFe^+$(PhI) under such conditions. A methyl or a second chloro



Scheme 13.



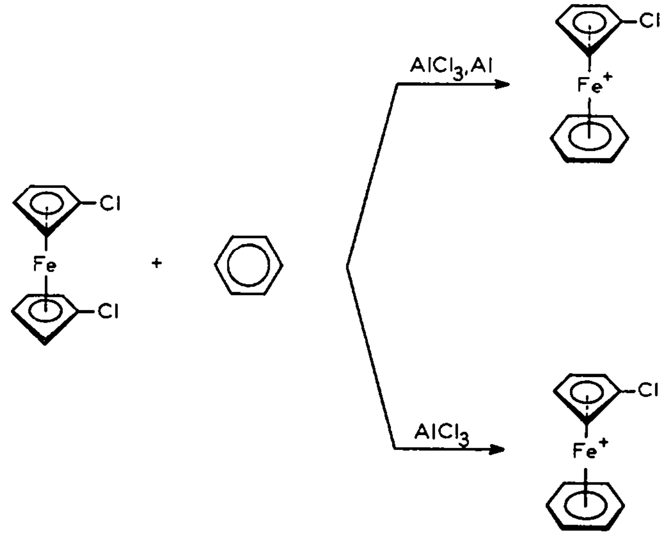
Scheme 14.



Scheme 15.

substituent favors the loss of chlorine upon complexation of chlorobenzene derivatives. Halogenonaphthalenes complex on the unsubstituted ring but bromonaphthalenes always give some debrominated and hydrogenated complex even at 80°. Dehalogenation and hydrogenation of fluoro- and chloronaphthalenes were found to occur only at more elevated temperatures. Although the previously proposed mechanism again implies anion (X^-) abstraction by $AlCl_3$ to give a dicationic Fe(III) intermediate, it is possible that dehalogenation proceeds via one-electron reduction to a Fe(I) intermediate,[60] a process that might parallel the one-electron reduction of free halogenoarenes. Indeed the CpFe(I) (ArX) complexes could be characterized by EPR at low temperature, but are much less stable than non-halogenated analogues.[67]

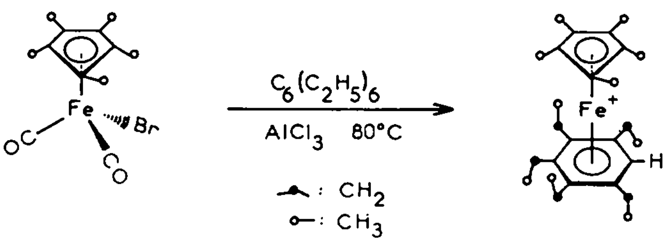
Similarly, dechlorination occurs in the course of the ligand exchange between 1,1′-dichloroferrocene and benzene only if Al dust is added to the reaction mixture (Scheme 16).[88]



Scheme 16.

3.2.5.3 *Dealkylation of peralkylarenes.*[40] The Fischer–Haffner complexation of transition metals to arenes induced by $AlCl_3$ often gives complexes in which the polyalkylarene has isomerized or lost one or several alkyl groups. Fortunately, this side reaction shows less tendency to proceed with first row than with second and third row transition metals. In particular, it does not occur in the ligand exchange between ferrocene and polymethylbenzenes whereas it does in analogous reactions with ruthenium.[141] However, tetramethylthiophene and hexaethylbenzene loose one alkyl group upon complexation with $CpFe^+$ at high temperatures (above 120–130°). These side reactions are enhanced when water is added to the reactants.[125] However it is possible to synthesize cleanly $CpFe^+(C_4Me_4S)$ and $CpFe^+(C_6Et_6)$ at moderate temperatures (80–100°), for example in refluxing heptane.[125] Similarly, 1,1′-diacylferrocenes and Fe salts give bis(arene) iron dication in which the arenes ($C_6H_nMe_{6-n}$) are isomerized when reactions are carried out in the presence of unsublimed $AlCl_3$.[78]

The most remarkable case of the loss of one alkyl substituent of an arene was found in the reaction of $C_5Me_5Fe(CO)_2Br$ with C_6Et_6.[40] Even at a reaction temperature as low as 50°, one ethyl group was specifically replaced by an hydrogen in the complex (but not in the free arene). The $\{^1H\}$ ^{13}C NMR spectrum clearly indicates that the product formed is pure (eqn 29).

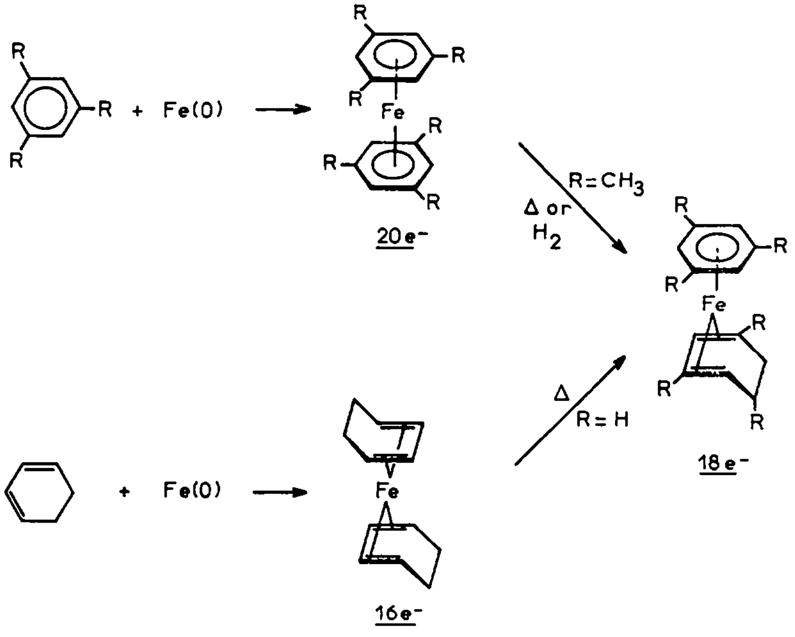


(eq.29)

By comparison, the reactions of ferrocene with C_6Et_6 and $C_5Me_5Fe(CO)_2Br$ with C_6Me_6 give cleanly the expected salt without loss of an alkyl at 110°. Thus the loss of an alkyl is clearly induced sterically and, since it depends on the metal (Fe or Ru) and ligand, intervenes in the course of—or after—complexation, not before. Conformational aspects also are important since (i) in the above reaction (eqn 29) only one ethyl group is lost even at 130°; (ii) the crystal structure of $CpFe^+(C_6Et_6)$ (cf. §2.2.2) indicates that the three arene carbons eclipsed (or nearly so) by Cp carbons bear ethyl groups directed away from the metal.[39] A related observation is that bis (hexaethylbenzene) transition metal sandwiches are highly unstable even at low temperatures.[142] The source of the H atom which replaces ethyl is neither the C_5Me_5 nor the C_6Et_6 groups, as verified by deuterium labelling experiments, but rather proton-containing impurities in commercial aluminium chloride. It is probable that protonation occurs at some non-sandwich stage of the transition state, lowering its energy by relief of steric strain.

3.3 *Metal vapor syntheses of neutral complexes*

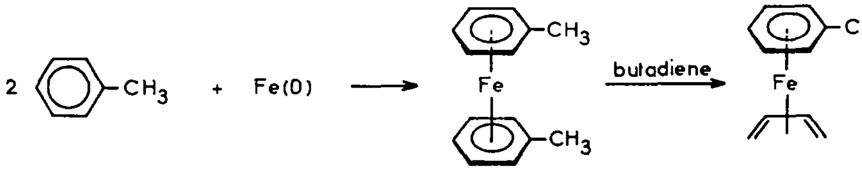
The condensation of metal vapor with arenes is very successful with chromium[142,143] because the bis(arene) transition metal sandwich fulfils the 18-electron-rule; it was applied to other transition metals such as Ti, Vb, Nb, Ta[144] giving sandwiches in which the central metal has at least 16 valence electrons. However, attempts with iron face serious obstacle since bis(arene)Fe(0) sandwiches bear 20 electrons in the iron valence shell. Co-condensation of iron atoms with benzene gives a black solid which explodes upon warming to −50°; with hexafluorobenzene, explosion occurred at −40°. With mesitylene, however, a stable complex was found in which one ligand had abstracted two H atoms from other mesitylene molecules, so that an 18-electron (arene) (cyclohexadiene) iron(0) structure was obtained.[16c] An analogous structure can be attained by co-condensation of iron atoms with 1,3-cyclohexadiene; since 1,3-bis(cyclohexadiene)iron, a probable intermediate, would have an unfavorable 16-electron configuration, it releases two hydrogen atoms to give the stable 18-electron complex $(C_6H_6)(\eta^4\text{-}1,3\text{-}C_6H_8)Fe$ (Scheme 17).



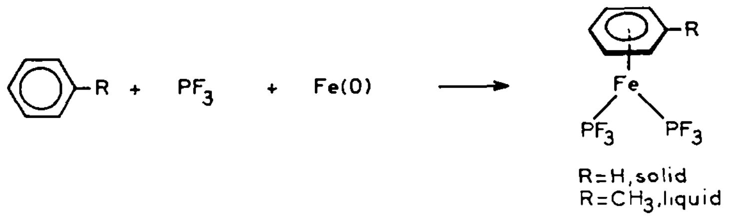
Scheme 17.

An alternative preparation consists of adding a two- or four-electron ligand at low temperature after condensation of iron atoms with an arene. Exchange between an arene ligand and one four-electron or two-two-electron ligand(s) is a straightforward process leading to 18-electron arene $(L_2)Fe(0)$ complexes.[51] For example, co-condensation of iron vapour with toluene followed by addition of butadiene gives toluene (η^4-butadiene)Fe(0), a volatile red compound (eqn 30). Co-condensation of benzene or toluene with PF_3 could be performed because PF_3 has low volatility[18];

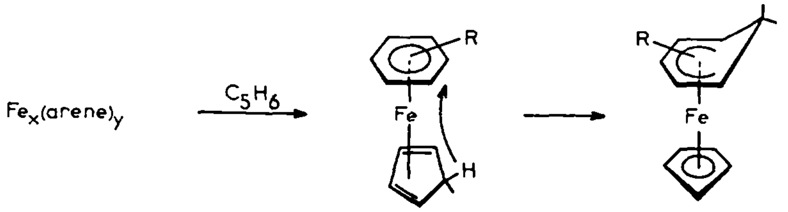
the red, volatile, air-sensitive complexes arene $(PF_3)_2Fe(0)$ are obtained; at 20°, the benzene complex is a solid whereas that of toluene is a liquid (eqn 31). Addition of cyclopentadiene after co-condensation of iron atoms with benzene, toluene or t-butylbenzene does not give the Fe(0) complex (arene) (η^4-cyclopentadiene)Fe complex but rather the rearranged cyclohexadienyl (η^5-cyclopentadienyl)Fe(II) resulting from hydrogen transfer from the diene ligand to the arene (eqn 32).[17] It is also possible to modify an arene ligand in the unstable 20-electron complex bis(arene)Fe(0) by adding H_2 subsequent to co-condensation. Complexes (arene)(cyclohexadiene)Fe^0 are thus obtained as in Scheme 17 (toluene, t-butylbenzene) and the parent (benzene)(cyclohexadiene)Fe complex is now also available by this route.[17,51]



(eq.30



(eq.31)



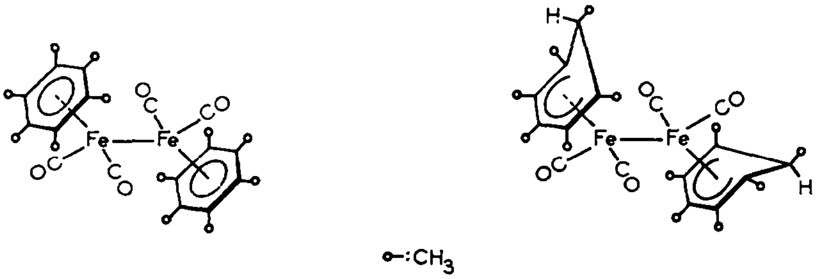
eq.32

3.4 *Photolytic complexations*

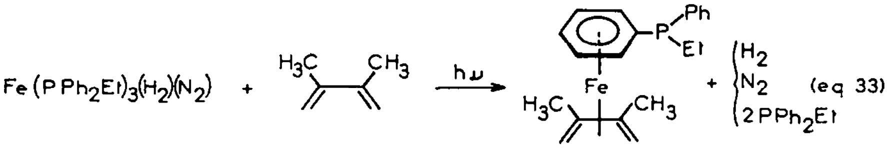
The complex (benzene)(η^4-cyclohexadiene)Fe(0), now available via the metal vapour synthesis described above, was first obtained by reacting $FeCl_3$ with i-PrMgBr and 1,3-C_6H_8 under UV irradiation according to:

$$Fe(i\text{-}Pr)_3 + 2(1,3\text{-}C_6H_8) \xrightarrow[35^\circ]{h\nu} C_6H_6(C_6H_8)Fe + 3/2C_3H_8 + 3/2C_3H_6 + H_2.$$

Ultraviolet irradiation of $Fe(CO)_5$ in the presence of excess hexamethylbicyclo(2.2.0) hexadiene has been claimed to produce a 0.3% yield of dimeric $\{C_6Me_6Fe(CO)_2\}_2$.[145] Later, this product was suggested to have a hexamethylcyclohexadienyl structure.[16b]



Photolysis of $(PPh_2Et)_3FeH_2N_2$ with 2,3-dimethylbutadiene gives orange (η^6-C_6H_5PPhEt)Fe(η^4-2,3 dimethylbutadiene); the phosphine ligand remaining in the reaction product behaves as an hexapto arene ligand with an uncoordinated phosphorus substituent (eqn 33).[146]

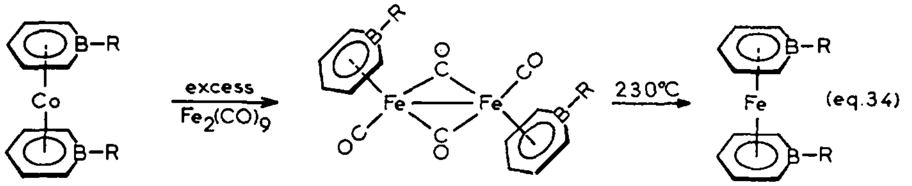


Photolysis of $CpFe^+$ (p-xylene) PF_6^- in sunlight permits the replacement of p-xylene by various ligands,[120,147,148,166], among which are C_6Me_6 (76% yield) and (2.2)paracyclophane (88% yield). In principle, only arene ligands more basic than the leaving p-xylene can be complexed using this reaction (basicity: arene 2 > arene 1):

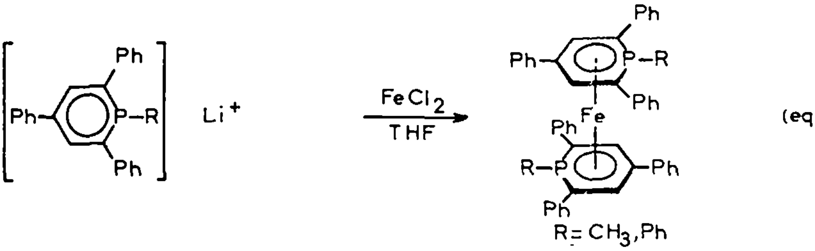
$$CpFe^+(\text{arene 1}) + \text{arene 2} \xrightarrow[CH_2Cl_2]{h\nu(\text{sun})} CpFe^+(\text{arene 2}) + \text{arene 1}.$$

3.5 *Complexation of bora- and phosphabenzene*

3.5.1 *Borabenzene.*[149] Borabenzene is a five-electron ligand behaving as a cyclopenta- or hexadienyl. The cobaltocene analogue bis(borabenzene)cobalt(II) reacts with excess $Fe_2(CO)_9$ in refluxing toluene to give the dimer $\{\text{borabenzene } Fe(CO)_2\}_2$ which can be transformed into the ferrocene analogue upon heating to 230° (eqn 34).



3.5.2 *Phosphabenzene.*[150] A brief report describes the reaction of phosphoryl lithium derivatives with $FeCl_2$ in THF to give stable neutral sandwiches (eqn 35).



3.5.3 (*arene*)*metallocarborane iron complexes.*[77] Bis(arene)iron(II) salts (arene = mesitylene or hexamethylbenzene) react with $Tl(3,1,2\text{-}TlC_2B_9H_{11})$ in THF to produce neutral, air stable $(\text{arene})C_2B_9H_{11}Fe$ complexes in low to moderate yields. A single crystal X-ray structure has established the closo sandwich geometry of the mesitylene complex isoelectronic to $CpFe^+$(mesitylene) cation. The Fe–arene (centroid) distance is 1.60 Å.

4. DECOMPLEXATION AND ARENE EXCHANGE PHENOMENA

A number of means have been used to exchange or decomplex arenes, e.g. thermolysis, photolysis, one-electron reduction, oxidation, nucleophilic attack, and reaction with β-diketones. Arene exchanges are little known, in contrast to $Cr(CO)_3$ series, and appear limited in scope. The most useful ways to decomplex the arene ligand from the cationic complexes are (i) thermolysis (ii) photolysis and occasionally (iii) nucleophilic displacement. Decomplexation of the arene from neutral complexes (18, 19 or 20-electron) is best effected by thermal displacement with two or four-electron ligands. A useful decomplexation method for cyclohexadienyl complexes is their oxidation with aqueous $KMnO_4$ or $(NH_4)_2[Ce(NO_3)_6]$.

4.1 *Decomplexation*

4.1.1 *Photochemistry*. The action of sunlight or UV irradiation on $CpFe^+(arene)BF_4^-$ in various solvents was shown to give ferrocene, $Fe(BF_4)_2$ and free arene.[158] The reaction was proposed to proceed via a solvent to metal charge transfer to give the 19-electron neutral intermediate; however, it is now clear that this mechanism is incorrect since photolysis of $CpFe^+(C_6Me_6)$ also leads to fast decomposition rather than to the photolytically stable 19-electron complex.[32] In dichloromethane or acetone, the action of sunlight on $CpFe^+$ (p-xylene) in the presence of excess two-electron ligand or arene gives $CpFe^+L_3$ or arene exchange (cf. §3.4). In acetonitrile, photolysis of various $CpFe^+$(arene) complexes in the presence of 1 mol L ligand per mol complex gives $CpFe^+(NCMe)_2L$ ($L = CO$, phosphine, olefin).[154] With the C_5Me_5 analogue, $C_5Me_5Fe^+(NCMe)_3$ could also be isolated as the crystalline purple PF_6^- salt in 90% yield in the absence of L ligands.[154] A metal to ligand charge transfer creating an unstable dicationic Fe(III) center is believed to account the photolytic decomplexation of $CpFe^+$(arene) cations.[32]

4.1.2 *Thermolysis*. The thermal decomplexation $CpFe^+$(arene) salts does not always proceed cleanly since high temperatures are required due to the stability of these complexes. However, it has been found possible to decompose under vacuum $CpFe^+$(polyarene) salts in which the polyarene was hydrogenated in the course of its complexation (cf. §3.2.5); substituted mesitylenes were also recovered by thermolysis of mesitylene (cyclohexadienyl) iron salts[65] (cf. §5.3.2).

Thermolysis of $CpFe^+$ (arene) PF_6^- (arene = nitro-, amino- or chloro-arene) in the presence of excess $P(OEt)_3$ gives $CpFe^+P(OEt)_3$.[151b,156] Thermal decomposition of $CpFe^+$ $(PhN_3)PF_6^-$ gives amino-ferrocene and $CpFe^+(PhNH_2)$ via an assumed nitrene intermediate.[157]

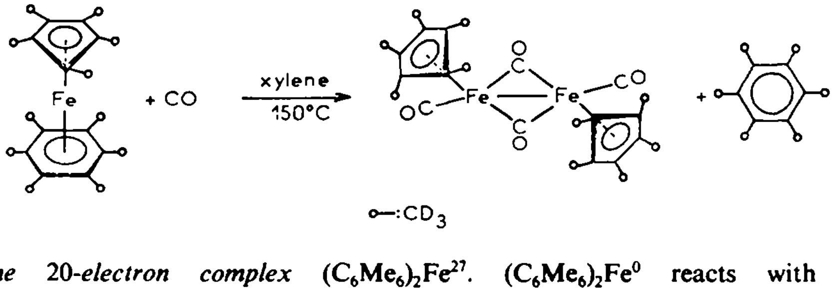
4.1.3 *Nucleophiles and one-electron reducing agents*. $CpFe^+(C_6H_6)$ undergoes decomposition to ferrocene, inorganic iron and benzene under the influence of C_2H_5ONa, NaOH, $NaNH_2$, Na/Hg, C_2H_5Li, CH_3Li, tBuLi, C_2H_5MgBr.[158] Most reactions were carried out in THF (except for C_2H_5ONa and NaOH in ethanol) during 2–6 h at 20–70° (cf. §5.3.1). The situation is different for alkyl substituted $CpFe^+$(arene) derivatives which undergo dimerization under the influence of one-electron reducing agents.[32] Similarly, cathodic reduction on Hg in 0.1 N NaOH leads to decomplexation of the parent benzene complex[57-59] and dimerization of many alkylsubstituted complexes.[159,160]

Decomplexation of aqueous solutions of soluble $(arene)_2Fe^{2+}(Cl^-)_2$ by basic reagents is immediate, whatever the arene (these solutions are obtained subsequent to hydrolysis of complexation reaction mixtures); this reaction is useful to remove these complexes from $CpFe^+$(arene) salts which are relatively stable in basic aqueous media (see §3.2.3).

4.1.4 *19-electron complexes*. Decomposition subsequent to electron-transfer $CpFe^+(arene) \xrightarrow{e^-} CpFe(arene)$ is a favorable process because the metal-ligand bonds are weaker due to the presence of an electron in an antibonding orbital in the 19-electron complexes. However it can be limited to the liberation of the arene in the presence of a two-electron ligand.[151] For instance, a 70% yield of $Cp_2Fe_2(CO)_4$ is obtained from $CpFe(C_6H_6)$ and CO in THF (eqn 36a).

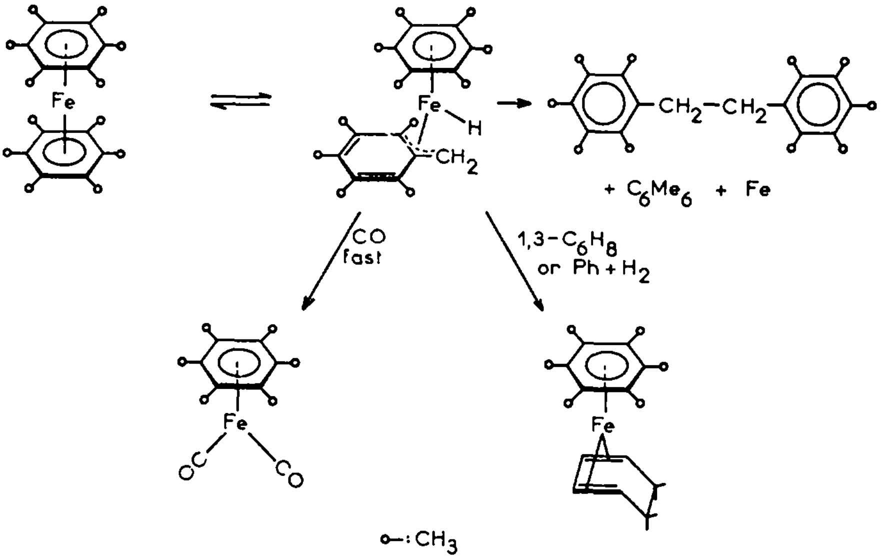
$$CpFe^I(C_6H_6) \xrightarrow[THF]{CO} \{CpFe(CO)_2\}_2 \qquad \text{(eq. 36 a)}$$

When the rings are permethylated, the stable 19-electron complex gives the analogous reaction at 150° in xylene in an autoclave; this was used for the synthesis of deuterium-labelled complexes (eqn 36b).[40]



(eq 36b)

4.1.5 *The 20-electron complex* $(C_6Me_6)_2Fe^{27}$. $(C_6Me_6)_2Fe^0$ reacts with CO (fast), 1,3-cyclohexadiene (cf. §3.3) and acetylene to give free C_6Me_6 and $(C_6Me_6)FeL_2$ complexes which have the d^8 Fe^0 configuration. In the absence of L ligand, decomposition produces free C_6Me_6, iron metal, H_2 and $(C_6Me_5CH_2\text{-})_2$. The kinetics of the CO reaction are 1st order in complex and independent of CO concentration at 21° in the range 4.10^{-2} to $1.4.10^{-1}$ M, which was interpretated in terms of an intramolecular oxidative addition of a CH_3 substituent as a primary step initiating ligand exchange or decomposition (Scheme 18).



Scheme 18.

4.1.6 *β-Diketones.*[161,178] Acetylacetone, dibenzoylmethane and benzoyltrifluoroacetone react readily with $CpFe^+$(arene) cations to liberate the free arene and give the chelate $CpFeA_2$ in high yields. Under more vigorous conditions, the Cp ring is also displaced from iron, to give iron(III) tris β-diketonates FeA_3.

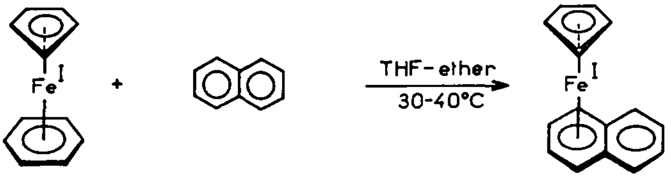
4.1.7 *Oxidation of cyclohexadienyl complexes.* In some cases, the reaction of N-bromosuccinimide in methanol with exo-substituted CpFe(η^5-cyclohexadienyl) complexes followed by extraction with boiling benzene gives the decomplexed substituted arene compound[122] (cf. §5.3.1).

(Mesitylene) (cyclohexadienyl) iron cations bearing exo substituents CN, CH_2NO, $CHCH_3NO_2$, CH_2CO_2tBu are oxidized by ceric ammonium nitrate giving 1/1 mixtures of mesitylene and the substituted mesitylene[66] (cf. §5.3.2).

4.2 *Arene exchange phenomena*

4.2.1 *Photolysis of CpFe$^+$(arene) salts.*[120,147,148] Photolytic exchange of p-xylene in $CpFe^+$ (p-xylene) with C_6Me_6 and [2,2]paracyclophane has been effected recently using sunlight and CH_2Cl_2 or acetone as solvent (cf. §3.4 and 5.1.1).

4.2.2 19-*Electron complexes.*[151,152] The benzene ligand is replaced by naphthalene in 6% yield in the 19-electron complex CpFe(I)(C_6H_6) at 30° in THF (eqn 37).



(eq.37)

Similarly, in CpFe(I)(naphthalene), arene exchange occurs with benzene or mesitylene to give CpFe(I)(C_6H_6) or CpFe(I)(mesitylene) in low yields. Thus 19-electron complexes are not good sources of CpFe units in arene exchange reactions.

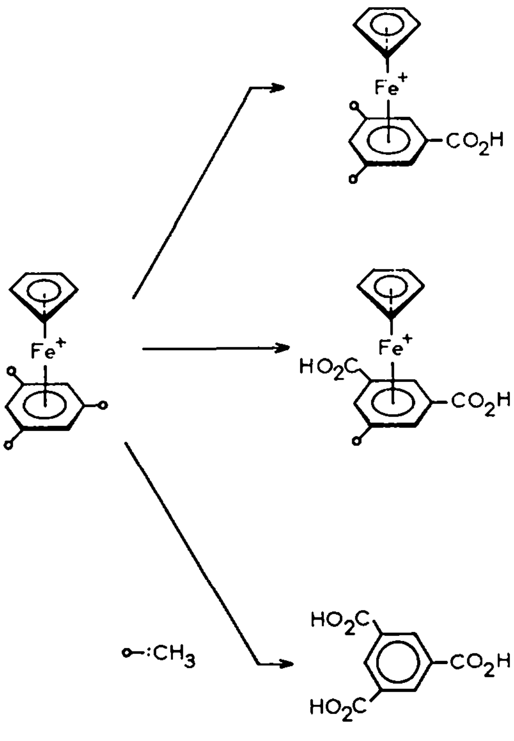
5. REACTIONS OF COMPLEXES AND MODIFICATION OF THE COORDINATED ARENE

5.1 *Oxidation of side chains*

$CpFe^+$ (arene) cations are remarkably stable towards the action of strong oxidants such as concentrated H_2SO_4, HNO_3, peroxides, bichromate, permanganate and $H_2O_2/NaOH$. Thus bications $CpFe^{++}$(arene) have not been isolated; recently, it has been reported that these species can be characterized by EPR upon oxidation of the monocation by SbF_5 in CH_2Cl_2 at 203 K[162] (arene = CH_3OPh, PhOPh, p-FPh–Ph, Ph–Ph, $C_{10}H_8$, $C_{14}H_8$).

The remarkable stability of the $CpFe^+$(arene) salts towards strong oxidants has allowed extensive investigation of the oxidation of alkyl substituents on the arene and Cp ligands to give acids and, in a few cases, to ketones.

5.1.1 *Oxidation of the alkyl chains to acids.* Since the $CpFe^+(C_6H_6)$ sandwich is not decomposed upon boiling an aqueous $KMnO_4$ solution of its salts, an alkyl side chain on either ring can be oxidized to a carboxylic substituent; $CpEtFe^+(C_6H_6)$ and $CpFe^+$(toluene) were oxidized to $CpCO_2HFe^+(C_6H_6)$ and $CpFe^+(PhCO_2H)$ respectively under these conditions in high yields.[163] $CpFe^+$(mesitylene) is oxidized similarly in a neutral medium. Depending on the proportion of oxidant, one- two or three methyl groups are oxidized to acids (Scheme 19). In the latter case, decomplexation of trimesic acid occurs under the drastic reaction conditions, presumably because the cumulative withdrawing effect of the three CO_2H groups weakens the metal–ligand bonds.

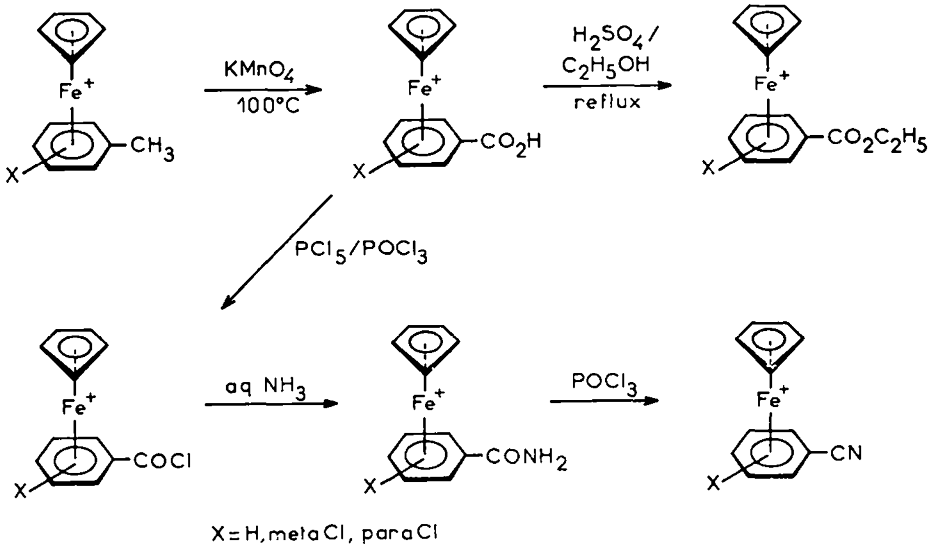


Scheme 19.

The organo-iron acids obtained are stronger than benzoic- and ferrocene carboxylic acids. As expected, $CpFe^+(C_6H_5CO_2H)$ is a stronger acid than its isomer $CpCO_2HFe^+(C_6H_6)$; a parachloro substituent on the benzoic acid complex enhances its acidity still further:[164]

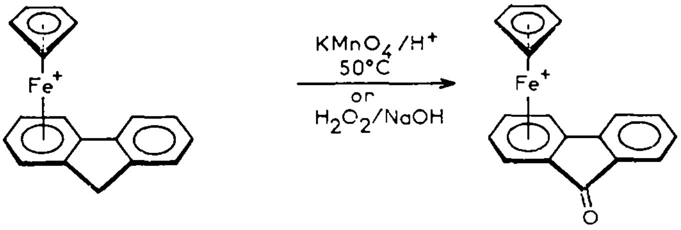
	pKa (50% aq. ethanol, 25°)[164]
$C_6H_5CO_2H$	5.73 ± 0.04
$CpFe^+(C_6H_5CO_2H)$	3.04 ± 0.04
$CpFe^+(p\text{-}ClC_6H_5CO_2H)$	2.87 ± 0.04
$CpCO_2HFe^+(C_6H_6)$	3.53.
$CpCO_2HFeCp$	6.11

A series of CpFe$^+$(arene) complexes have been prepared by oxidation of alkyl side chains bearing various substituents.[165] The acids were esterified or converted to acid chlorides and thence to amides and nitriles (all these reactions being effected in fair to good yields; Scheme 20); this chemistry also applies to the CpEt ring with benzene or chlorobenzene as an ancillary ligand. Nucleophilic substitution of the halogen (cf. §5.5) was effected with complexes of chlorobenzoic acids.[166]



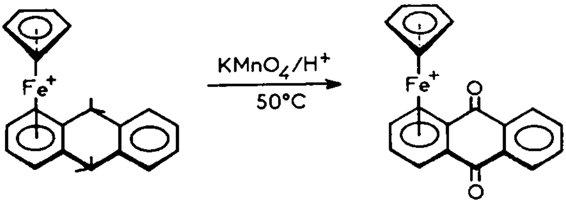
Scheme 20.

5.1.2 *Oxidation of aralkyl chains to arylketones.*[155] The synthesis of CpFe$^+$(ketoarene) complexes is a difficult problem since ligand exchange reactions cannot give such complexes (cf. §3.2.2). When the arene ligand is diphenyl methane or an analog such as fluorene, dihydroanthracene, xanthene or thioxanthene, a methylene group is activated by two arene groups, one of which bears a CpFe$^+$ unit. These CpFe$^+$(arene) complexes have recently been oxidized to the diarylketone complexes by heating with KMnO$_4$ at 50° the aqueous solutions resulting from hydrolysis of ligand exchange reactions between the diarylalkanes and ferrocene. Complexes of fluorenone, 9,10-anthraquinone, benzophenone, xanthone, thioxanthone and thioxanthen-9-one10,10-dioxide were obtained in 18–42% yields based on ferrocene. In the case of the fluorene complex only, it was also possible to obtain the diarylketone complex by oxidation with H$_2$O$_2$/NaOH at 25° (eqn 38).



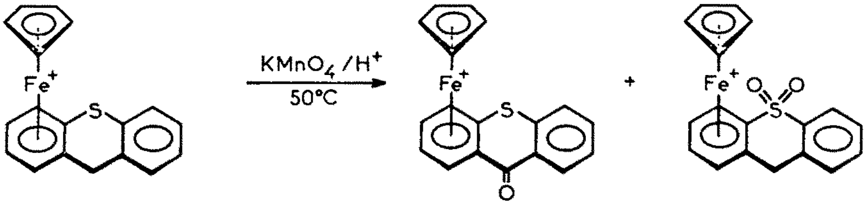
(eq 38)

The dication (CpFe$^+$)$_2$ fluorene was also oxidized by KMnO$_4$ to (CpFe$^+$)$_2$ fluorenone. With dihydroanthracene, only the anthraquinone complex could be obtained (eqn 39); attempts to synthesize the anthrone complex resulting from the oxidation of only one CH$_2$ failed.



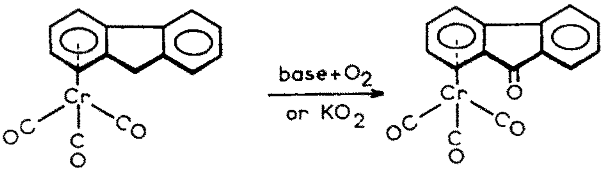
(eq.39)

$KMnO_4$ oxidation of the thioxanthene complex gave a mixture of the complexes of thioxanthone and of the corresponding sulfone. The ratio $CpFe^+$(thioxanthone)/$CpFe^+$(sulfone) is 7/3 under the usual equimolecular conditions but 1/4 when the amount of $KMnO_4$ was raised to 1.2 molar equivalents and the reaction time increased from 3 to 5 h; the two cations were easily separated by removing the thioxanthone complex with acetone (eqn 40).



(eq.40)

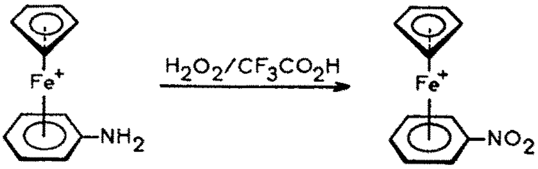
Attempted oxidation to carbonyls failed with the complexes of tetralin, o-chlorotoluene, 9,10-dihydrophenanthrene and acenaphthalene. The oxidation of diarylalkane complexes has precedents in the related chemistry of the arene $Cr(CO)_3$ series. Diarylketone $Cr(CO)_3$ complexes were obtained by treating the corresponding hydrocarbon complex with either a base $+O_2$ or with KO_2[168] (eqn 41).



(eq 41)

It should be noted that the oxidation of such hydrocarbons to diarylketones or acids are long known, facile organic reactions[169] which do not require activation by transition metals.

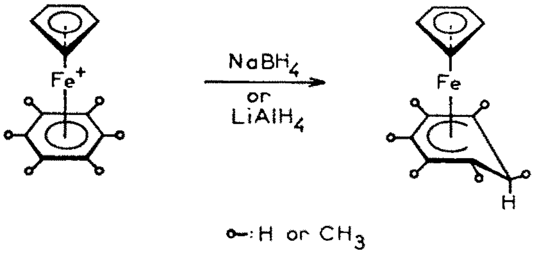
5.1.3 *Oxidation of an amino substituent to a nitro group.* Hydrogen peroxide in CF_3CO_2H effects the oxidation of the aniline derivatives to the nitroarene complexes (eqn 42),[156] a reaction similar to the oxidation of aminocobalticinium salts.[172]



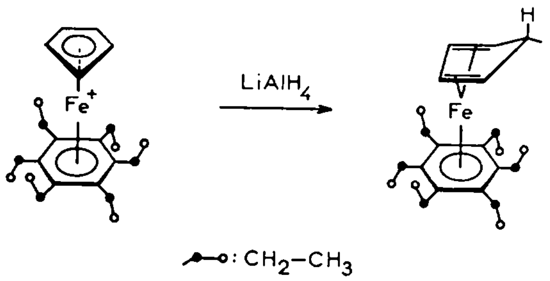
(eq.42)

5.2 *Reactions with metal hydrides*

5.2.1 $CpFe^+$(arene) *complexes.* The reaction of $LiAlH_4$ or $NaBH_4$ with the yellow salts $CpFe^+(C_6H_6)\,X^-$ ($X = BF_4$, PF_6, BPh_4) has long been known to give a neutral orange product,[170] the structure of which was found by ^1H NMR to be the d^6 Fe(II) complex CpFe (η^5-cyclohexadienyl)[171] rather than the d^8 Fe(0) complex (η^4-cyclopentadiene) Fe(η^6-C_6H_6). The same type of structure is found even when the benzene ligand is permethylated[48] (eqn 43). The only exception is the reaction of the hexaethyl benzene complex where reduction proceeds specifically at the cyclopentadiene ring (eqn 44).[67]



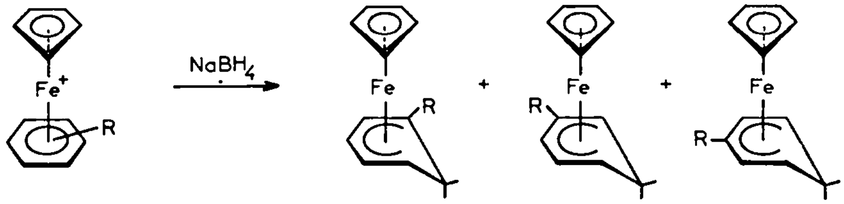
(eq 43)



(eq 44)

In all cases, the attack occurs exclusively *exo*. A strong exo C–H stretch is generally found at 2750 cm^{-1} for organometallic complexes of cyclohexadienyl and cyclopentadiene.[173,174] The reaction with perdeuterohydrides shifts this IR frequency.[48]

When the arene is monosubstituted, attack always occurs at an unsubstituted arene carbon.[48,91,92] Directing effects of Me,[48] Cl,[91] OMe[92] and CO_2Me[175] substituents are shown in Scheme 21. Cl and CO_2Me groups favor ortho attack whereas a OMe group favors meta attack. These results parallel those found for arene manganese tricarbonyl cations.[176]

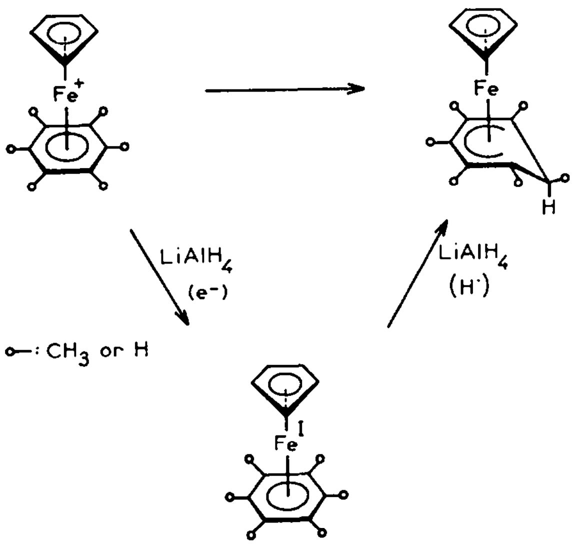


	relative site reactivities		
	ortho	meta	para
R = CH_3	1	1	0.5
Cl	4	1	0
OCH_3	0.2	1	0.6
CO_2CH_3	12.7	1	1

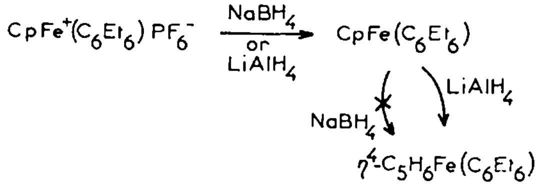
Scheme 21.

The reactions of hydrides and other nucleophiles with organometallic cations were rationalized in terms of charge control.[177] Nucleophilic attack occurs at an even closed cyclic polyene (arene) rather than at an odd one (cyclopentadienyl). Schematically, the even ligand donates electron pairs to the metal whereas the odd ligand—a radical—requires one electron from the metal; thus the positive charge on the mixed cation is more delocalized onto the former. This hypothesis is confirmed experimentally and it is convenient in the case of $CpFe^+$(arene) cations because reactions at the arene are desired while the ancillary Cp ligand remains unchanged. This was confirmed by INDO calculations[68] but it has also been proposed that the products of nucleophilic addition are not always kinetically controlled.[68,177] Although the reactions of hydrides with organometallic cations were generally believed to occur through attack of H^-, it was found recently that this is often not so, especially in the case of $CpFe^+$(arene) cations.[67] The reactions of $CpFe^+(C_6R_6)$ (R = H, D, Me) with $LiAlH_4$ at low temperature in THF allows the virtually quantitative formation of the dark green one-electron transfer products which could be extracted (Scheme 22). Alternatively, warming up the reaction mixture gives the exo H atom transfer in a second step. Reaction of an isolated sample of the thermally stable 19-electron Fe(I) complex $CpFe(C_6Me_6)$ with $LiAlH_4$ gave the cyclohexadienyl complex in a similar manner.

$NABH_4$ also reacts with $CpFe^+(C_6Me_6)$ to give first the d^7 Fe(I) complex as an electron-transfer intermediate but this step is now slower than the H atom transfer step, and only minute steady amounts are detected. With $CpFe^+(C_6Et_6)$, this $NaBH_4$ reaction gives the electron-transfer Fe(I) complex as the final reaction product; even forcing conditions do not give the hydride transfer product, which can, however, be obtained with $LiAlH_4$ via preliminary electron transfer (eqn 45).



Scheme 22



$$\mathrm{CpFe^+(C_6Et_6)\,PF_6^-} \xrightarrow[\mathrm{LiAlH_4}]{\mathrm{NaBH_4}\ \text{or}} \mathrm{CpFe(C_6Et_6)} \xrightarrow{\mathrm{LiAlH_4}} \eta^4\text{-}\mathrm{C_5H_6Fe(C_6Et_6)}$$

(eq.45)

Very unstable Fe(I) complexes such as $CpFe(C_6H_5F)$ and $CpFe(C_4Me_4S)$ best synthesized by reaction of $LiAlH_4$ with the corresponding cations at −80°[172] could be characterized by EPR and/or Mössbauer spectroscopy or extracted with cold pentane.

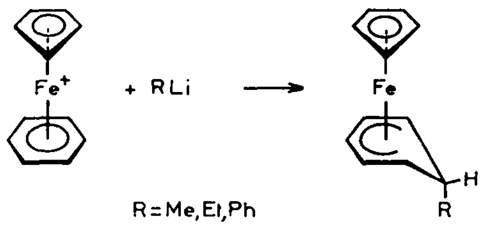
5.2.2 *Bis(arene)iron dications and (cyclohexadienyl) (arene)iron monocations.* Hydrides also react with the bis(arene) iron dications to give the monocationic hydride transfer product (cyclohexadienyl)(arene) iron cation[63,67] or the neutral double hydride transfer product[67] (η^4-cyclohexadiene)(η^6-arene) iron. No electron transfer was found in the first reduction; but the second hydride transfer was found to consist of an electron transfer followed by an H-atom transfer. The 19-electron Fe(I) complex $(C_6Me_6)_2Fe^+$ synthesized independently also reacts with hydrides by an electron transfer path giving the 20-electron complex $(C_6Me_6)_2Fe(0)$ which is not further changed by hydrides (Scheme 23).

5.3 *The addition of nucleophiles*

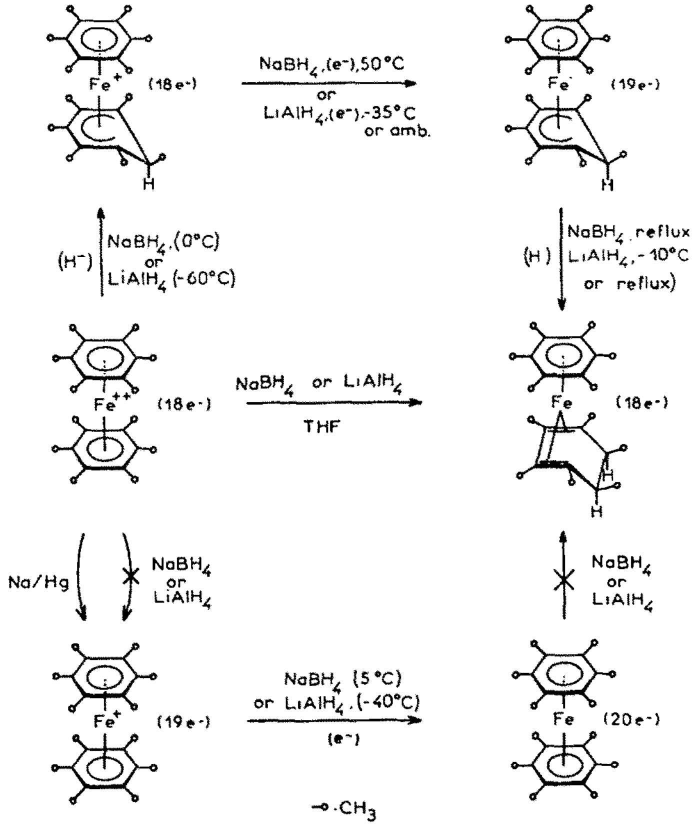
5.3.1 $CpFe^+$(arene) *cations.* Six types of reactions were found between $CpFe^+$(arene) cations and nucleophiles. (i) Decomplexation by attack at the metal center, (ii) addition of nucleophilic carbanions, (iii) electron transfer, (iv) nucleophilic substitution of halogens, (v) ring opening, (vi) deprotonation of the alkyl side chain.

We discuss in this section the addition of carbanions.

Addition of phenyl-, methyl- and ethyllithium to $CpFe^+(C_6H_6)$ gives the cyclopentadienyl (6-exo-cyclohexadienyl) iron complexes (eqn 46).

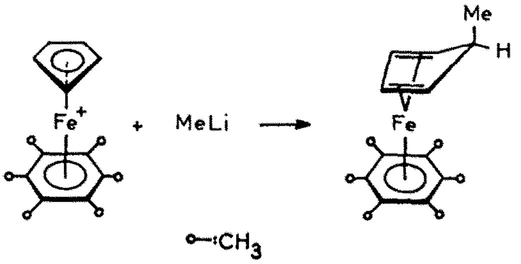


(eq 46)



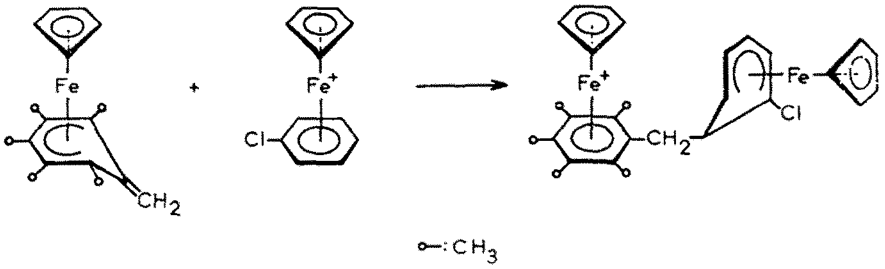
Scheme 23.

These reactions were extended to CpFe$^+$(polymethylbenzene) complexes. Both PhLi and MeLi attack unsubstituted arene carbons.[111] In contrast to hydrides, methyl lithium reacts with the cyclopentadienyl ring of CpFe$^+$(C$_6$Me$_6$) (eqn 47). Similar reactions were found with other carbanions and with CpFe$^+$(C$_6$Et$_6$).[181]



(eq 47)

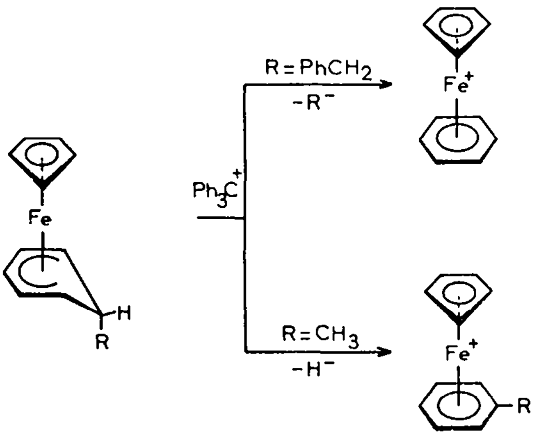
Small amounts of complexes resulting from addition to the Cp ring were also found in the reactions of the durene and pentamethylbenzene complexes.[111] Methide adds ortho to chlorine.[181] The neutral carbon nucleophile CpFe(η^5-C$_6$Me$_5$CH$_2$) reacts with CpFe$^+$(C$_6$H$_5$Cl) to give a binuclear complex[184,185] (eqn 48).



(eq.48)

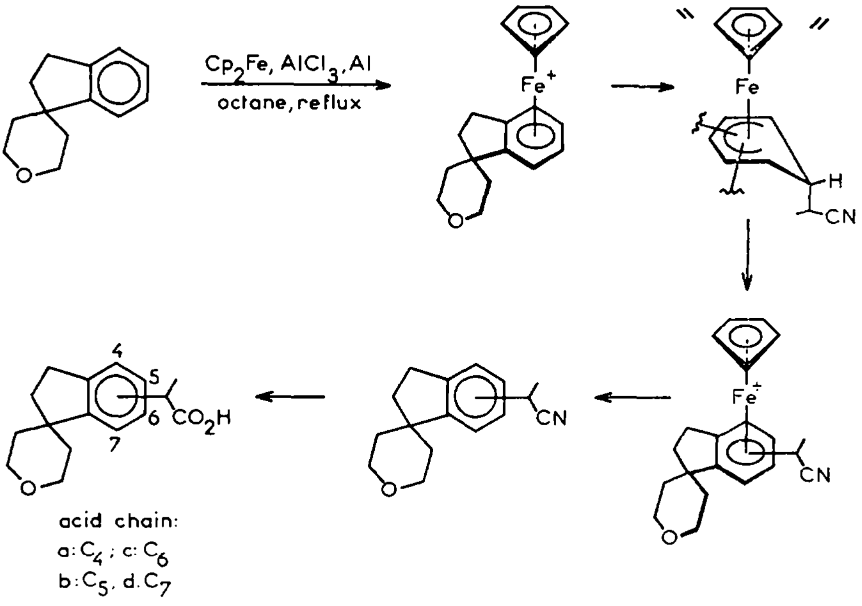
Like the organolithium reagents, $PhCH_2MgBr$ reacts in THF/ether at 0° to give the 6-exo-benzylcyclohexadienyl complex.[182,183]

The reaction of $Ph_3C^+BF_4^-$ or N-bromosuccinimide (NBS) with CpFe(η^5-cyclohexadienyl) gives the hydride abstraction product $CpFe^+(C_6H_6)$. Cyclohexadienyl complexes bearing an exo alkyl substituent can give either exo-R abstraction or endo-H abstraction[180,181] (Scheme 24). The tendency for exo-R abstraction increases in the series: $R = CH_3 \sim Ph < C_5H_5 < C_2H_5 < PhCH_2$.



Scheme 24.

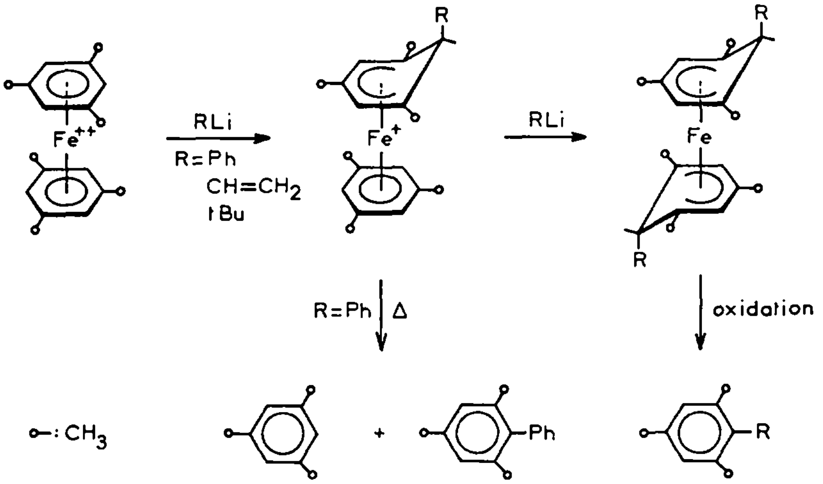
A large excess of oxidant favors the abstraction of R. These features were applied to an attempted synthesis of the acid b (Scheme 25) which has useful pharmacological properties.[186] The nucleophile used was the ^-CHMeCN anion and the desired acid was to be obtained by reaction of the nitrile with KOH in MeOH[122] (Scheme 25).



Scheme 25.

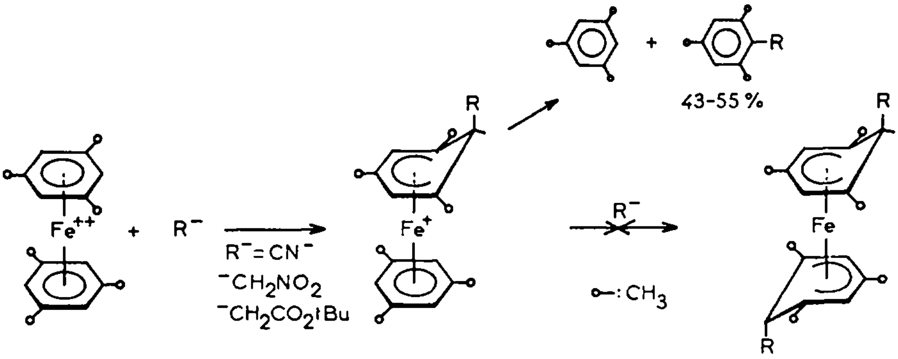
The reaction of LiCHMeCN with the precursor $CpFe^+$(arene) cation in THF or DME at – 30° gives a mixture of cyclohexadienyl complexes which were not isolated but oxidized using NBS. Alkaline hydrolysis provides 49% overall yields of acids; these were separated by HPLC and found to be present in the proportion a/b/c: 43/14/41. Thus the desired acid b is formed in minor amounts. By contrast the use of the $Cr(CO)_3$ complex gave a regioselective formation of 79% of b in a similar process, due to favorable conformational effects of this tripod unit.

5.3.2 *Bis(arene)dications.* The reaction of phenyl-, t-butyl- and vinyllithium with bis-(mesitylene) iron dication bis hexafluorophosphate at −70° gives mono- and bis-adducts (the latter being fluxional) depending on the stoichiometry[65] (Scheme 26). Thermolysis of the cationic monoadduct (R = Ph) at 216° gave mesitylene and phenylmesitylene. But the more advantageous synthesis of the latter is the oxidation of the neutral bis-adduct with dilute aqueous $KMnO_4$ (35% overall yield from PhLi); the older synthesis of phenylmesitylene from bromomesitylene, $CoCl_2$ and PhBr proceeds in only 15% overall yield from bromomesitylene. Oxidation of bis (vinyl- or t-butyl cyclohexadienyl) iron with dilute aqueous $KMnO_4$ gives a 27% overall yield of vinylmesitylene or a 9% overall yield of t-butylmesitylene respectively; the best previous synthesis of the latter proceeds in only 3% yield from $C_6H_2Me_3MgBr$ and t-BuCl.



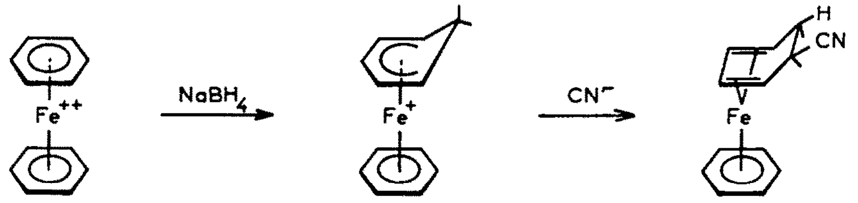
Scheme 26.

With functional carbanionic nucleophiles such as LiCN, $LiCH_2NO_2$, $LiCHMeNO_2$ and $LiCH_2CO_2tBu$, only the monoadducts are formed (48–85% yields); their oxidation by ceric ammonium nitrate gives the expected free aromatics [65b] (Scheme 27).



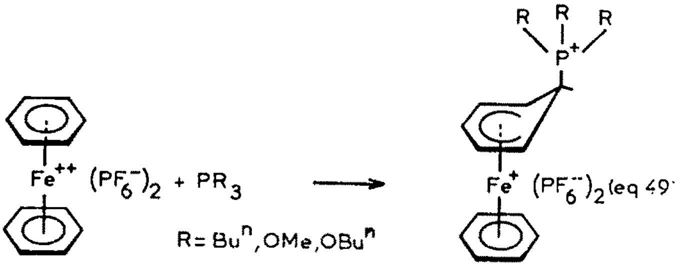
Scheme 27a.

Attempts to form the corresponding bis adducts failed, probably because the second addition is sterically inhibited by the methyl groups. Indeed $NaBH_4$ reduction of $(C_6R_6)_2Fe^{2+}(PF_6^-)_2$ (R = H, D, Me) gives $(C_6R_6)Fe^0(\eta^4\text{-}C_6R_6H_2)$ rather than $(\eta^5\text{-}C_6R_6H)_2Fe$ and carbanions such as CN^- react with $(C_6H_6)Fe^+(\eta^5\text{-}C_6H_7)$ to give $(C_6H_6)Fe^0(\eta^4\text{-}1,2\text{-}C_6H_7CN)$. These latter reactions (Scheme 27b) are violations of Green's rule; compare the reaction of NaOMe and NaC_5H_5 with $(CpCoC_6H_6)^{2+}$ which gives the bis adduct related to Cp(1,3-cyclohexadiene)Co.[69]



Scheme 27b.

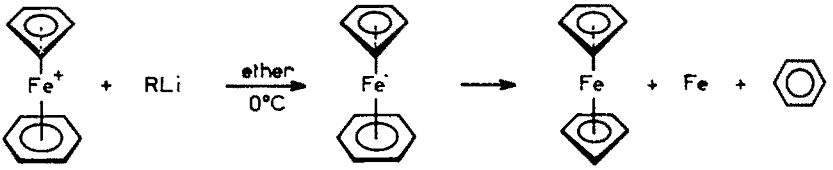
Phosphites $P(OR)_3$ (R = Me, nBu) add to $(C_6H_6)_2M^{2+}$ (M = Fe, Ru) to give a monoadduct which catalyses the hydrolysis of excess phosphite to phosphonate $HP(O)(OR)_2$[187] (eqn 49).



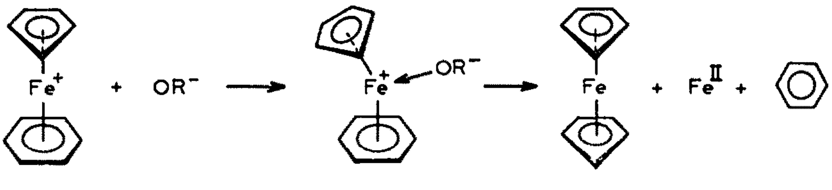
Addition of excess triaryl or trialkyl phosphines also gives monoadducts.[64]

5.4 *Electron transfer reactions by nucleophiles and other reducing agents*

5.4.1 $CpFe^+$(arene) *complexes*. It was stated in §5.2 that main group metal hydride can react with various $CpFe^+$(arene) complexes via electron transfer. Several carbon nucleophiles do so as well (eqn 50) whereas O and N nucleophiles such as sodium ethoxide and amide react with $CpFe^+(C_6H_6)$ in THF at 20–70° to give iron(II), ferrocene and arene by what is presumably a nucleophilic attack at the metal center[158] (eqn 51). Both reactions give decomplexation products but metallic iron resulting from the disproportionation of Fe(I) is found in electron-transfer reactions. Electron-transfer paths are strongly solvent dependent; for instance the reaction of methyl- and ethyllithium is a nucleophilic addition to the benzene ligand in THF at low temperature but an electron transfer reaction in ether at low temperature or in THF at room temperature. The reaction of t-butyllithium in THF at 20° with $CpFe^+(C_6H_6)$ also leads to disproportionation as in eqn (50). While benzylmagnesium bromide gives the addition product at 0° in THF/ether, the ethyl Grignard reagent gives ferrocene (Scheme 28). Cyclopentadienyl sodium was also reported to give either ferrocene or the addition product under different conditions.[182,183]

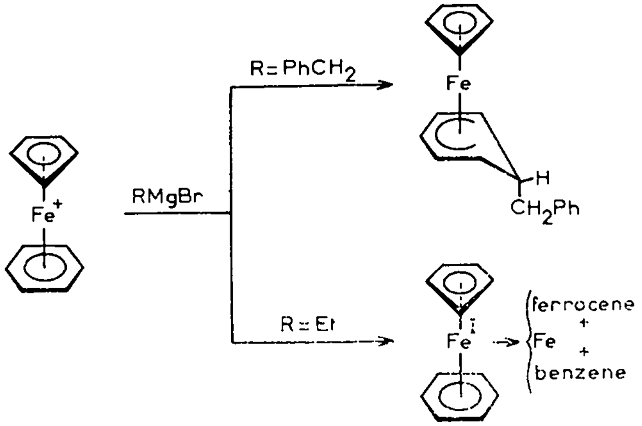


(eq.50)



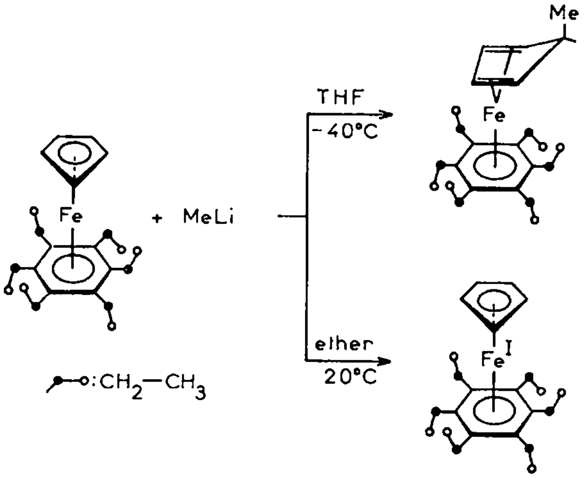
(eq.51)

In the early studies mentioned above, only the decomposition products were isolated subsequent to electron transfer reactions of carbanions. In the reaction of MeLi with $CpFe^+(C_6Et_6)$, the neutral addition product is obtained in THF as solvent (−20°, 5 min) whereas the thermally stable electron



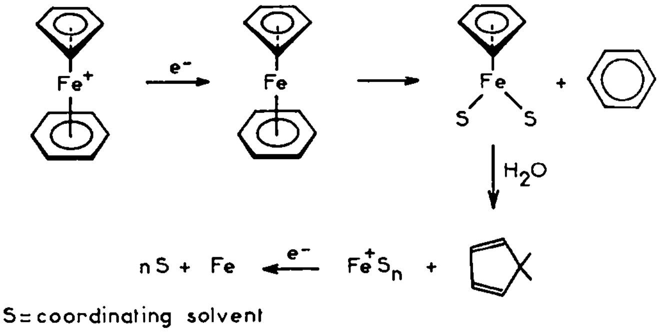
Scheme 28.

transfer Fe(I) product is isolated upon reaction in ether (20°, 4 h; Scheme 29). Note that this solvent effect is just the opposite of that found in reactions of hydrides with the same complexes (cf. §5.2).



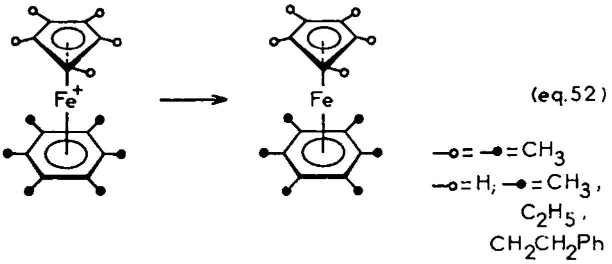
Scheme 29.

Reducing agents such as sodium naphthalene, sodium amalgam and sodium metal react with CpFe$^+$(C$_6$H$_6$) at 20° to give ferrocene, benzene and iron.[158] The cathodic reduction on Hg in 0.1 N NaOH (− 1.56 V) gives benzene, cyclopentadiene and metallic iron after passage of two moles of electrons[57–59] (Scheme 30).



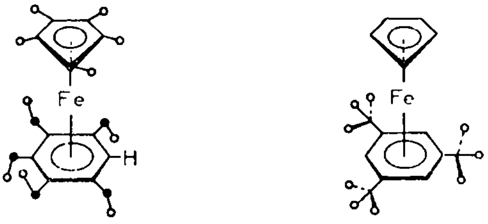
Scheme 30.

Reduction of a series of CpFe$^+$(arene) complexes in DME or THF at low temperature gives thermally unstable neutral CpFe(I)(arene) complexes[36,37] which were characterized by EPR[188–193] despite the lack of hyperfine coupling (arene = benzene, toluene, p-xylene, mesitylene, durene, biphenyl, diphenylmethane, naphthalene, dihydroanthracene, phenanthrene, tetralin); reactions with O_2 and water regenerating the CpFe$^+$(arene) cations and thermal decomposition as mentioned above was also reported. The Na/Hg reduction of CpFe$^+$(C_6H_6) in pentane + water gives some neutral Cp(cyclohexadienyl) iron, which was interpretated in terms of protonation of the intermediate 20-electron anion CpFe$^-$(C_6H_6).[195] When the arene ligand is peralkylated,[32,38–40,194] thermally stable 19-electron Fe(I) complexes could be synthesized in high yields at room temperature, crystallized as dark green micro- and monocrystals and thoroughly characterized (eqn 52).

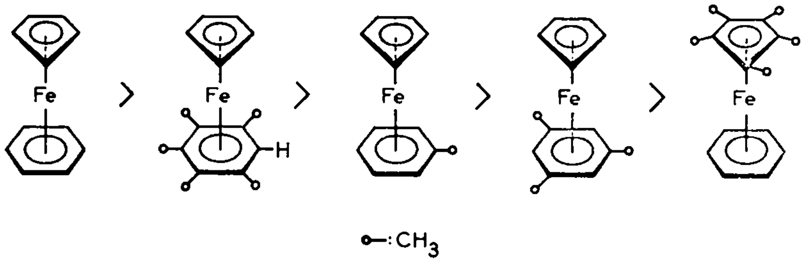


(eq.52)

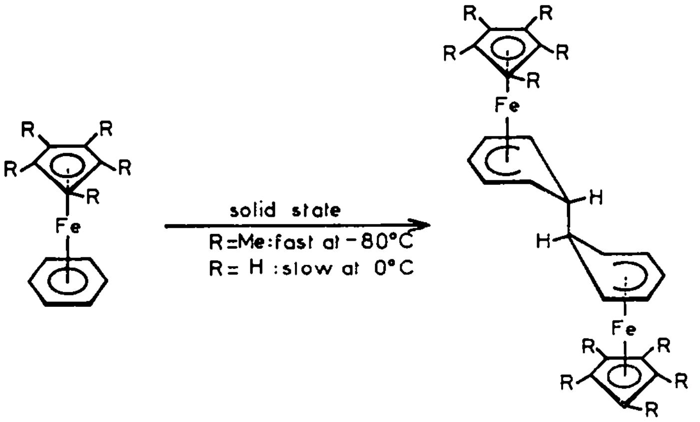
Only very few examples were found for which the Fe(I) complex is thermally stable despite incomplete peralkylation of the arene ligand:[39,40]



Although the arene fulfills this condition in the complex CpFe(I)$C_6Me_5NH_2$, it is stable only up to −10° in DME,[196] giving ferrocene, iron and $C_6Me_5NH_2$ at 20° in a few seconds. The parent complex CpFe(I)C_6H_6 (also stable at −10°) is more stable in the solid state than Fe(I) analogues bearing methyl substituents, the order of stability being as follows:[32]

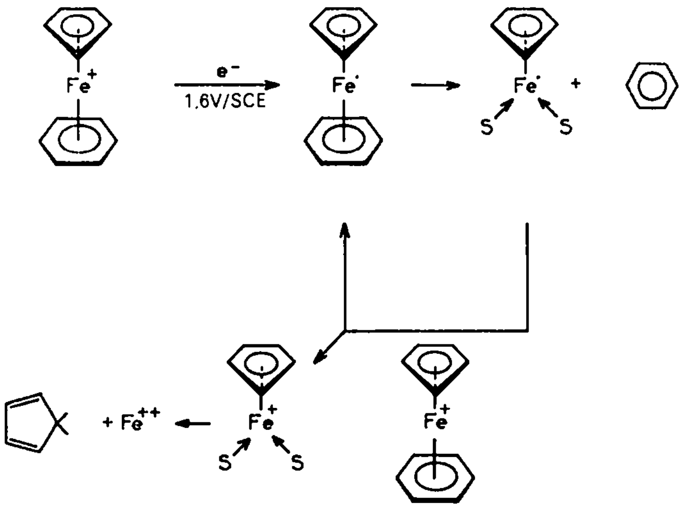


Only C_5Me_5Fe(I)(C_6H_6) could not be isolated in the solid state at low temperature. These methyl substituted Fe(I) complexes spontaneously give the dimers in the solid state but this dimerization is much slower in pentane.[32] CpFe(I)(C_6H_6) also dimerizes in this fashion but minor amounts of benzene, iron and ferrocene are also formed (eqn 53).[37b]



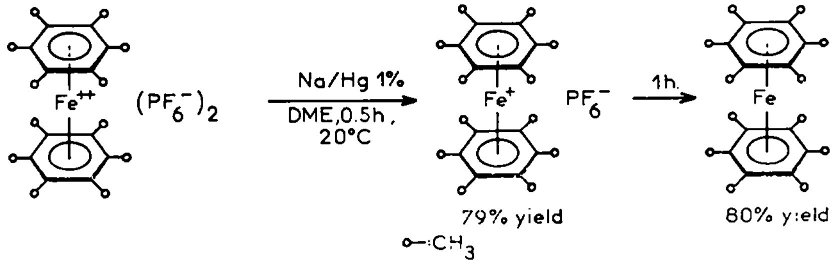
(eq.53)

Dimerization is also observed during cathodic reduction (− 1.8 V, Hg, aq. NaOH 0.1 N) of the methyl substituted $CpFe^+$(arene) cations since neutral Fe(I) intermediates precipitate is the medium;[160] in alcohol, the Fe(I) intermediates are soluble and decompose autocatalytically (much less than 1 F being consumed per mole of $CpFe^+$(arene) complex). Indeed, this is an example of electrocatalysis (Scheme 31).



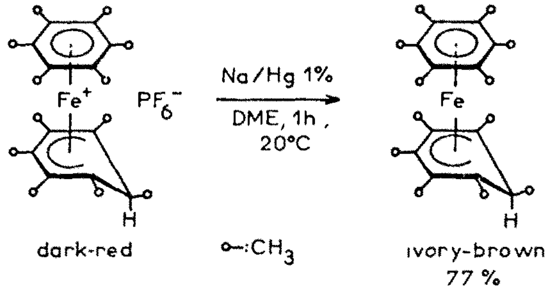
Scheme 31.

5.4.2 *Bis(arene) iron mono- and dications and (arene)(cyclohexadienyl) iron cations.* (The Fe(I) complex $(C_6Me_6)_2Fe^+PF_6^-$ was first synthesized by reaction of the dication with dithionite under N_2. Reaction with alkaline dithionite (KOH) gives the 20-electron Fe(0) neutral complex $(C_6Me_6)_2Fe$ which is light-, air- and thermally sensitive.[25] The synthesis of $(arene)_2Fe^+PF_6^-$ salts was also reported using dithionite buffered with sodium acetate (arene = mesitylene or hexamethylbenzene).[22] Naphthyl sodium was used to synthesize $(C_6Me_6)_2Fe$ from the dication in 65% yield.[166] Improved syntheses of both the Fe(I) and Fe(0) complexes of C_6Me_6 were found using Na/Hg in DME[28] (eqn 54).



(eq 54)

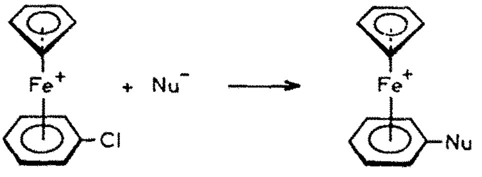
However this reaction leads to decomposition of the mesitylene analog. Bis(benzene)iron dication is sensitive to hydrolysis, being decomplexed if the hydrolysis of the reaction mixture resulting from its Fischer–Haffner synthesis is carried out at 20° (cf. §3.1). The reaction of the hydrides $LiAlH_4$ and $NaBH_4$ in THF with $(C_6Me_6)_2Fe^{2+}$, described in §5.2.2, gives first $(C_6Me_6)(C_6Me_6H)Fe^+$ which can be reduced in high yield either by continuation of the hydride reaction or by Na/Hg; the dark-red hexafluorophosphate salt of this monocation gives 77% of ivory-brown crystals of the 19-electron d^7 complex $(C_6Me_6)(\eta^5\text{-}C_6Me_5H)Fe(I)$ upon reaction with Na/Hg in DME for 1 hr, followed by recrystallization from pentane[67] (eqn 55).



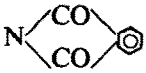
(eq 55)

5.5 *Nucleophilic substitution at coordinated aryl halides*

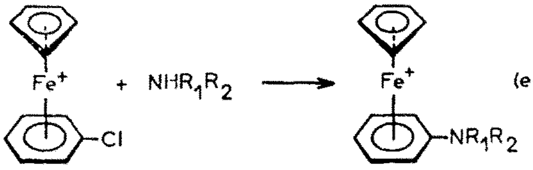
While a chlorine substituent activates and directs the nucleophilic addition of H^- and carbanions towards ortho positions N, O and S nucleophiles replace the halogen atom itself on the benzene ring under mild conditions (30–60°; 20–30 min) in ethanol or acetone[197] (eqn 56).



(eq 56)

Nu = OH^-, OPh^-, CN^-,  $^-$ (acetone); SH^- (acetonitrile), OEt^-, $CH_3CO_2^-$, SPh^- (ethanol), N_3^- (DMF).

Even NH_3 displaces chlorine when heated with $CpFe^+(PhCl)BF_4^-$ at 50° in an autoclave.[197] Replacement by amines has also been reported[156] (eqn 57).

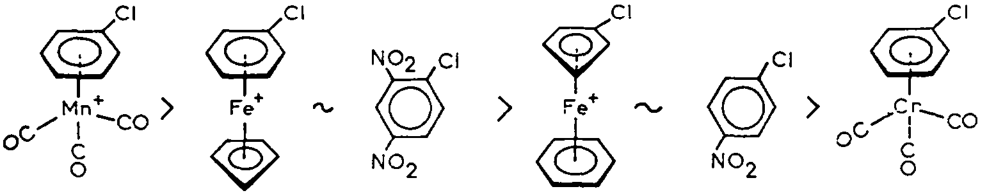


(eq 57)

$R_1 = R_2 = H$ (neat, 50°).
$R_1 = H$; $R_2 = CH_3$, $CH_2CH_2NH_2$, CH_2Ph, cyclohexyl.
$R_1 = R_2 =$ Et, cyclohexyl in CH_2Cl_2 (20°, 16 h).

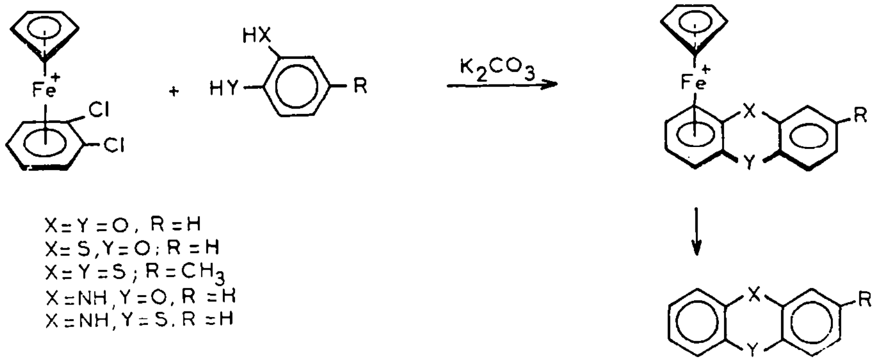
Replacement of the chlorine in substituted $CpFe^+$(chloroarene) cations was also effected with OEt and SPh (p-chlorobenzoic acid), with NH_2, OCH_3 and CN (p-chlorotoluene) and with several amines mentioned above (o-, m-, and p-chlorotoluene).

The chlorine substituent on the cyclopentadienyl ring of $C_5H_4ClFe^+(C_6H_6)$ has also been replaced by OEt, SPh, NH_2, phthalimido anion, piperidino anion and n-$C_5H_{11}NH$, although at somewhat higher temperature compared to substitution on the arene.[198] Kinetic studies on the relative rates of the reaction of sodium methoxide with the isomeric complexes $CpFe^+(C_6H_5Cl)BF_4^-$ and $C_5H_4ClFe^+(C_6H_6)BF_4^-$ indicates that the chlorine in the chlorobenzene complex is almost three orders of magnitude more reactive than the chlorine in the chlorocyclopentadienyl complex and several orders of magnitude more reactive than that of p-chloronitrobenzene; its mobility is similar to that of 1-chloro-2,4-dinitrobenzene.[90,93,199] Thus, one may state that the CpFe$^+$ unit is as electron withdrawing as two nitro groups. Since CpFe$^+$ is not so strong an activating unit as $Mn(CO)_3{}^+$ [a fluorine substituent is removed upon simple hydrolysis of $(CO)_3Mn^+(C_6H_5F)$ whereas it is hydrolytically stable in $CpFe^+(C_6H_5F)$], the order of reactivity for the displacement of an halogen (and presumably for other reactions) follows the order:



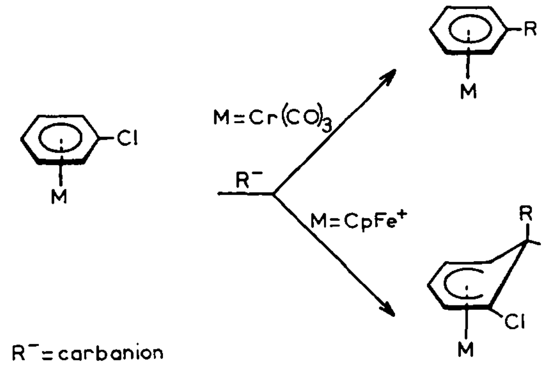
Kinetic evidence has been obtained that the cationic complexes form ion pairs with methoxide, resulting in a reduction of their reactivity towards nucleophilic substitution.[199]

Using the o-dichlorobenzene complex, heterocycles have been obtained by reactions with various o-disubstituted arenes and subsequent thermolysis[200] (Scheme 32).



Scheme 32.

A dichotomy of behavior is noteworthy between CpFe$^+$ and $Cr(CO)_3$ complexes of chlorobenzene with respect to reactions of carbanions: the chlorine is displaced only in the latter complex (Scheme 33).

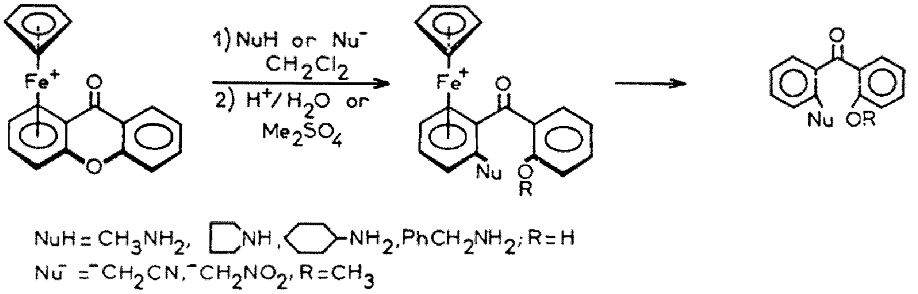


Scheme 33.

CpFe$^+$ complexes of fluoroarenes show essentially the same behavior as the chloro analogues, e.g. easy displacement of the halogen by amines and ortho addition of H$^-$ and carbon nucleophiles (see also §5.2.1). Rate studies have shown that the fluorobenzene complexes are more reactive than the chlorobenzene analogs.[199]

5.6 *Ring opening of xanthone by nucleophiles*

$CpFe^+(\eta^6$-xanthone) undergoes cleavage of the heterocyclic carbon–oxygen bond upon reaction with carbanions or amines under mild conditions in 55–85% yields,[201] the reaction parallels that known for 2,7-dinitroxanthone.[202] o,o′-disubstituted benzophenones could be obtained upon photolysis (Scheme 34). For example, o-hydroxy, o′-pyrrolidylbenzophenone (NuH = ▭NH) could be synthesized in 75% yield from the iron complex of xanthone.



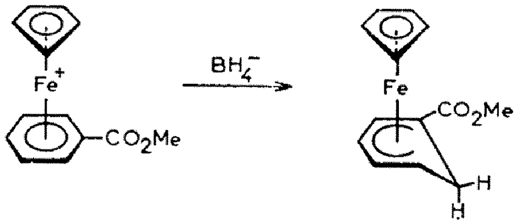
Scheme 34.

However, in some instances, e.g. with $NaBH_4$ and CH_3Li, nucleophilic attack on the xanthone complex occurs at the carbonyl group[203] (*vide infra*, §5.7).

5.7 *Reduction and nucleophilic attack of exocyclic carbonyls and the stereochemical consequences in polycyclic systems*

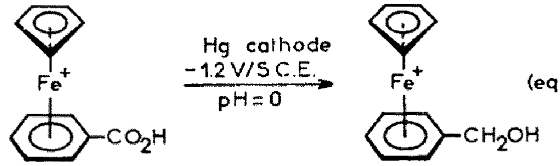
Reduction of or nucleophilic attack at exo-cyclic carbonyl groups attached to the benzene or to the Cp ring in $CpFe^+$(arene) complexes is activated by the cationic organo-iron unit.

However, there is competition between reaction at the carbonyl group and the benzene ligand. $CpFe^+(PhCO_2Me)$ is reduced by $NaBH_4$ exclusively at the benzene carbon (mostly ortho, eqn 58).[175]



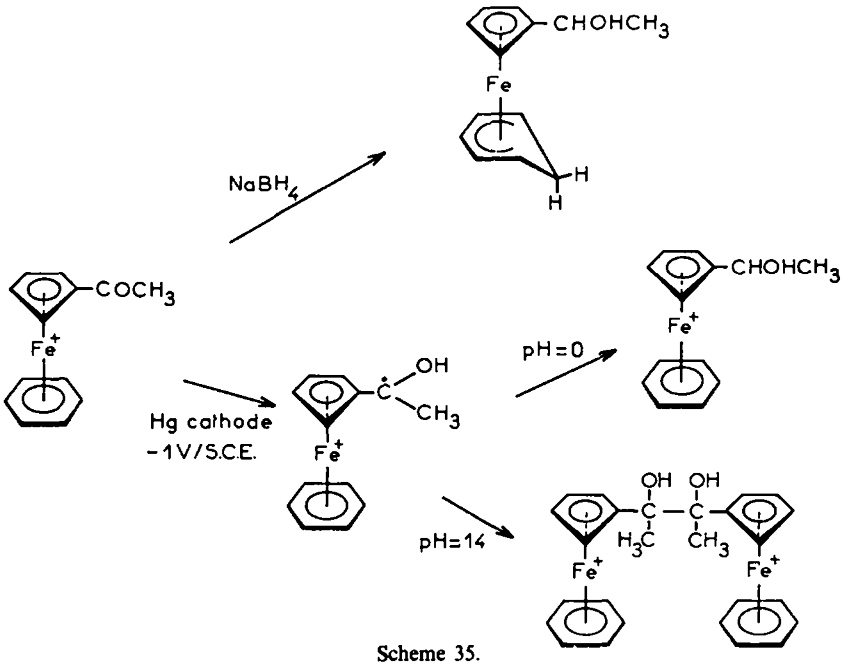
(eq. 58)

The regiospecificity is reversed when the related acid is reduced on an Hg cathode at −1 V and the primary alcohol could be synthesized on a preparative scale by electroreduction[204,205] (eqn 59).



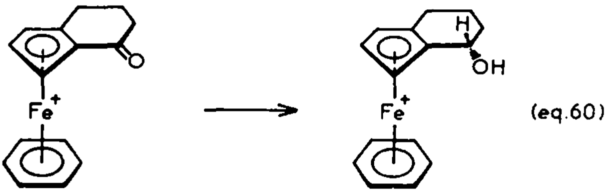
(eq. 59)

Reduction of ketones by $NaBH_4$ occurs both at the carbonyl and the benzene ring. However, electroreduction of the same ketone on an Hg cathode at −1 V/sce occurred regiospecifically at the carbonyl. In controlled potential electrosyntheses, good yields of cationic secondary alcohols or pinacols were obtained depending on the working pH (Scheme 35).

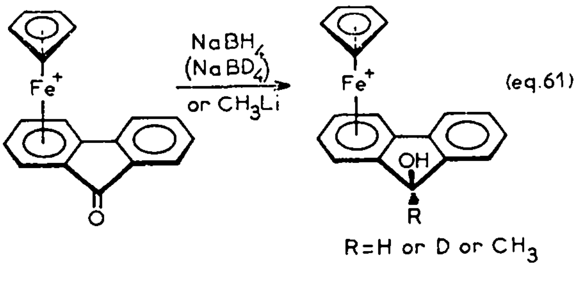


Scheme 35.

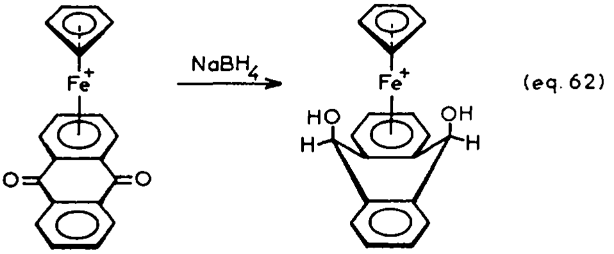
In the case of a cyclic ketone, electroreduction under these conditions occurs stereospecifically, giving the endo alcohol as in eqn (60).



It was recently shown that $NaBH_4$ and CH_3Li react stereospecifically with $CpFe^+$(ketoarene) complexes giving respectively the secondary and tertiary endo alcohols derived from fluorenone (eqn 61), benzophenone or xanthone as ketoarenes.[202]

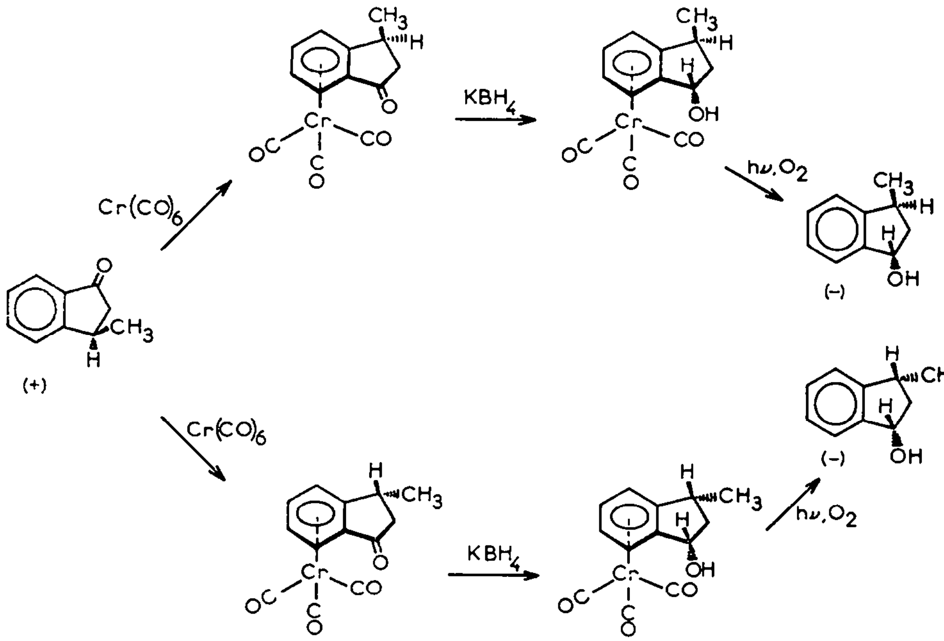


The reduction of $CpFe^+$ (anthraquinone)[203] gives a diol for which a quasi axial structure is proposed based on IR absorptions at 3574 cm^{-1} (Fe...HO) and 3430 cm^{-1} (intramolecular OH...OH, eqn 62).



On the other hand, exo addition of the anions of acetonitrile and nitromethane to CpFe$^+$(ketoarene) complexes could be carried out successfully only with the fluorene complex. With other ketoarene complexes, unchanged starting material or CpFe$^+$(C$_6$H$_6$) was recovered. With the xanthone complex, a ring opening reaction occurs as is mentioned in §5.6.

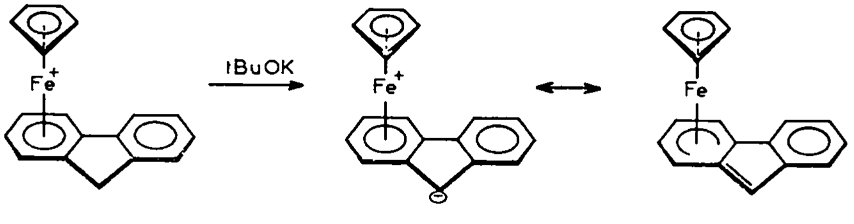
Apparently, the CO group of bis-aryl or bis-benzoketone complexes is sufficiently activated to undergo reaction prior to arene reduction (which would give a cyclohexadienyl complex). It is as yet difficult to state whether a CO group attached to the arene ligand and bearing an aliphatic or alicyclic substituent would behave similarly since such simple complexes are not presently accessible. Note that a methoxy substituent on the carbonyl prevents reduction by NaBH$_4$.[175] These considerations serve to emphasize the advantage of electrosynthesis in some cases. By way of comparison, it should be noted that hydride reduction and nucleophilic addition of carbanions find many precedents in the related chemistry of arene chromium tricarbonyl complexes, especially for the synthesis of optically active aromatics.[106,206] In this series, competition between reduction of the arene ligand and the carbonyl does not pose problems insofar as the organo-metallic group is neutral. Moreover, chromium carbonyl complexes are available with a variety of diarylketones. An example of the well known synthetic strategy using Cr(CO)$_3$ is shown in Scheme 36.



Scheme 36.

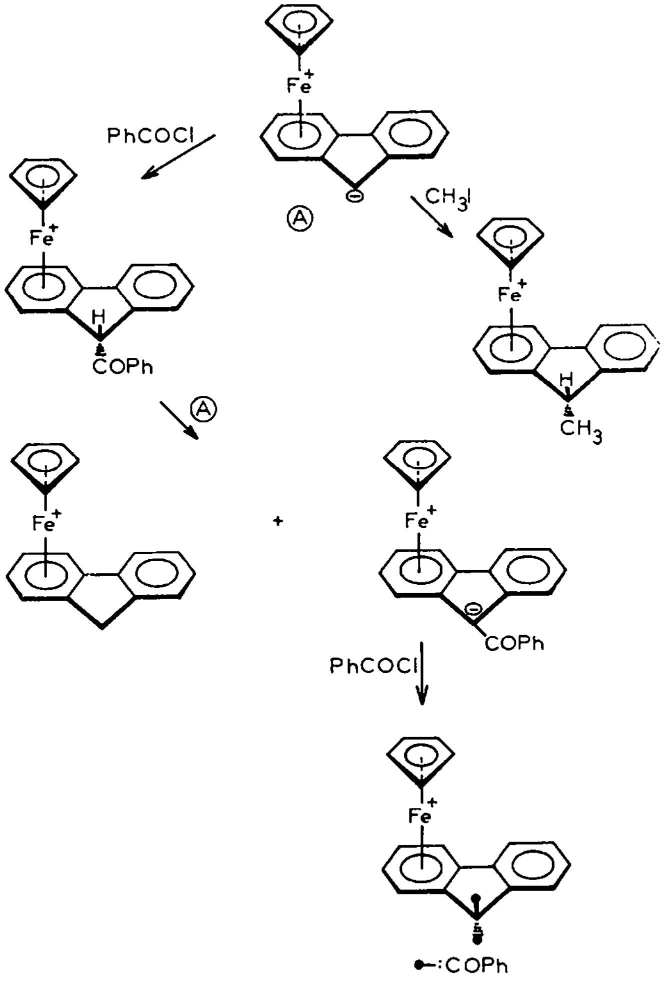
5.8 *Deprotonation of the arene side chain and reactions of deprotonated species*

It is known that benzylic protons of an arene can be activated by a transition metal unit since both exo benzylic protons of indane chromium tricarbonyl can be replaced by deuterium under the influence of NEt$_3$ in DMSO.[207] This property was used to alkylate alkylarenes via the intermediacy of their Cr(CO)$_3$ complexes.[208,209] The first example of deprotonation of a CpFe$^+$(arene) cation used fluorene and t-BuOK, giving a thermally stable blue zwitterion, the X-ray structure of which indicates an angle of 11° between the plane of the complexed ring and that of the uncomplexed ring.[210,211] This angle is significant and indicates a slight cyclohexadienyl contribution to the structure (eqn 63).



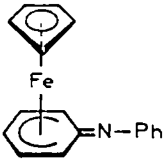
(eq.63)

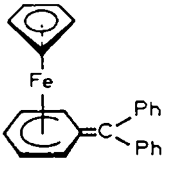
No shift in the complexation by CpFe was found in contrast to what occurs in the $Mn(CO)_3$ analog. The zwitterion could be alkylated in THF by CH_3I (1 day, 20°) or CH_3SO_3F (a few minutes, 20°) to give the 9-exo methyl fluorene complex, but reaction with benzoyl chloride did not give the 9-exo-benzoyl fluorene complex; the 9-endo hydrogen is very acidic and protonates the zwitterion. Thus the resulting complex is the bis benzoylated cation (Scheme 37).

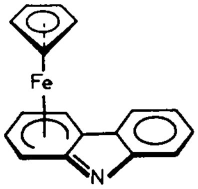


Scheme 37.

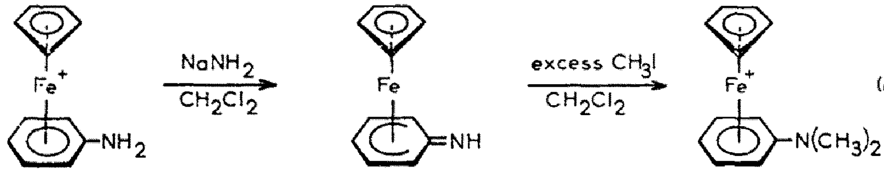
Other stable, neutral complexes resulting from the deprotonation of $CpFe^+$(arene) cations (arene = triphenylmethane, diphenylamine, carbazole, benzimidazole) were synthesized using sodium amide in liquid NH_3 or sodium bis(trimethylsilyl) amide.[116] These deprotonated complexes were formulated as cyclohexadienyls and the ^1H NMR chemical shifts indicated that the structures were intermediate between η^6-zwitterions and η^5-cyclohexadienyls with more cyclohexadienyl character for the triphenylmethane complex.



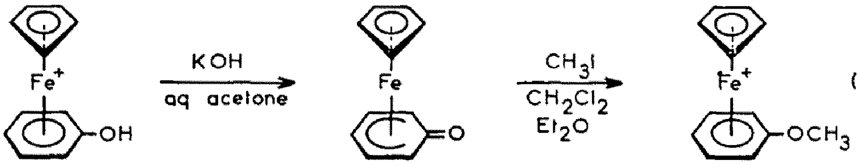




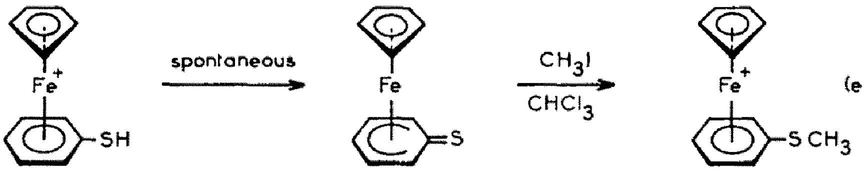
CpFe$^+$(arene) complexes bearing an exo-cyclic heteroatom (aniline, phenol, thiophenol) were also readily deprotonated[113,117,118] and the relatively stable, neutral cyclohexadienyl species were alkylated by CH_3I at 20°. In the case of the thiophenol complex, deprotonation was spontaneous.[113] Reaction of CH_3I with the iminocyclohexadienyl complex gave only the dimethylaniline complex because of the acidity of the monomethylated intermediate[117] (eqns 64–66).



(eq 64)

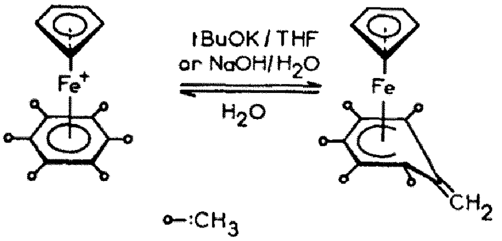


(eq.65)



(eq.66)

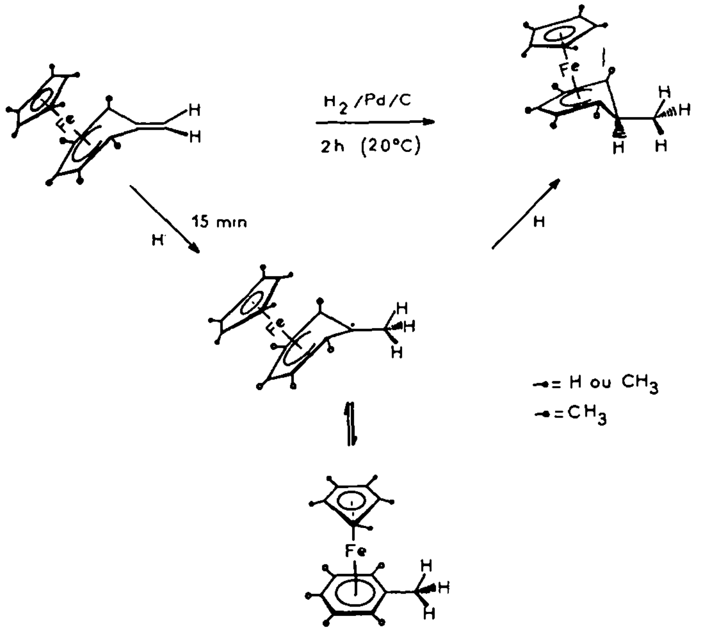
Similarly, the o-, m- and p-toluidine complexes are deprotonated at nitrogen and the deprotonated iminocyclohexadienyl complexes react with CH_3I and acylating agents to give the N-alkyl or -acyl derivatives. CpFe$^+$(arene) cations bearing an alkyl side chain such as methyl were also deprotonated[184,185,212-214] but deprotonated species are only stable in the cases of peralkylbenzene ligands.[184,185,212] The X-ray crystal structure of $Cp(C_6Me_5CH_2)Fe$ indicates that the dihedral angle is 32°, close to that found in cyclohexadienyls[184] (around 40°). The location of the two CH_2 hydrogens reflects a slight twist of the methylene group (11°) due to the steric constraints of the two ortho methyls. The iron–Cp and iron–arene distances are as in ferrocene and iron–arene complexes respectively (eqn 67). The deep red, pentane-soluble deprotonated complex is clearly of



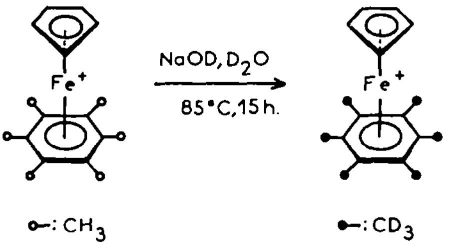
(eq.67)

the cyclohexadienyl type and not a zwitterion although it could be reduced by Na to a 19-electron radical anion species.[193] $Cp(C_6Me_5CH_2)Fe$ can be hydrogenated as an ordinary olefin by H_2–Pd/C at 20° and 1 atm in 2 h. $CpFe(I)(C_6Me_6)$, the monohydrogenated species, is shown by Mössbauer and IR spectroscopy to be an intermediate in this hydrogenation[215] (Scheme 38).

Heating $CpFe^+(C_6Me_6)\ X^-$ ($X^- = OD^-$, obtained from $CpFe(C_6Me_5CH_2) + D_2O$) in D_2O/NaOH at 85° for 15 h results in the replacement of the 18 methyl hydrogens by deuteriums (90%; eqn 68).[40]

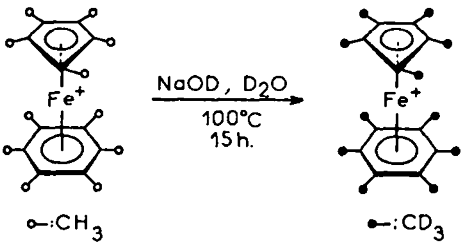


Scheme 38.



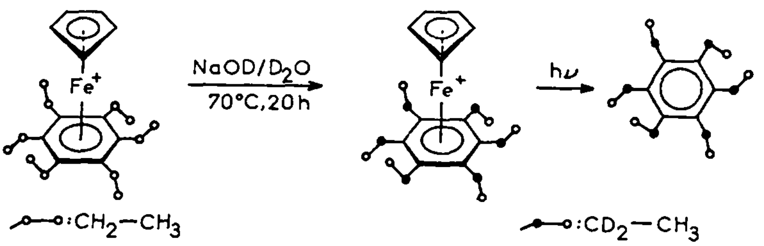
(eq.68)

A similar treatment of $C_5Me_5Fe^+(C_6Me_6)OD^-$ not only results in the deuteration of the methyls of the arene ligand but also of those of C_5Me_5 (eqn 69).[40]



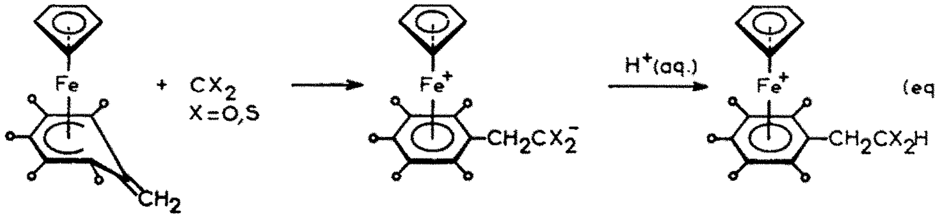
(eq.69)

However, treatment of $C_5Me_5Fe^+(C_6H_6)$ with bases does not give the deprotonated fulvene complex η^4-$C_5Me_4CH_2Fe^0(C_6H_6)$ but rather the product of nucleophilic addition to the benzene ligand.[40] Reaction of $CpFe^+(C_6Et_6)$ with D_2O/NaOD also gives the perdeuteration of the benzylic hydrogens. Subsequent photolysis gives the free arene in 84% yield (eqn 70).[40]

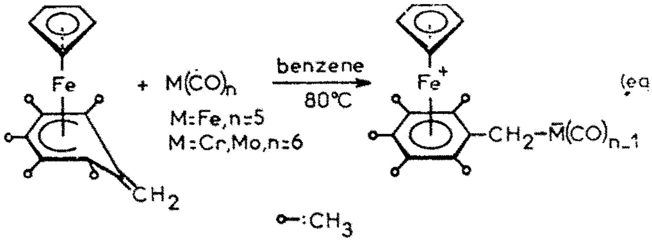


(eq.70)

$CpFe(C_6Me_5CH_2)$ reacts readily with a large variety of nucleophiles to form bonds between the CH_2 carbon and D, C, N, P, Si, Fe, Mn, Cr, Mo.[184,185,211] Reactions with CO_2 and CS_2 give zwitterions of the formula $CpFe^+C_6Me_5CH_2CX_2^-$ (X = O, S) which can be acidified at pH 1 to the acid and dithioacid (eqn 71). Reaction with iron–, chromium– and molybdenum carbonyls also give zwitterions after the loss of one carbonyl ligand (eqn 72).

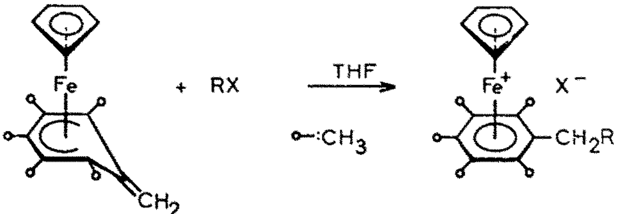


(eq.71)



(eq 72)

A very general reaction is that found with halides. Not only halogens and alkyl, acyl, silyl and phosphorous halides, but also $CpFe(CO)_2Cl$, $CpMo(CO)_3Br$ and $Mn(CO)_5Br$ undergo nucleophilic displacement of the halide. Reactions with transition metal halides are carried out at −20° to avoid extensive electron transfer side reactions (eqn 73).



(eq 73)

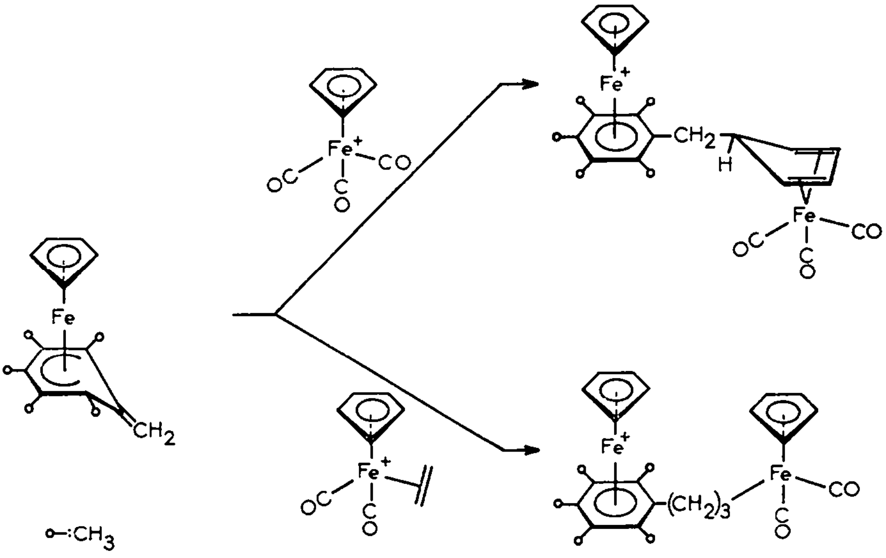
RX = CH_3I, PhCOCl, $SiMe_3Cl$, PPh_2Cl, I_2, Br_2, Cl_2, $CpFe(CO)_2Cl$,
$CpMo(CO)_3Br$, $Mn(CO)_5Br$

Hydrocarbons activated by cationic transition metal units give nucleophilic addition reactions providing C–C bond formation according to the rule of Davies, Green and Mingos (Scheme 39).

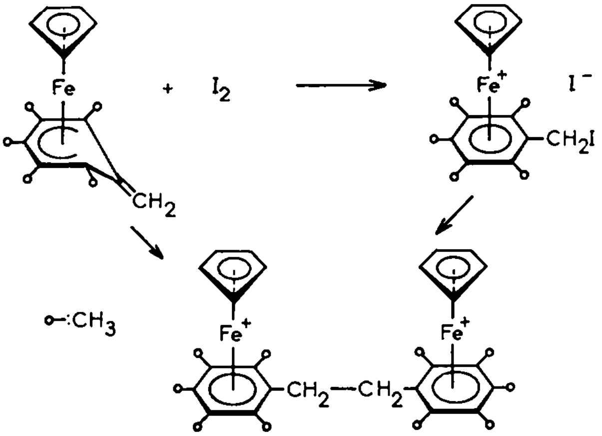
Double nucleophilic substitution can occur upon reaction with I_2. In fact the reaction product depends upon the order of addition of the reactants (Scheme 40).[184,185]

A number of other analogous $CpFe^+$(alkylbenzene) cations have also been deprotonated by tBuOK and alkylated *in situ* by CH_3I at low or ambient temperatures (arene = $Ph(CH_3)_n$, n = 1, 2, 3, o-$ClPhCH_3$, Ph_3CH, tetralin, 9-10 dihydroanthracene, xanthene). Monomethylation products were formed in 20–95% spectroscopic yields but were contaminated with starting materials and sometimes with dimethylation products. Intermediate deprotonated species are not stable in the cases of simple alkyl benzene complexes and were only characterized by these alkylation reactions.[213,214] The deprotonated complexes clearly seem to be stabilized by an alkyl substituent on the benzylic carbon or by peralkylation of the arene, e.g. when both ortho benzene carbons bear alkyls. Functionalization has similarly been effected on benzylic carbons by reactions with functional halides subsequent to deprotonation of the toluene, ethylbenzene, isopropylbenzene and fluorene complexes.

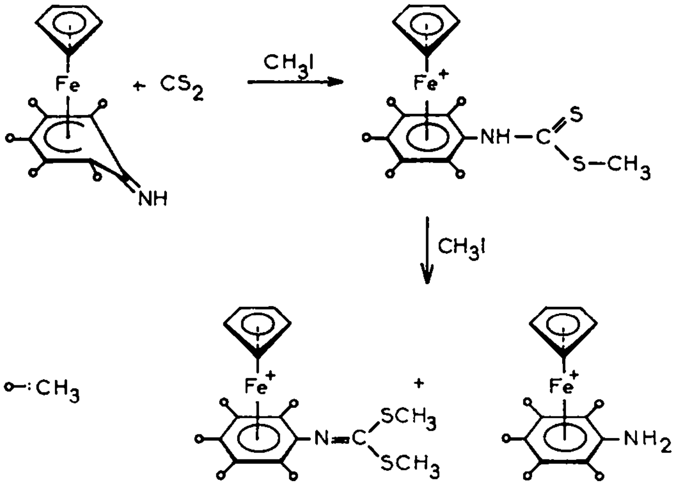
Attempted functionalization of derivatives of $CpFe^+$(aniline) cation subsequent to deprotonation at nitrogen is complicated by the deprotonation of the intermediate functionalized $CpFe^+$(arene) cation by the imine (Scheme 41).[113]



Scheme 39.

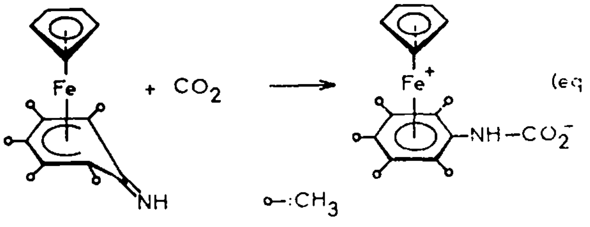


Scheme 40.



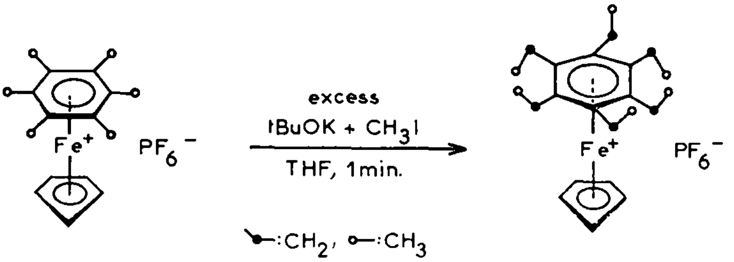
Scheme 41.

However, the monofunctionalized complex could be isolated when the remaining benzylic hydrogen is less acidic than those of the cationic primary amine complex. Using crystalline samples of $CpFe(C_6Me_5NH)$, the carbamate zwitterion was isolated in good yields upon reaction of this imine with CO_2 (eqn 74).[196]

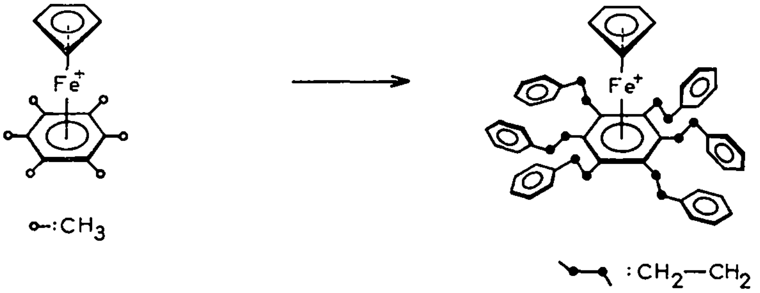


(eq 74)

Reaction of $CpFe^+(C_6Me_6)PF_6^-$ with excess CH_3I and tBuOK in THF gives $CpFe^+(C_6Et_6)PF_6^-$ quantitatively after *ca* 1 min of mild reflux (eqn 75).[39] Reactions with $PhCH_2X$ (X = Cl, Br) give a similar result after 15 min, (X = Br) or after 3 hr at reflux (X = Cl), (eqn 76).[39]



(eq.75)



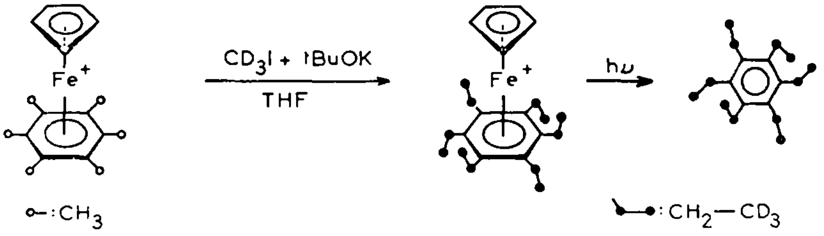
(eq.76)

Decomplexation provides the free ligand in 58% overall yield from C_6Me_6 (Scheme 42).

$$\begin{tikzcd}
CpFe^+(C_6Me_6)\,PF_6^- \arrow[r, "80\%"] & CpFe^+[C_6(CH_2\text{-}CH_2\text{-}Ph)_6]\,PF_6^- \arrow[d, "80\%"] \\
C_6Me_6 \arrow[u, "90\%"] \arrow[r, Rightarrow, "58\%", "\text{via } CpFe^+"'] & C_6(CH_2\text{-}CH_2\text{-}Ph)_6
\end{tikzcd}$$

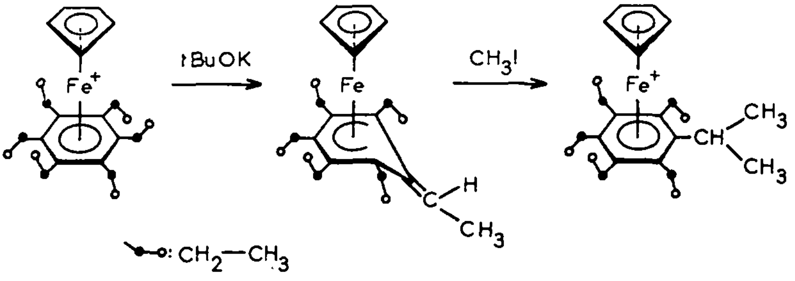
Scheme 42.

The permethylation reaction was applied to the synthesis of $C_6(CH_2CD_3)_6$ from C_6Me_6 using CD_3I and an overall yield of 77% was obtained (eqn 77).



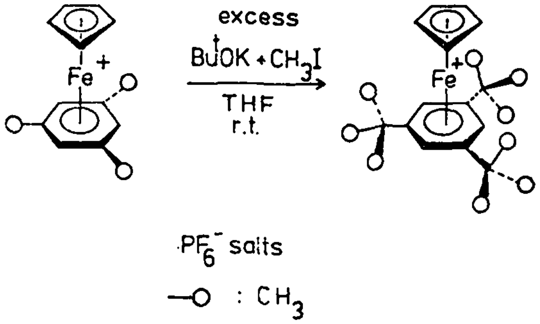
(eq77)

The permethylation of $CpFe^+(C_6Me_6)PF_6^-$ is limited by steric bulk and reaction of excess CH_3I and tBuOK with each other competes with alkylation, preventing the formation of isopropyl substituents on the arene. Indeed, if $CpFe^+(C_6Et_6)PF_6^-$ is treated with 1 mol tBuOK in THF, deprotonation occurs, giving $CpFe(C_6Et_5CHMe)$. The IR absorption of the exo-cyclic double bond is shifted to 1640 cm^{-1} in pentane indicating less conjugation with the cyclohexadienyl system than in $CpFe(C_6Me_5CH_2)$ (1600 cm^{-1}). Alkylation by CH_3I proceeds in 10 h in THF at 65°, giving the pentaethylisopropyl complex[39] (eqn 78).



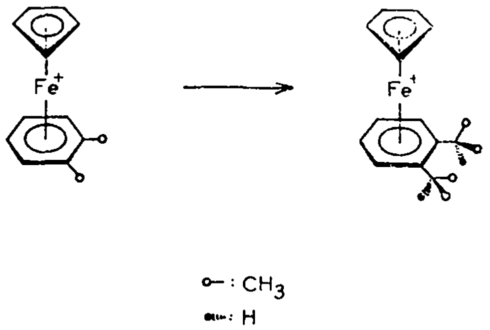
(eq.78)

In the mesitylene complex, steric inhibition is not a factor and complete permethylation occurs giving the 1,3,5 tris-(t-butyl)benzene complex (eqn 79).

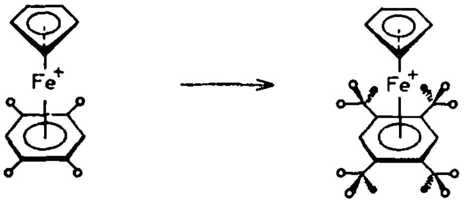


(eq 79)

The cases of the o-xylene and durene complexes are intermediate. Reaction with excess tBuOK and CH_3I results in the replacement of two hydrogens out of three by methyl groups on each methyl substituent (eqn 80 and 81).[39]



(eq 80)



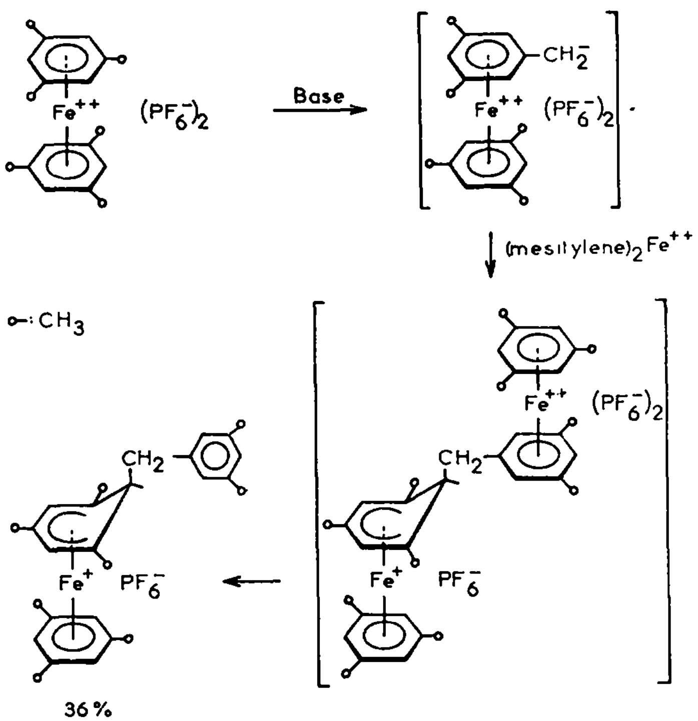
(eq.81)

Attempts to effect permethylation of $C_5Me_5Fe^+(C_6Me_6)$ give a complex mixture even under forcing conditions:

$$C_5Me_5Fe^+(C_6Me_6)PF_6^- \xrightarrow{\text{excess tBuOK} + CH_3I} C_5Me_xEt_{5-x}Fe^+(C_6Me_yEt_{6-y})PF_6^-$$

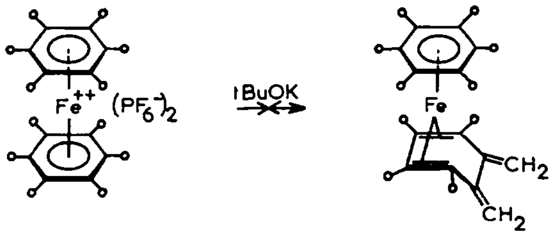
$$2 < \bar{x} < \bar{y} < 3.$$

Nitrogen and oxygen bases such as $LiNMe_2$, $NaN(SiMe_3)_2$ (in benzene), LiOMe (in MeOH), $LiNH_2$ and tBuOK (in THF) deprotonate the bis(mesitylene) iron dication to give up to 36% yields of addition products of the (arene) (cyclohexadienyl) iron cation type. It is assumed that the deprotonated mesitylene complex acts as a carbon nucleophile on another molecule of dicationic complex[66] (Scheme 43).



Scheme 43.

It is probable that this reaction is relevant to the instability of deprotonated $CpFe^+$(arene) cations[216] (protonation of the latter species regenerate these cations). Recently it was shown that the reaction described in Scheme 43 could be avoided using the hexamethyl complex, but double deprotonation by tBuOK in THF at low temperature does not give $(C_6Me_6)Fe\{(\eta^4\text{-}C_6Me_4(CH_2)_2\}$, *vide infra* §5.10.2 (eqn 82).[224]



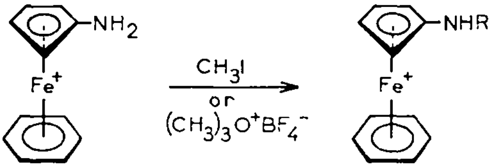
(eq.82)

The 36 methyl hydrogen in $(C_6Me_6)_2Fe^{2+}(PF_6^-)_2$ could be exchanged with deuteriums in D_2O in the presence of a base.[66]

Attempted permethylation of this complex using CH_3I and tBuOK gave a complicated mixture of $(C_6Me_xEt_{5-x})_2Fe^{2+}(PF_6^-)_2$.[224]

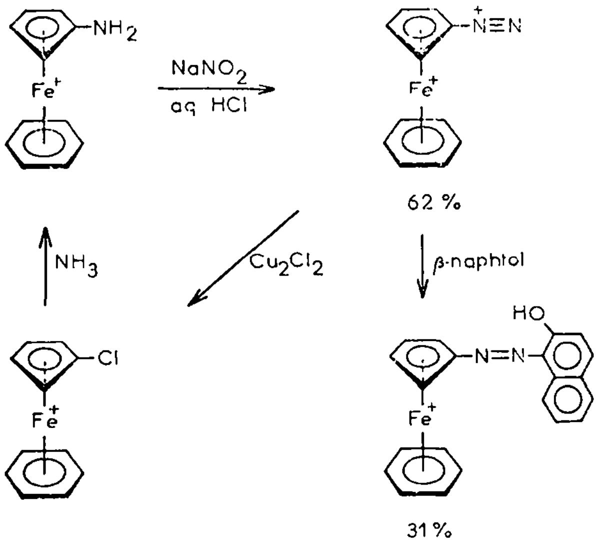
5.9 $CpFe^+$(arene) *complexes bearing an amino group*

$C_5H_4NH_2Fe^+(C_6H_6)BF_4^-$, prepared by reaction of $C_5H_4ClFe^+(C_6H_6)BF_4^-$ with NH_3 in autoclave,[198] can be alkylated at nitrogen even without deprotonation. Reaction with triethyl oxonium tetrafluoroborate at 0° in CH_3CN or with methyl iodide in DMF at room temperature for 75 days gives the N-alkylaniline complex[217] (eqn 83).



(eq 83)

Diazotation with sodium nitrite in HCl at 0° gives the diazonium dication, stable to 90° as a bright red PF_6^- salt (62% yield). The classical coupling with β naphtol was effected, giving the dark red azo complex in 31% yield. Liberation of nitrogen (Sandmeyer reaction) occurs only in the presence of Cu_2Cl_2 (Scheme 44) leading to formation of the chlorocyclopentadienyl complex. Attempted preparations of the iodo and hydroxy compounds failed.

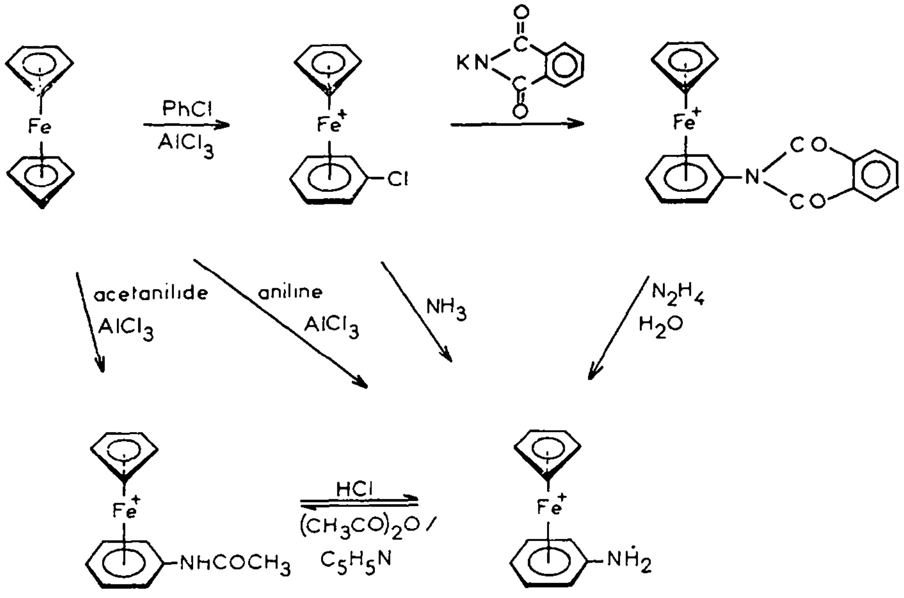


Scheme 44.

An attempted synthesis of $C_5H_4NH_2Fe^+(C_6Me_6)PF_6^-$ by nucleophilic displacement of Cl in $C_5H_4ClFe^+(C_6Me_6)PF_6^-$ failed.[60]

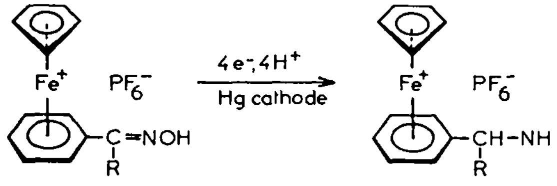
The two isomeric amines $C_5H_4NH_2Fe^+(C_6H_6)$ and $CpFe^+(C_6H_5NH_2)$ are very weak bases; the pKa values are respectively $+0.20$ and -1.07. The aniline complex is the weaker base as can be expected since delocalization of the positive charge is more important on the benzene ring; diazotation of this amine failed.[218] It can be synthesized either by direct ligand exchange between a ferrocene ring and aniline in 60% yield[117] or by reaction of $CpFe^+(C_6H_5Cl)$ and NH_3 in autoclave.[197] It is also formed by reaction of the phthalimide derivative with hydrazine (Scheme 45). It reacts with acetic anhydride in pyridine to provide the acetanilide complex from which the aniline complex can be regenerated upon reaction with HCl (Scheme 45).[197]

Deprotonation at nitrogen of the aniline and toluidine complexes[113,118] together with alkylation and acylation of the iminocyclohexadienyl complexes formed were described in the preceding section (§5.7). This sequence may be compared to the long-known alkylation and acylation reactions described above, which do not require deprotonation.



Scheme 45.

Electroreduction of the oximes $CpFe^+(C_6H_5CR=NOH)PF_6^-$ on an Hg cathode gives the amines (eqn 84).[219]

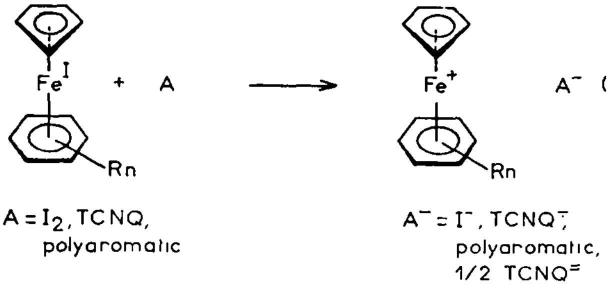


(eq 84)

The attempted Fischer–Haffner type synthesis of $(C_6Me_5NH_2)_2Fe^{2+}$ failed.[60]

5.10 *Reactivity of* 19- *and* 20-*electron complexes*

5.10.1 19-*electron* CpFe(I)(arene) *complexes* are strong one-electron reducing agents and behave as "electron reservoirs". Reactions with classical acceptors such as I_2,[36,37] TCNQ[220] and polyaromatics[220] give simple electron-transfer products (eqn 85).

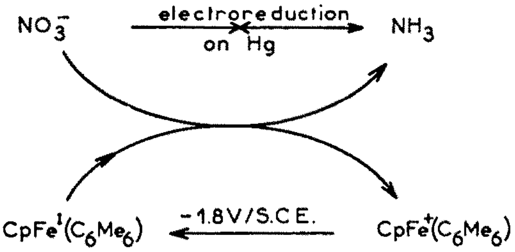


(eq.85)

Reduction of H_2O proceeds at various rates, depending on whether the medium is homogeneous.[36,37,221]

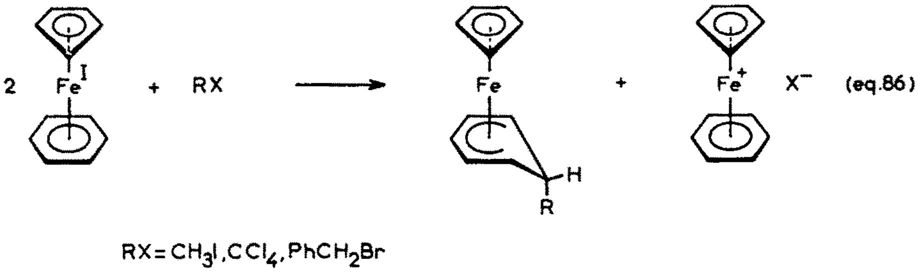
$$CpFe(I)(C_6Me_6) + H_2O \rightarrow CpFe^+(C_6Me_6)OH^- + 1/2H_2\uparrow.$$

Cathodic reduction of $CpFe^+$(arene) cations at -1.8 V/sce on Hg in aq. NaOH 0.1 N gives H_2, the Fe(I)/Fe(II) redox system behaving as a redox catalyst. When the arene ligand is C_6Me_6, the Fe(I) form is stable and the redox catalyst is more efficient.[211] In this medium, nitrate ion is reduced rapidly and catalytically, the process being effected with the soluble zwitterion $C_5H_4CO_2{}^-Fe^+(C_6Me_6)$,[221] which is best synthesized from ferrocene, CO_2, $AlCl_3$ and C_6Me_6[131] (Scheme 46).

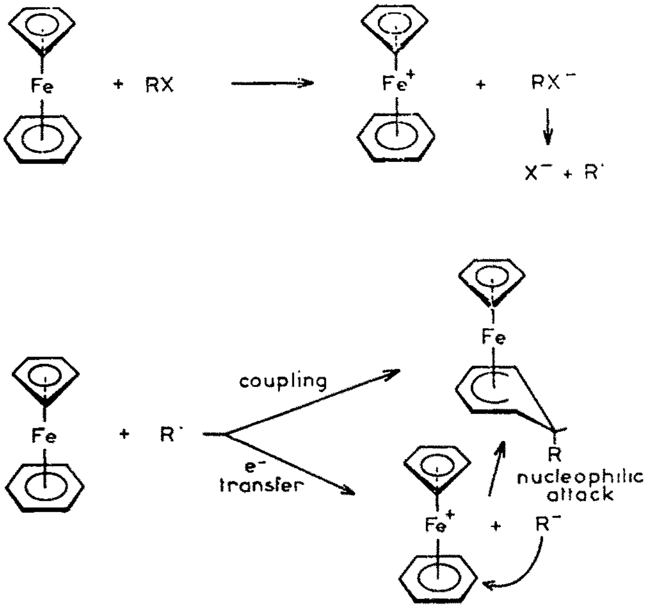


Scheme 46.

$CpFe(I)(C_6H_6)$ reacts with various alkyl halides to give equimolecular amounts of Cp(cyclohexadienyl) iron and $CpFe^+$(arene) cation (eqn 86).[222]

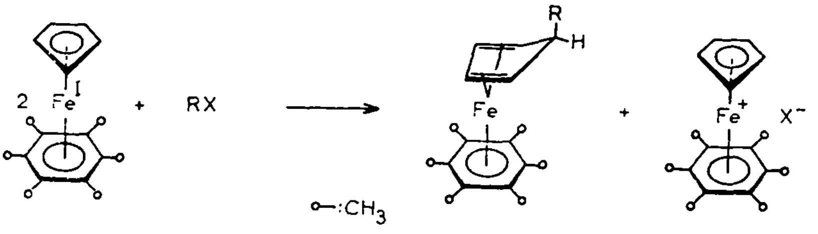


The first step is an electron transfer from the Fe(I) complex to the alkyl halide giving the radical anion of the latter. The alkyl radical resulting from the loss of the halide can either couple with another molecule of Fe(I) complex or oxidize it to give a carbanion, which then adds nucleophilically to the activated benzene ring (Scheme 47).



Scheme 47.

With $CpFe(I)(C_6Me_6)$, permethylation of the arene changes the reaction site and substituted cyclopentadiene Fe^0(arene) complexes are now obtained (eqn 87).[223]

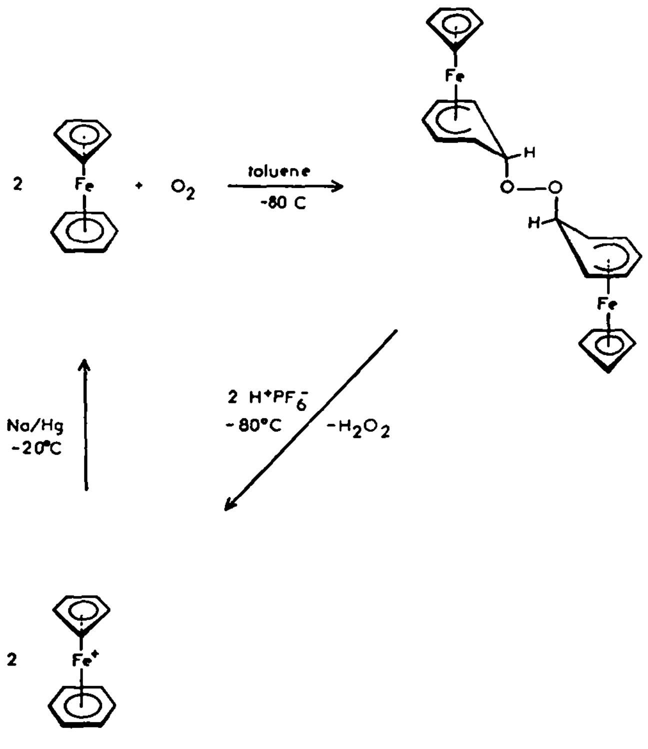


(eq 87)

With the fully methylated complex $C_5Me_5Fe(I)(C_6Me_6)$, the regiospecificity is changed again and attack proceeds on the arene ligand as in the parent complex $CpFe(I)(C_6H_6)$.[223]

Dimerization of the Fe(I) complexes, which is observed for most cases where the arene ligand is not hexasubstituted[32,101,124] (solid state or pentane solution) is an intramolecular electron transfer, the metal being oxidized from Fe(I) to Fe(II) and the benzene ring reduced to a cyclohexadienyl. Although the odd electron has high metal character, dimerization proceeds through an arene carbon. This dimerization, slow at 20° in pentane (12 h), is dramatically accelerated in the presence of O_2 (fast at $-80°$). In this case the dimer is bridged by a peroxo group.[128,225] O_2 is even able to induce the dimerization of the thermally stable complex $CpFe(I)(C_6H_3tBu_3)$ which does not dimerize in its absence. These dimerizations consume 1/2 mol O_2 per mol of Fe(I) sandwich.

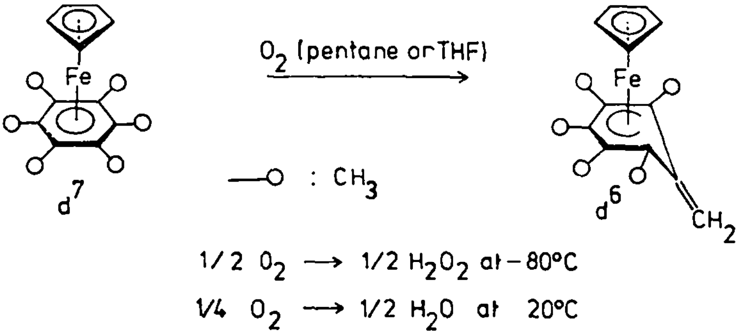
Upon reaction of O_2 with the Fe(I) sandwich at $-80°$, the green solution turns orange. Hydrolysis with $H^+PF_6^-$ gives yellow $CpFe^+$(arene) PF_6^- and 1/2 mol H_2O_2. The IR spectra of the orange dimeric peroxides show a peroxo stretch at 860 cm^{-1}. It is thus proposed that the peroxo dimers are formed either by coupling with O_2 or by electron transfer to O_2 to form $O_2^{\cdot -}$ followed by nucleophilic attack of $O_2^{\cdot -}$ on the $CpFe^+$(arene) cation (Scheme 48).



Scheme 48.

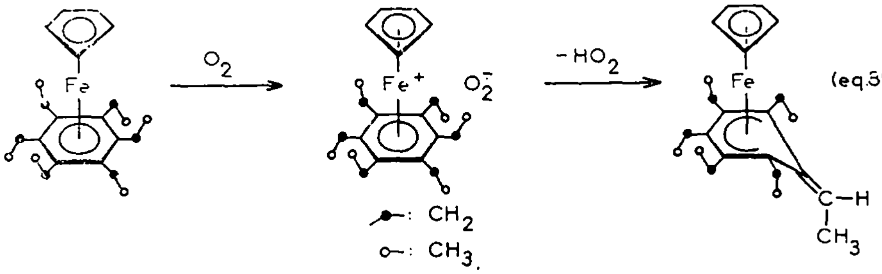
This activation of O_2 occurs whatever the solvent but, in THF, the presence of $NaPF_6$ induces a dramatic change in reactivity. Simple electron transfer gives a yellow precipitate of $CpFe^+$(arene)

PF_6^- and Na_2O_2.[128] In those cases where the arene ligand bears benzylic hydrogen(s), the reaction of O_2 is totally different,[184,185,212] at least in the absence of $NaPF_6$; it gives a dark red complex resulting from H atom abstraction, accompanied by 1/2 mol H_2O_2 (at −80°) or H_2O (at 20°). With the hexamethylbenzene ligand, the yield of the stable complex $CpFe(C_6Me_5CH_2)$ is 97% (eqn 88).



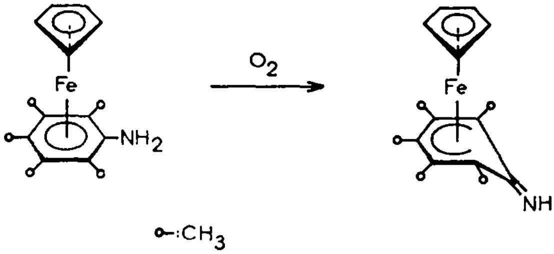
(eq 88)

The reaction proceeds similarly whatever the number of methyl group(s) on the arene but neither the Fe(I) complex nor the H atom abstraction complex is stable when the arene bears less than six methyl groups. $C_5Me_5Fe(I)(C_6Me_6)$ also reacts in this fashion, the H atom being regiospecifically abstracted from an arene methyl group. With $CpFe(I)(C_6Et_6)$, the reaction is much slower and proceeds in a few minutes at −20°; the intermediate electron-transfer product $O_2^{\cdot -}$ could be detected in this case (eqn 89).[185]



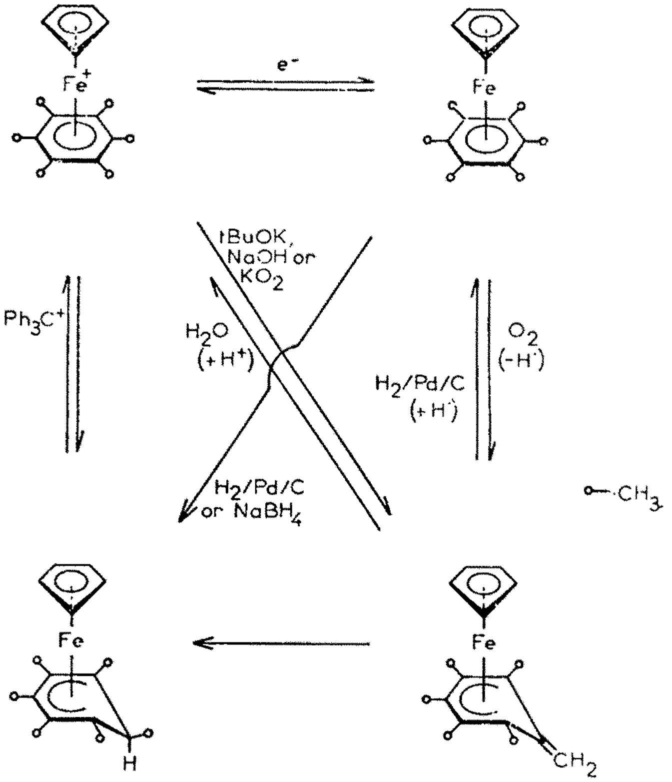
(eq.89)

Consistent with an outer-sphere electron-transfer mechanism followed by deprotonation, KO_2 deprotonates $CpFe^+(C_6Me_6)$ to give $CpFe(C_6Me_5CH_2)$ and the unstable 19-electron complex $CpFe(I)(C_6Me_5NH_2)$ reacts with O_2 giving the stable crystalline iminopentamethylcyclohexadienyl complex in 80% yield (eqn 90).[196]



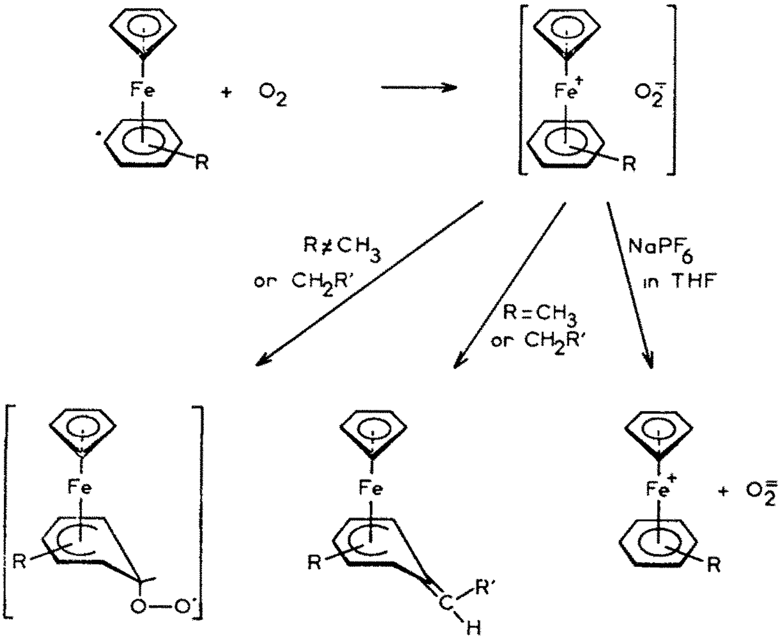
(eq.90)

The fast outer-sphere electron-transfer between the Fe(I) complex and O_2, which accounts for the various reactions described here, is due to the large difference (≃ 1 V) between the redox potentials of the reversible organometallic system (≃ − 1.8 V/sce) and $O_2/O_2^{\cdot -}$ (≃ − 0.7 V/sce). The general Scheme 49 accounts for all the reactions connecting the CpFe (hexamethylbenzene) complexes, emphasizing the electron- and hydrogen-atom transfer reactions.



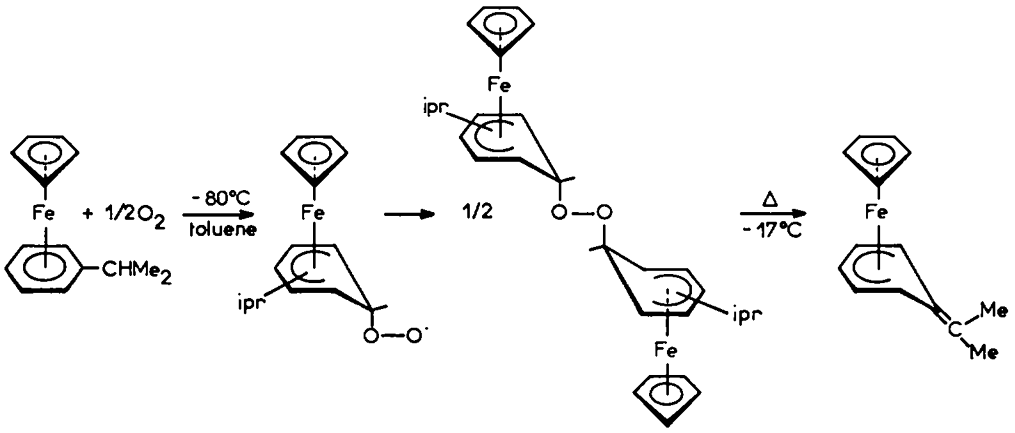
Scheme 49.

The fate of the reactive superoxide radical anion in the ion pairs formed by electron transfer from the Fe(I) complex to O_2 depends on whether the arene ligand carries benzylic protons, and, if the medium is THF, whether it contains $NaPF_6$; it may react via (i) nucleophilic attack on the coordinated arene, (ii) deprotonation of a benzylic substituent or (iii) disproportionation (Scheme 50).[226]



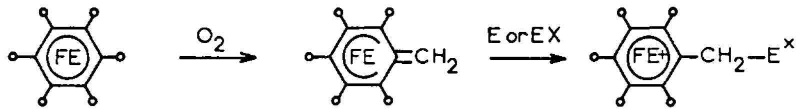
Scheme 50.

When the arene ligand bears an isopropyl substituent, an intermediate situation is found. The reaction of O_2 with $CpFe(I)(C_6H_5CHMe_2)$ at $-80°$ in pentane gives a soluble orange compound of the peroxo dimer type. Warming to $-17°$ results in a sharp colour change to deep red, indicating formation of a CpFe(II) (cyclohexadienyl) complex bearing an exocyclic methylene group (cf. eqn 88). In this case, its formation requires H atom abstraction via a radical type mechanism. Steric bulk about the tertiary benzylic hydrogen disfavors deprotonation by $O_2^{\cdot-}$ with respect to nucleophilic addition of this species to the arene ligand (Scheme 51).[128]



Scheme 51.

This H-atom abstraction by O_2 under mild conditions is of synthetic interest, as it provides a clean route to $CpFe(II)(C_6Me_5CH_2)$ and thus access to its rich chemistry, including bond formation with a variety of elements via reactions with organic and inorganic electrophiles (eqn 91, see also §5.7).[185]



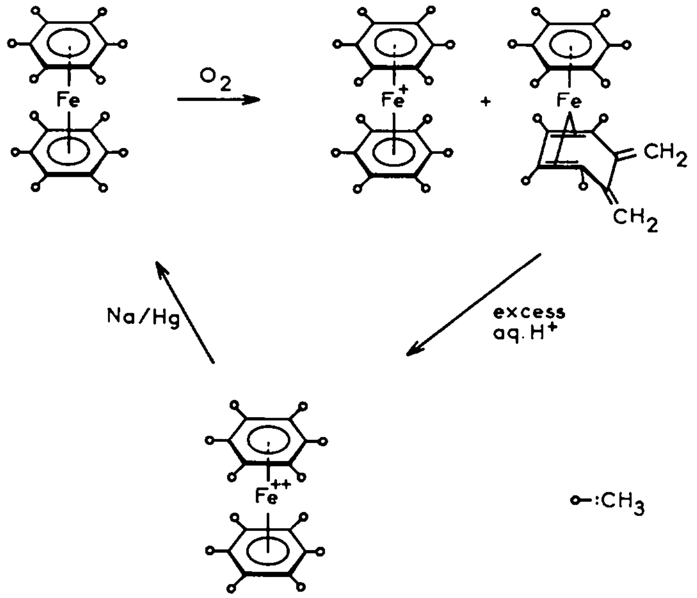
(eq.91)

(x = -1 or 0)

E = D,C,P, Si, Fe, Mn, Cr, Mo, halogens
X = halogen
FE = η^5-C_5H_5Fe; o— : CH_3

5.10.2 *The twenty-electron complex* $(C_6Me_6)_2Fe^0$ reacts with O_2 in toluene to give a substantial amount of the 19-electron complex $(C_6Me_6)_2Fe^+$, 1/2 $O_2^{=}$ as a purple precipitate, accompanied by a deep red compound identified as the double H atom abstraction product $C_6Me_6Fe\{\eta^4\text{-}C_6Me_4(CH_2)_2\}$.[224] (Scheme 52).

Reaction of $(C_6Me_6)_2Fe$ with benzene gives the cyclohexadiene complex $(C_6Me_6)Fe(\eta^4\text{-}1,3\text{-}C_6H_8)$.[16b] The extra H atoms come from C_6Me_6. The rate of reaction is enhanced in the presence of H_2. This process is induced by an intramolecular decomplexation of C_6Me_6 via oxidative addition of a methyl group and exchange reactions with other ligands proceed similarly (§4.1.5, Scheme 18).[16b]



Scheme 52.

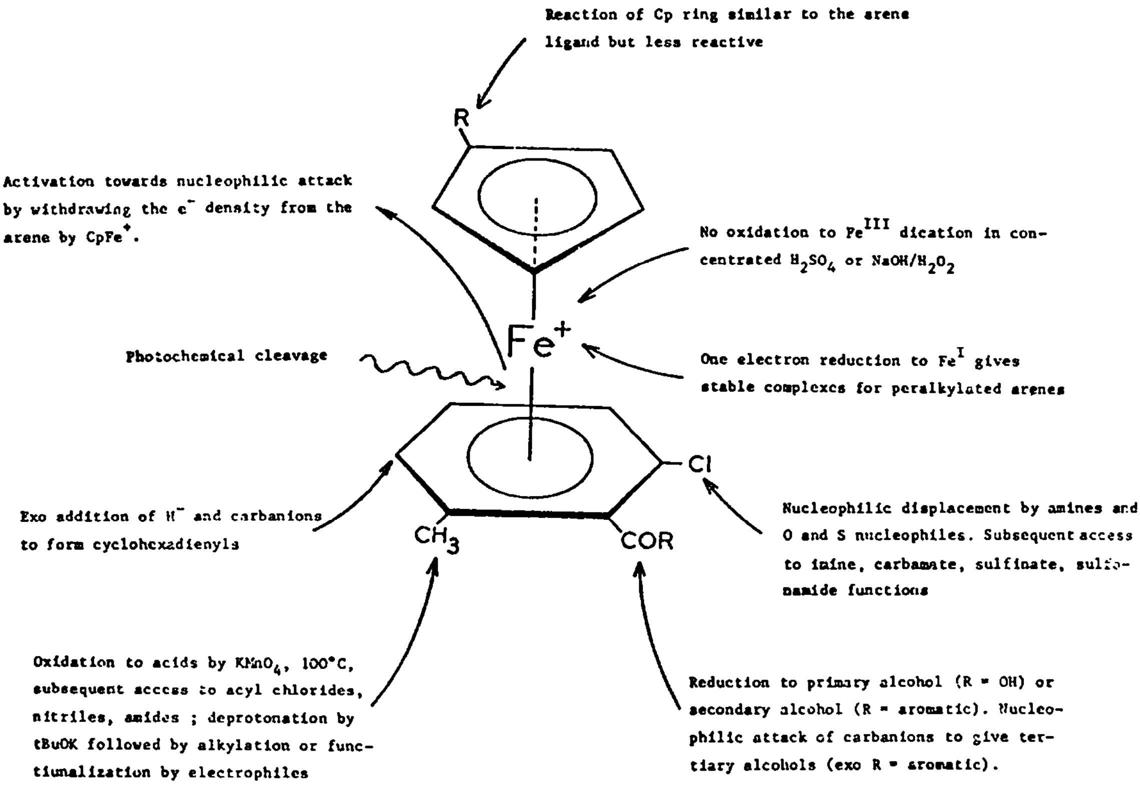
6. SUMMARY, CONCLUSION AND PROSPECTS

The twenty-year old finding[87] that arenes can be complexed to the $CpFe^+$ unit by $AlCl_3$-induced ligand exchange with ferrocene has led to the synthesis of several hundred cationic complexes of aromatic ligands. This reaction is an example of the general Fischer–Haffner process for the synthesis of transition metal sandwiches, among which the bis(arene) iron dications are especially useful.

The chemistry of $CpFe^+$(arene) cations has attracted considerable attention because these complexes are extremely stable to heat, air, water and concentrated acids such as H_2SO_4 (NMR spectra could be recorded using the latter solvent).

In addition, the chemistry of complexed arenes is completely opposite to that of the free aromatics. Thus they do not undergo any of the reactions of nucleophilic aromatics such as acylation, arylation, metallation, bromination, nitration, or substitution by free radicals.[12] On the contrary, they undergo many useful reactions with nucleophiles. These include the exo-addition of hydrides and carbanions, nucleophilic displacement of chloride by neutral amines and O and S anions under mild conditions, benzylic deprotonation by t-BuOK followed by various functionalizations of deprotonated species, ring opening of xanthone by neutral amines, and reduction and nucleophilic addition at an exo-cyclic carbonyl.

The chemistry of bis(arene) iron dication is far less studied but follows similar trends. The greater reactivity of the arene ligands in this series as compared to that found in the mixed $CpFe^+$(arene) cations is illustrated by the nucleophilic addition of phosphites to the bis(arene) complexes. A feature specific to this series is that reduction by hydrides proceeds at one arene ligand only to give cyclohexadiene complexes. Substituted cyclohexadienes are accessible using this strategy. In this respect, the comparative reactivity of $CpFe^+$(arene) and cyclohexadienyl Fe^+(arene) complexes should be studied and the results analyzed in the light of Green's rule. This rule works nicely *inter alia* in the $CpFe^+$(arene) series: the greater reactivity of the arene as compared to Cp results from the larger delocalization of the positive charge onto the even arene ligand than onto the odd cyclopendadienyl one. Consequently, the role of the Cp ligand is mostly that of an ancillary ligand, when desired. A useful Cp chemistry ressembling that of the arenes is also observed occasionally, but its purpose has been more comparison of physical measurements or functionalization of organo-metallics than organic syntheses since decomplexation leads to Cp polymerization. Interestingly the modified aromatic could always be recovered free by photolysis, or thermolysis; oxidation of cyclohexadienyl complexes with dilute aqueous $KMnO_4$ or ceric ammonium nitrate was equally useful.



Reaction of Cp ring similar to the arene ligand but less reactive

Activation towards nucleophilic attack by withdrawing the e^- density from the arene by CpFe$^+$.

No oxidation to Fe^{III} dication in concentrated H_2SO_4 or $NaOH/H_2O_2$

Photochemical cleavage

One electron reduction to Fe^{I} gives stable complexes for peralkylated arenes

Exo addition of H^- and carbanions to form cyclohexadienyls

Nucleophilic displacement by amines and O and S nucleophiles. Subsequent access to imine, carbamate, sulfinate, sulfonamide functions

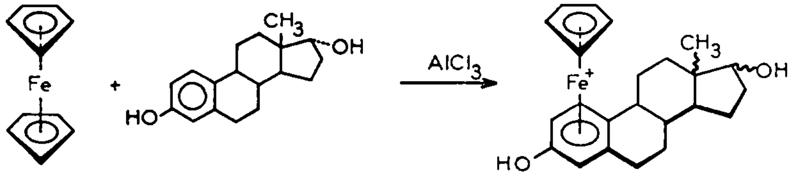
Oxidation to acids by $KMnO_4$, 100°C, subsequent access to acyl chlorides, nitriles, amides ; deprotonation by tBuOK followed by alkylation or functiunalization by electrophiles

Reduction to primary alcohol (R = OH) or secondary alcohol (R = aromatic). Nucleophilic attack of carbanions to give tertiary alcohols (exo R = aromatic).

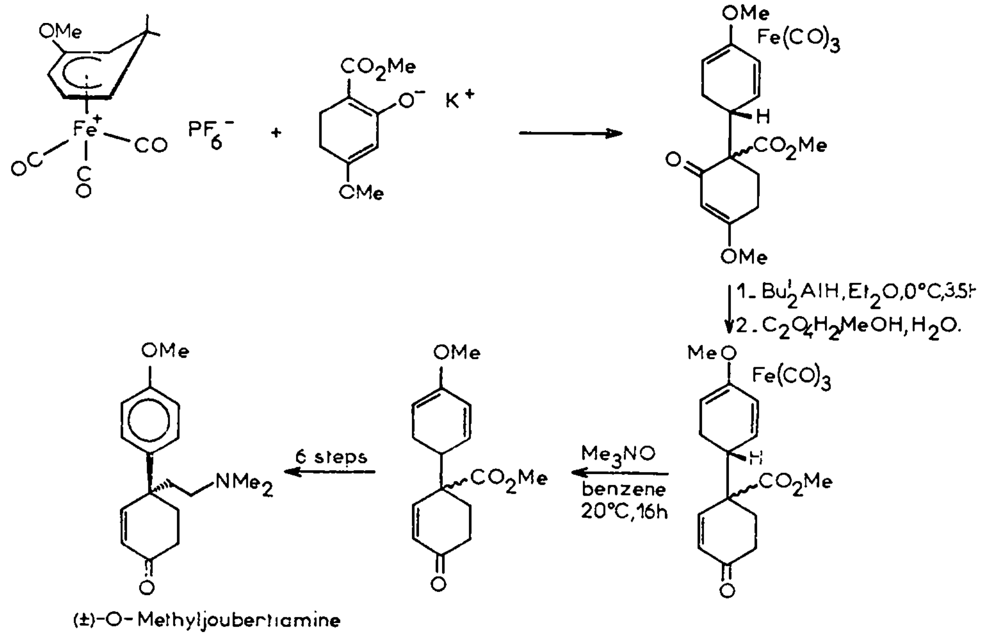
Stereochemical advantages from complexation on one face of the arene were obtained upon reduction of the anthraquinone complex and in the formation of 9,10-*cis*-dihydro 9,10-dimethylanthracene in the course of the ligand exchange of ferrocene with 9,10-dimethylanthracene. However, these examples are limited and no general method has been found to obtain iron complexes of aromatic ketones.

The complexation of arenes by iron(II) in bis(arene) iron dications is restricted to benzene and its various methyl substituted derivatives. The use of $AlCl_3$ to induce the complexation reaction implies that arenes cannot be complexed when they bear an exocyclic unsaturation (in particular carbonyls). This is presently a severe limitation on the chemistry of arene–iron cationic complexes. Indeed, the $Cr(CO)_3$ unit is much more useful in inducing stereoselectivity through temporary complexation of one face of the arene, allowing the syntheses of optically active polycyclic aromatics. Although ketones do not complex readily to $Cr(CO)_3$, they can be synthesized after complexation, which is generally not the case with the CpFe$^+$ unit.

Another important feature of the cationic iron–arene complexes is that they are readily converted to neutral complexes by one- or two-electron reduction or by action of hydrides or carbanions. Relatively stable 19- or 20-electron complexes can be synthesized, which display novel chemistry involving electron transfer. Dioxygen can be activated under mild conditions and a variety of reactions of the radical anion $O_2^{\cdot-}$ ensue (deprotonation, nucleophilic addition and disproportionation). A reaction of synthetic interest is simple H atom abstraction from CpFe(I)(alkylarene) complexes upon contact with O_2 which can be followed by bond formation with a great variety of elements upon reaction with organic and inorganic electrophiles. Reactions between CpFe(I)(arene) complexes and alkyl halides give substituted cyclohexadienyl and cyclopentadiene complexes. Besides applications in aromatic synthesis, 19-electron CpFe(I)(arene) complexes are of interest as "electron reservoirs". For instance, they are redox catalysts, effecting the rapid reduction of nitrate to ammonia. Based on their ionization potentials determined by He(I) photoelectron spectroscopy, they are the most electron-rich molecules known thus far. Various physical and theoretical studies indicate they are essentially metal-centered rather than organic free radicals, although the latter form is suggested by the coupling reaction of the benzene ligands. It is probable that 20-electron bis(arene) iron(0) complexes and related arene (cyclohexadiene) iron systems, synthesized either by conventional means or by metal vapor techniques, will provide additional synthetic possibilities for aromatics in the near future. Note that these species are related to the (cyclohexadienyl)(arene) iron cations and to bis(arene) iron dications by the addition or abstraction of one or two hydrides. More generally, any means affording arene–iron sandwiches without the use of $AlCl_3$ will be of interest since more functional groups may withstand complexation; in this way it will be possible to complex aromatic steroids and other natural products. Such complexes have not been reported with iron as yet whereas $Cr(CO)_3$ complexes of aromatic steroids[227,228] and morphine derivatives[229] have been known for some years; moreover the latter were used in the modification of the aromatics. Recently, however, β-estradiol has been complexed to $CpFe^+$.[216]



It is also worth mentioning that while the inorganic unit $Fe(CO)_3$ cannot complex simple arenes, it forms stable 18-electron (cyclohexadienyl) $Fe^+(CO)_3$ cations upon hydride abstraction by $Ph_3C^+BF_4^-$ from cyclohexadienene $Fe(CO)_3$; these complexes may occasionally be useful in the synthesis of natural products, as in the recently reported process leading to (±)-O-methyljoubertiamine and shown in Scheme 53.[201]



Scheme 53.

Note that the inorganic $Fe(CO)_3$ unit is isolobal to the organic one (η^6-arene)Fe, but at the same time their electronic properties are very different. Extensive chemistry of model hexahapto arene iron complexes is now available which should make the as yet little explored modification of aromatic natural products an outstanding challenge for the future.

Note added in proof. The side of hydrogenation of anthracene upon complexation by $CpFe^+$ depends on whether $C_5H_5Fe^+$ or $C_5Me_5Fe^+$ is used. $C_5Me_5Fe(CO)_2Br$ gives red $\{C_5Me_5Fe\ \eta^6\text{-1,2,3,4-tetrahydroanthracene}\}^+$ as the major cationic reaction product.[236]

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