Review

η^6-ARENE- η^5-CYCLOPENTADIENYL IRON CATIONS AND RELATED SYSTEMS

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1. Introduction

Since the publication of a comprehensive review [1] on (η^6-arene)
(η^5-cyclopentadienyl)iron cations in 1977 a large number of papers have been
devoted to the chemistry of these systems. The area has been partially
reviewed [2a-d] and described briefly in a short chapter [3] but no
comprehensive review has appeared. The present article complements the
earlier review and covers works published on (η^6-arene) (η^5-Cp) iron cations
(Fig.1-I) and related systems: (η^5-cyclohexadienyl) (η^5-Cp) iron
(Fig.1-IIa-c); electroneutral (η^6-arene) (η^5-Cp) iron (Fig.1-III) and
(η^6, η^6-arene) di[(η^5-Cp)iron] dications (Fig.1-IV) up to late 1983.

Fig. I.

(I) (IIa) (IIb) (IIc)

(III) (IV)
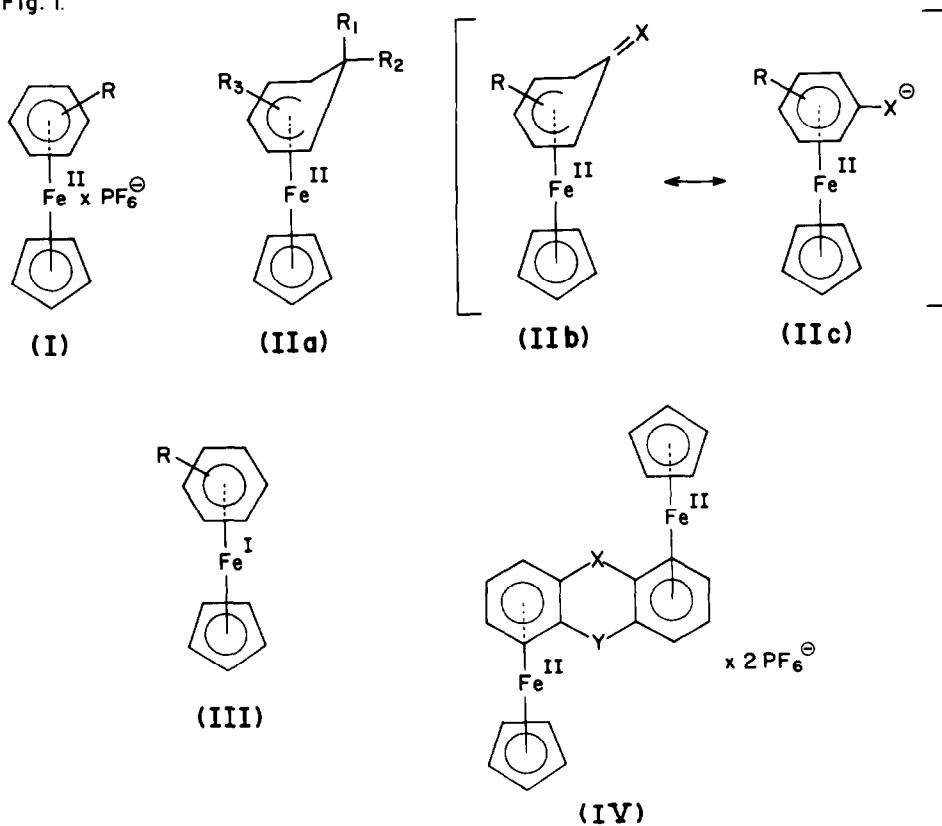
2. Crystal and electronic structure

The structure of 1.1^1-trimethylenebenzenecyclopentadienyliron PF_6[4],

([2.2] paracyclophane) (Cp) iron BF_4 [5],

bis[(2,5-dimethyl-3,4-cyclobutabenzo)-1,5-cyclooctadienyl] (Cp) iron PF_6 [6],

$[2_5](1,2,3,4,5)$ cyclophane (Cp) iron PF_6 [7], (exo-9-methylfluorene) (Cp) iron

PF_6 [8,9] (only partially), (hexaethylbenzene) (cyclopentadienyl) iron PF_6

[10] and [3a-7a-η^6(hexahydro-2,2^1,3,3^1,5,6-spiro (1H-indene-1:4 pyrane))]

(Cp) iron PF_6 [11] of the type I; (η^6-fluorenyl)(Cp) iron [8,9] and

(pentamethylbenzyl)(Cp)iron [12] of type II and (hexamethylbenzene) (Cp) iron

[13] of the type III have been determined in order to confirm their structure.

Generally, the Cp ligand is nearly planar in all of the structures; the

dihedral angle between η^6-arene ring plane and Cp plane do not exceed $3^\bullet$ with

the exception of the $7^\bullet$ angle found in the bridged trimethylenebenzene

cyclopentadienyliron cation. Carbon-carbon atom distances in the Cp ring are

in the range of 1.34Å [6]-1.52Å[4] with an average of 1.42Å; for complexed

arene rings this distance averages 1.39Å(1.3Å [4] to 1.44Å[5]). The distance

between iron atom and the center of gravity of arene rings vary from 1.52Å [6]

to 1.60Å while the distance to the Cp ring varies from 1.62Å [4] to 1.79Å for

the electroneutral hexamethylbenzene (Cp) iron complex [12].

The geometry of complexed arene ring (complexes type I and III) shows no

changes upon complexation with exception of interatomic carbon-carbon

distances.In the case of the cyclohexadienyl complexes of type IIb, which can

also be depicted as IIc, "zwitterionic", Johnson and Treichel [8,9] and Hamon,

Astruc et al. [11] determined the structures of deprotonated ligands to find

out which depiction is more precise. For the fluorenyl anion complexed by

(Cp) iron moiety, Johnson and Treichel found that carbon C10 (Fig. 2a) is

further from iron and shows a longer iron-carbon C10 bond length (2.316Å or

2.300Å for two independent crystals in unit) than for the other complexed ring

carbons (range 2.039Å to 2.152Å or 2.032Å to 2.175Å, respectively). The

dihedral angle between the planes of carbons 1,2,3,4,11 and carbons 11,10 and 9 is 11.0° or 10.1° . Distance C9-C13 is longer than C9-C10 by about 0.063Å. The data shows that neither limiting structure IIb nor IIc defines completely the bonding in the molecule, but on the basis of reactivity of the complex the authors have assumed it to be closer to the zwitterionic form (IIc).
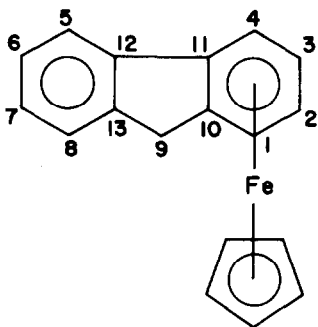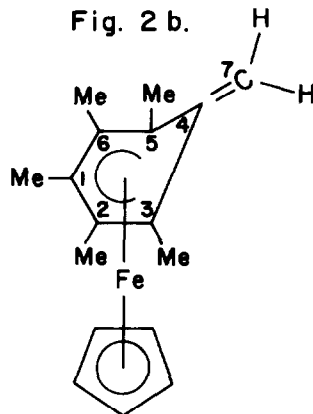
Fig. 2 a.

Fig. 2 b.

Hamon, Astruc et al. [11] who determined the structure of (pentamethylbenzyl) (Cp) iron complex, (Fig. 2b), found the dihedral angle between planes of carbons 1,2,3,5,6 and carbons 3,4,5 to be 32.6° -three times larger than in fluorenyl complex but below the range (39-50°) given for other cyclohexadienyl metal complexes [14]. The exocyclic carbon C7 is not exactly in the plane of carbon atoms C3,4 and 5 but is bent slightly upward by 10° and twisted in the plane of C7, H,H by 11° due to steric interaction with methyl groups. Bond C4-C7 is 1.376Å long -typical length of a double bond. Its ability to undergo nucleophilic substitution reaction, solubility in pentane and easy hydrogenation over Pd/C catalyst are considered as additional proofs of the cyclohexadienyl structure of the complex. Johnson and Treichel [9] found that fluorenyl complex gives only a 5% yield of hydrogenation product; but the fluorenyl structure is rigid and so the five membered ring posseses a restricted ability toward deformation from the plane.

Dications (type IV) usually have a structure in which the two Fe(Cp) moieties are trans [15-18]. Recently, Lee et al. [19] have reported the

synthesis of dications with the Fe(Cp) fragments _cis_ in case of bent heterocycles such as thianthrene and phenoxathiin. Assignment was initially based on the analysis of ^{1}H and ^{13}C NMR spectra.

The electronic structure of the arene-metal complexes has been reviewed recently [2a] therefore only major contributions are discussed here. INDO SCF-MO calculations were carried out for a number of d^6 sandwich complexes including (benzene) (Cp) iron cation and systems obtained therefrom by addition of one electron. Clack and Warren [20] postulated that the additional electron should be located on the ligand orbitals rather than on the metal and that the neutral complex is nearly equienergetic with its parent cation although less stable. Results obtained by Astruc, Ammeter et al. [21] by semiempirical calculations for (benzene) (Cp) iron and data extracted from Mössbauer and ^{1}H NMR spectra suggest that the additional electron enters metal orbitals giving d^7 configuration in contrast with the above calculations.

The unrestricted Hartree-Fock method has been used in the INDO approximation for calculations of the electronic structure of (arene) (Cp) iron cations, their derivatives and ferrocene analogs [22]. Unsymmetrical distribution of the cation charge density was found with the greater positive charge on the arene ring of the (arene)(Cp)iron complexes. INDO molecular orbital calculations for substituted cations (X-benzene) (Cp) iron have been done for nucleophilic addition reactions (and compared to calculations for free ligands) [23]. The results are in agreement with the proposals of Davies, Green and Mingos [2d] concerning the relationship between the site of attack and hapticity of arene ligand but no influence of the charge or LUMO on that site in complex has been found. The electronic structure of the electroneutral complexes (type III) has also been discussed by Nesmeyanov and coworkers [24,25] and by Astruc and coworkers [13,21,26,27] on the basis of EPR, Mössbauer and photoelectron spectra. Schmitt et al. [28] used Iterative Extended Huckel Model calculations of the energy contents, bond orders and

charge distribution to confirm the structure of $(\eta^6$-coronene) (Cp)iron PF_6 where the coordination of Fe(Cp) moiety was to the outer ring of the arene.

3. $(\eta^6$-Arene) $(\eta^5$-cyclopentadienyl) iron (II) cations and dications

3.1 Synthesis

The Ligand Exchange Reaction between ferrocene and arene in the presence of $AlCl_3$ and Al has remained the most exploited synthetic route for the preparation of (arene)(Cp)iron monocations and the only route leading to (arene)[(Cp)iron]$_2$ dications [1]. Various arenes - benzene and substituted benzenes [4,10,26,29-63,96-103], polycyclic arenes [8,9,28-30,52,53,55,64-70,76,77], cyclophanes [71-74], heterocycles -tetramethylthiophene [75], benzimidazole [29], heterocycles related to fluorene [16,29] or anthracene [16,19] have been employed in reactions with ferrocene, substituted ferrocenes [4,26,35,36,40-48,57,59,61], biferrocenyl (mono- and bis-arene) [67] and azaferrocene [79].

Influence of the reaction conditions in ligand exchange reaction, i.e. ratio of the substrates, temperature, solvent and the time of reaction on the yield of the products have been examined [30,66,68,70] but the most important factor enhancing the yield of the cations up to 90% in some case is the presence of water or concentrated HCl [77]. $HAlCl_4$ appears to be the active catalyst and the key step involves formation of the [(Cp)$_2$FeH] $AlCl_4$ which then undergoes exchange. Astruc et al. [37] have reported a one-pot synthesis of the acids $(\eta^5$-$C_5H_4CO_2H)Fe(\eta^6$-arene) BF_4 from ferrocene, $AlCl_3$, arene and CO_2 at atmospheric pressure. The reactions of carboxylation of Cp ring and ligand exchange are both induced by $AlCl_3$ and proceed successively. Roman et al. [46,47] obtained optically active (arene)(substituted Cp) iron cations from optically active substituted ferrocenes in ligand exchange reactions.

Ligand exchange reaction is accompanied by side reactions : dehalogenation [64-66] and hydrogenation [64-66,68-70] have been observed. Stereospecific

cis-hydrogenation of the 9 and 10 position in 9,10-dimethylanthracene occurred [65,66] and possible mechanisms of the hydrogenations observed for naphthalene, anthracene, phenanthrene, 9,10-dimethylanthracene, 9,10-dimethylphenanthrene and pyrene have been discussed [64-66, 68-70]. Coffield synthesis of (arene)(Cp) iron cations has been applied to the synthesis of species with permethylated Cp ring when ligand exchange reaction failed to give expected cations [10,26,43,48,78]. Guerchais and Astruc [80] have found that the reaction of $(C_5Me_5)Fe(CO)_2Br$ with anthracene in the presence of $AlCl_3$ gives the mixture of 9,10-dihydrogenated and 1,2,3,4-tetrahydrogenated monocations in the ratio 2:3 while with $(C_5Me_5)Fe(CO)_2Cl$ as a starting material 1,2,3,4-tetrahydrogenated cation was obtained exclusively.

Gill and Mann have developed a photochemically induced arene replacement reaction. Starting from (p-xylene)(Cp) iron cation they have synthesized a variety of complexes [81-83]. Using CH_3CN as a solvent they have shown that complex $[(CH_3CN)_3(Cp)Fe]$ PF_6, stable at low temperatures, could be an intermediate in reaction [83]. Generally, using p-xylene complex as a substrate complexes of ligands more basic than p-xylene can be obtained. This method has been applied successfully to the synthesis of cyclophane cations [71-74,85]. Hemberger and Dunbar [86] have reported gas-phase ligand exchange reaction between ferrocene and arenes, as a result of direct association of the arene molecule with cation $[(Cp)Fe]^+$ obtained from ferrocene by high energy ionization under low pressure conditions. They observed formation of nitrobenzene complex which has not been synthesized by ligand exchange reaction and also dechlorination of chlorobenzene leading to formation of (benzene)(Cp) iron cation.

Many complexes have been obtained by chemical modification of (arene)(Cp) iron cations and those reactions will be described later (section.3.3).

Ligand exchange reaction is so far the only synthetic route leading to synthesis of $(\eta^6, \eta^6$-arene)[(Cp)iron]$_2$ dications. Several dications derived from polycylic arenes, specifically anthracenes and phenanthrenes [65,67,69], pyrene [70], cyclophanes [71-74], heterocycles related to fluorene and anthracene [16,19] have been obtained. Formation of dication from monocation [1,19] have confirmed previously proposed stepwise mechanism of formation of dications via monocations. Dications of the type $(\eta^6$-arene)$_2$[(Cp)iron]$_2$ were formed in reactions of arenes with biferrocenyl [67] and diphenylmethane [29].

3.2 Spectroscopy and mass spectrometry

Electronic absorption spectra of the cations (I) and related electroneutral complexes (III) have been studied by Solodovnikov et al.[25,87]. For the cations they have found two to three absorption bands in visible region which they attributed to d – d transitions and one to three absorption bands in UV region attributed to $\pi - \pi$ transitions. Hamon et al. [26] studied the effect of permethylation of ligands (Cp and benzene) on the energy of orbital levels. They have found that permethylation of benzene ring affects energy of e_2 molecular orbitals more than the permethylation of Cp ring. A similar conclusion was based on the observation that QS value of the Mössbauer doublet increases upon permethylation of the benzene ring. Their studies also suggested that the assignment of $\pi - \pi$ transitions in electronic spectra should be reexamined Green et al. [27] registered spectra of a few cations and applied the data extracted from them to analysis of the photoelectron spectra of electroneutral and cyclohexadienyl analogues.

^{1}H and ^{13}C NMR spectra data appear in the literature as a part of characteristics of the synthesized complexes and recently published data confirm the general remarks on the changes in chemical shifts upon complexation given previously [1,51]. Clack and Warren [88] carried out the INDO SCF MO calculations for a number of sandwich and tricarbonyl metal complexes of arenes and found a good correlation between observed shifts of

protons in ^{1}H NMR spectra and calculated changes in electron density upon diminution of aromatic character of an arene ring complexed by a metal. Steele et al. [51] have done an extensive study of ^{13}C NMR spectra of (arene)(Cp)iron cations (I) comparing shifts of carbon atom signals of complexed arenes against those of free arenes, intensities of the signals observed, influence of (Metal) L_3 moiety on shifts and the origin and nature of the upfield shift. ^{13}C[^{57}Fe] double resonance NMR study of iron complexes including (benzene)(Cp)iron cation and related cyclohexadienyl complex have been used as proof of direct iron participation in the stabilization of α-ferrocenylcarbocations [89]. Analysis of ^{1}H NMR spectra [73] or ^{1}H and ^{13}C NMR spectra [74] helped in the determination of the structures of complexed metacyclophanes. Both ^{1}H and ^{13}C NMR spectra also indicated the formation of both cis- and trans- (η^6, η^6-arene)[(Cp)iron]$_2$ dications from phenoxathiin and thianthrene [19]. Mössbauer spectra of cations (1) were compared to spectra of related electroneutral complexes [26,76].

Field desorption mass spectrometry has been applied successfully for the investigaton of non-volatile (arene)(Cp)iron PF$_6$ salts [90], the base peak observed agrees with the molecular weight of cation.

3.3 Chemical properties of cations

The (arene)(Cp)iron cations are very reactive species. Examples of reactions involving each part of the complex, i.e. Cp ring and its substituents, iron atom, complexed arene ring and its substituents and exchange of the arene ring have been reported. The most striking difference between the free and complexed arene is the lack of electrophilic substitution reactions and very high susceptibility for nucleophilic attack. In the reviewed period no electrophilic substitution on (arene)(Cp)iron cation has been observed. Nesmeyanov et al. [76] have shown that in (diphenylmethane)(Cp)iron cation only the uncomplexed phenyl ring undergoes electrophilic substitution. Chemistry of (arene)[(Cp)iron]$_2$ dications (IV) has not been

much explored, so far only one reaction, the oxidation of fluorene to fluorenone dication [91] has been reported.

3.3.1. Nucleophilic addition

Nucleophilic addition to arene ring in arene-metal complexes has previously been reviewed [2b,c,d,e]. These papers give full details on stereospecificity, regioselectivity, competitive and subsequent reactions. Davies, Green and Mingos [2d] formulated simple rules to predict the most favourable site of attack based on the structure and hapticity of complexed ligand in kinetically controlled rections. In the case of (arene)(Cp)iron cations nucleophilic addition leads to formation of (cyclohexadienyl)(Cp)iron complexes; hydride [9,44,45,56,57,59,92-95] and carbanions [50,60,95] have been applied as nucleophiles (section 4.1). Attempts to add hydride or ethyl anion to (naphthalene)(Cp)iron(II) BF_4 resulted in one-electron reduction to electroneutral (naphtalene) (Cp)iron(I) instead of addition to the complexed ring [24]. (Cyclohexadienyl)(Cp)iron complexes also react as nucleophiles; (pentamethylbenzyl)(Cp)iron reacts with the chlorobenzene cation, exclusively ortho to chlorine [12,48] (scheme 1).

Scheme I.
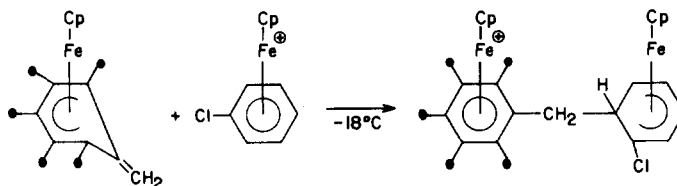
Addition of anions to arene complexes possesing a keto group gave different products from the cyclohexadienyl complexes. A carbonyl group in the substituent, bonded to arene or Cp ring, in position α to this ring undergoes addition more readily, than the complexed ring [44,45,91,96]; while in the case of carboxyalkyl group addition of anion to the arene ring occurs [56]. It has been found that addition of hydride or deuteride anions to complexed

fluorenone, anthraquinone, benzophenone [91] or xanthone [96] leads exclusively to formation of endo-alcohols. Similar results were found in addition of methide anion (from MeLi) to fluorenone or xanthone complex [96] or anions generated from acetonitrile, nitromethane and phenylacetylene, when formation of a C-C bond in the endo-alcohols was accomplished. Ylid Ph₃P=CHCO₂Et gave the mixture of E and Z isomers of esters [96] in reaction with fluorenone complex (scheme 2).

Scheme 2.
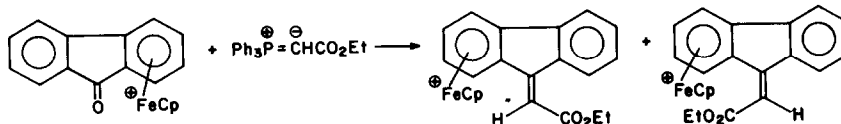
For the carbonyl group in (α-ketotetramethylene Cp)(arene)iron cations, addition of hydride to carbonyl group and to arene ring occurred simultaneously [45] (scheme 3).

Scheme 3.
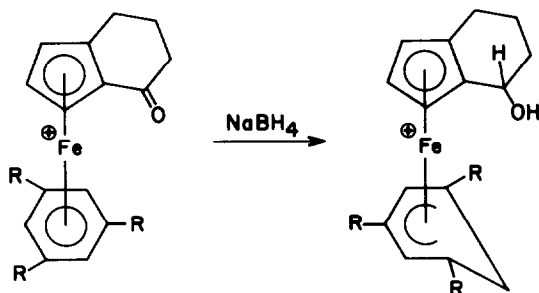
3.3.2. Nucleophilic substitution

Addition of a nucleophile is a key step in aromatic nucleophilic substitution reaction which occurs when the attacked aromatic ring has a good leaving group [2c]. In the period under review chlorine appeared to be the most used leaving group [33,34,58,62,63,97-102] although the aryloxy group was also utilised [96,103]. Kinetics of nucleophilic substitution of chlorine in (chlorobenzene)(Cp)iron PF₆ by piperidine [63] or methoxide [62] have been

studied. Litvak et al. established that the reaction is of first order for (PhCl)(Cp)iron PF$_6$ complex and second order in piperidine, which acts as a catalyst for elimination of hydrogen chloride from the intermediate σ complex. Furthermore, reaction of (R-C$_6$H$_4$-Cl)(Cp)iron PF$_6$ salts with sodium methoxide is of the second order and reaction rate constants increase in the order o-Me $\leqslant$ m-Me $\leqslant$ p-Me $\leqslant$ p-CO$_2$Na $\leqslant$ H. This does not correspond to the order for free arenes. Effects of the solvent and temperature of reactions were studied and energetic parameters reported. Kinetic study of reactions of haloarene complexes of Me(CO)$_3$ (Me = Cr, Mo, Mn$^+$) and [(Cp)iron]$^+$ with methoxide ion have been presented by Knipe et al. [58,97]. They established a readiness order of complexes undergoing S$_N$2Ar reaction as:

(CO)$_3$Cr $<$ (CO)$_3$Mo $\ll$ (Cp)Fe$^+$ $<$ (CO)$_3$Mn$^+$ when for complexed haloarenes is as: PhF $>$ PhCl $>$ MeC$_6$H$_4$Cl. The presence of NaClO$_4$ or LiCl retards reaction rates while addition of THF or dioxane to solvent (MeOH) accelerates them. They postulated formation of an ion-pair between the haloarene complex and methoxide anion, reducing the reactivity of complex, as a first step in reactions. Chlorine in chlorobenzene and chlorotoluene complexes has been replaced by various nucleophiles e.g.amines [34,98], azide [101,102], OH and SH anions [33,100], forming new amino, azido, hydroxy or mercaptobenzene complexes. (o-Dichlorobenzene)(Cp)iron complex undergoes a double S$_N$2Ar reaction, exchanging both chlorine atoms [99]. Such reactions with o-disubstituted benzenes lead to a synthesis of heterocycles related to anthracene (scheme 4). All of these reactions go smoothly under mild conditions.
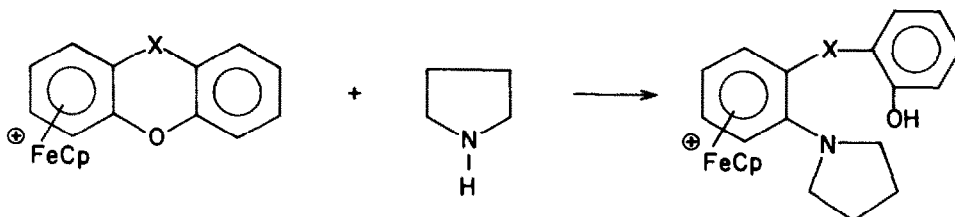
Scheme 4.
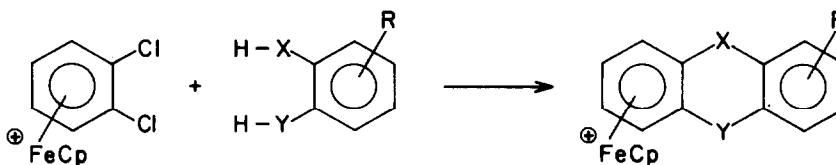
X,Y = (O; S; NH) ; R = (H; Me)

Pyrrolidine causes ring opening reaction of such heterocyclic complexes when oxygen is the heteroatom [96,103] (scheme 5).

Scheme 5.

X = direct bond; CH_2; CO; O; S;

Other nucleophiles such as amines and anions of acetonitrile and nitromethane react with the xanthone complex [96] to open the heterocycle ring yielding o,o'-disubstituted benzophenone complexes. Subsequent decomplexation reactions of modified complexes provide new synthetic routes to various aromatic compounds.

3.3.3. Deprotonation and subsequent reactions

The action of bases on complexes with -XH group (X = C,N,O,S), bonded to complexed benzene ring lead to formation of cyclohexadienyl complexes possessing exocyclic double bond (type IIb), also formulated as "zwitterionic" (IIc) (scheme 6).

Scheme 6.
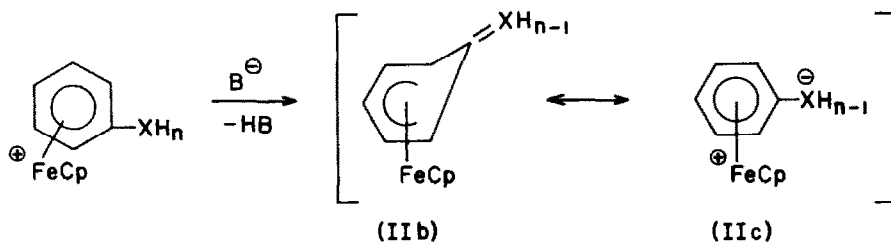
(II b)   (II c)

Many complexes (IIb — IIc) have been isolated and their reactivity is discussed (section 4.3). A number of papers deal with reactions of complexes (IIb — IIc) in situ - these reactions yield (Cp)iron cations with modified arene ligand. Deprotonation of alkyl or aralkyl substituted benzene (Cp) iron cations with base followed by addition of carbon electrophilic reagents lead

to formation of C-C bonds [8,9,10,52,53,104] (scheme 7).

Scheme 7.
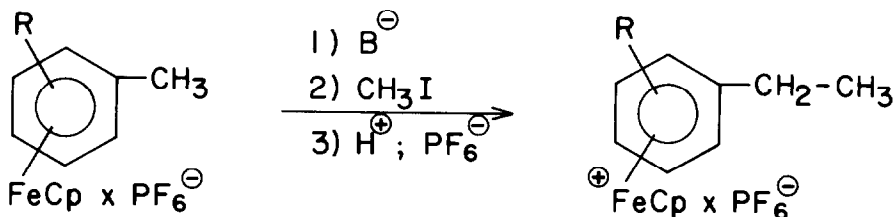
One-pot reactions of polymethylated benzene (n = 2,3,4,6) complex

$(C_6H_{6-n}Me_n)(Cp)$ iron lead to various alkyl or aralkylbenzene (Cp) iron

complexes [10]; excess of reagents in the case of n=6 gave hexasubstituted

products. For n=2 and 4, di- or tetraisopropylbenzene (C_5Me_5) iron complexes

were formed, while for n=3 (mesitylene), sym-tri(t-butylbenzene) (Cp) or

(C_5Me_5) iron cations were obtained. Attempts to alkylate cyclopentadienyl

methyl groups failed. A variety of organic halides, CO_2 and CS_2 have been

reacted with deprotonated alkyl, aralkyl, arenes, polycyclic arenes or

heterocyclic [52,53] ligands. Deprotonation of $-NH_2$ group (or NH) with

subsequent reaction with alkyl halides [33,35,53,54], acyl chlorides [39,54],

sulfonyl chloride [39], carbon dioxide or disulphide [54] lead to various

(N-substituted amino aryl)(Cp)iron complexes. Similarly, oxidation of

electroneutral (pentamethylaniline)(Cp)iron[I] complex (type III) followed by

reaction with carbon dioxide lead to analogous products [38]. Both protons

can be removed from NH_2 groups [33,54]. Deprotonation of -OH or -SH

substituents in benzene complex followed by methylation lead to methoxy- or

thiomethoxy benzene complexes [33] (scheme 8).

Scheme 8.

Y = OH; SH;   X = NH; O; S;   X' = O; S; NCH_3
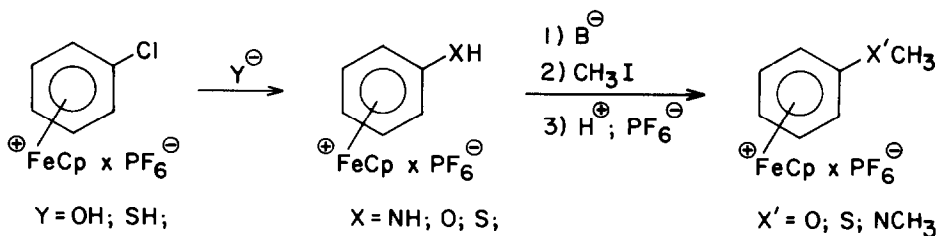
Formation of C-N bond was achieved by deprotonation of (ethylbenzene),
(diphenylmethane) or fluorene complexes followed by reaction with ethylnitrite
to give oximes [49];the oxime of benzophenone was transformed into the primary
amine by cathodic reduction on mercury.

3.3.4. Oxidation

Oxidation of side chain of complexed benzene ligands has been reviewed [1].
Since that time two reports dealing with oxidation of methylene groups bonded
to complexed ring in fluorene, diphenylmethane, 9,10-dihydroanthracene [91],
and in xanthene and thioxanthene [96], have appeared. This reaction leads to
complexes of ketones unavailable by ligand exchange reaction, the oxidation
was performed on the aqueous solution of the cation obtained in ligand
exchange reaction by $KMnO_4$ or in the case of fluorene complex [91] with
ethanolic KOH/air. Oxidation of 9,10-dihydroanthracene leads only to
anthraquinone complex, no anthrone complex was isolated. Oxidation of
thioxanthene [96] complex leads to formation of thioxanthone and corresponding
sulphone complexes. The ratio of ketone to ketosulphone depends on the amount
of $KMnO_4$, an excess of oxidant favors formation of the ketosulphone. Fluorene
dication formed the corresponding dication of fluorenone [91].

3.3.5. Arene ring contraction and expansion

Photolysis or thermolysis of (azidobenzene)(Cp)iron cation results in
formation of the (aniline)(Cp)iron complex and cyanoferrocene [101]
(scheme 9).

Scheme 9.
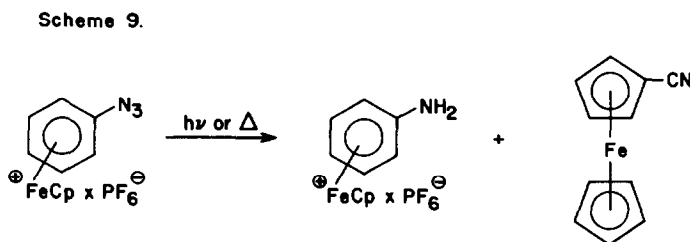
Photolysis experiments on o-,m-,p-azidotoluene complexes [102] gave

1-cyano-2-methylferrocene for ortho, a mixture (1:3) of 1-cyano-2-methyl and

1-cyano-3-methylferrocene for meta and 1-cyano-3-methylferrocene for para

complex. The reaction mechanism involves ready formation of complexed

phenylnitrene as an intermediate followed by ring contraction to give a useful

route to substituted cyanoferrocenes.

Expansion of benzene complexes to tropone complexes have been reported in

reactions of phenol or thiophenol complex with diazomethane [100].

3.3.6. Lability of arene ligands

Photochemically induced arene replacement reactions using the

(p-xylene)(Cp)iron cation have been described by Gill and Mann [81-84]. It was

observed that the arene ligand can be replaced by one-6-electron or three

2-electron donors (scheme 10).

Scheme 10.
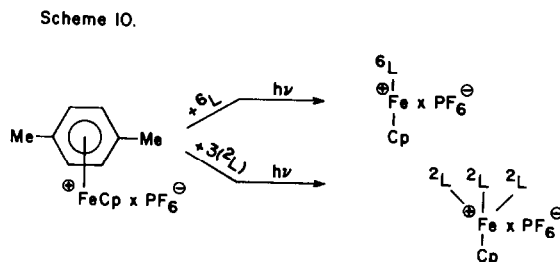
Hexamethylbenzene [81], (2.2)-paracyclophane, cycloheptatriene and

cyclooctatetraene [82] were 6-electron ligands in these reactions while

trialkyl or aryl phosphines, isocyanides and cyanides [81,82] or CO [81] have

been employed as 2-electron ligands. When acetonitrile was used as solvent in

the presence of phosphines, various mixed $(MeCN)_{3-n}(P)_n$ complexes were

obtained (P=phosphine ligand) [82,83]. Mechanism of reaction have been

studied [84]. In the case of MeCN as solvent formation of unstable

intermediate $(Cp)Fe(MeCN)_3 PF_6$ has been observed [83]. The reaction has been

employed to synthesize complexes of p- and m-cyclophanes [72-74,85]. Similar

substitution of arene ring by three 2-electron donors (phosphines) have been

accomplished thermally [98] and electrochemically [105]. Decomposition of

cationic complexes of type I aimed at liberation of modified arene ligand have been reported. NBS has been used as a reagent causing chemical decomposition allowing recovery of the free arene [50,60]. Pyrolytic sublimation [52,55,66,69,70,96] and photolysis [10,52,66,69] have been reported as efficient routes to generate free arenes from these complexes.

3.3.7. Chemical and electrochemical studies with or without change of iron oxidation state

One-electron reduction of cations I by Na/Hg lead to formation of electroneutral (arene)(Cp)iron(I) - type III complexes (scheme 11).
Scheme II.
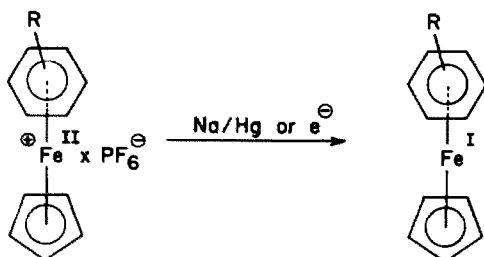
A number of studies have appeared recently on this reaction [13,24,38,94,106-111] and the chemistry of the electroneutral complexes (section 5). Electroneutral species also result when cation (I) reacts with base (t-BuOK) followed by treatment with sodium and Na/EtOH which involves the formation of anion-radicals as intermediates [109]. Studies on electrochemical reduction to electroneutral complexes (section 5) has also attracted attention [26,39,43,49,112,113]. In addition to qualitative data polarographic half-wave potentials in different media (range -1.40 to -1.70 V vs.SCE) were reported. Subsequent reactions observed after electroreduction are: decomposition to iron, dimerization to bis(cyclohexadienyl)complexes (type IIa), catalytic reduction of the medium [43,112] or compounds present in the reaction mixture [42]. Cathodic reduction on mercury transformed oxime to corresponding primary amine in the case of (benzophenone oxime)(Cp)iron cation [49]. Regio- and sterospecific electroreduction of carbonyl group in

(α-oxotetramethyleneCp)(arene)iron cation led to <u>endo</u>-alcohol while an open

chain α-keto groups bonded to Cp or arene ring gave aldehydes and next

alcohols or pinacols [44,45]. Conductivity measurements have been reported

for various anions pairing (p-xylene)(Cp)iron cation in different solvents

[84]. Cyclic voltammetric studies on cationic species were reported

[43,61,105,113] and one-electron reduction (reversible) discussed [43,61] in

terms of formation of electroneutral complexes. In the presence of

phosphines, electrochemically induced arene ligand replacement reaction (by

three 2-electron ligands) was reported [105]. Recently three reports appeared

on the investigation of complexes with higher and lower formal oxidation

states of iron in complexes I-III. Solodovnikov et al. [55] reported

oxidation of monocations (I) with various strong oxidizing systems; the

$SbCl_5$-CH_2Cl_2 system oxidized monocations at $-70°C$ to (arene)(Cp)iron(III)

dications which are isoelectronic with the ferricinium cation. They examined

the ESR spectra at $77°K$ extracting spectral parameters; on the basis of

observed splitting of the signals in ESR and NMR spectra for the

α-methylnaphtalene complex they reported the presence of both isomers of that

complex with (Cp)Fe(III) moiety complexing substituted or unsubstituted rings.

Polarographic reduction of (arene)(Cp)iron(II) cations (type I) revealed the

presence of two one-electron cathodic waves. Despite earlier reports on the

non-reversibility of the second one [112,114] recent reports [94,115] have

claimed that the second wave is reversible and this was attributed to the

unknown (arene)(Cp)iron anion (scheme 12).

Scheme 12.

cation   electroneutral   anion
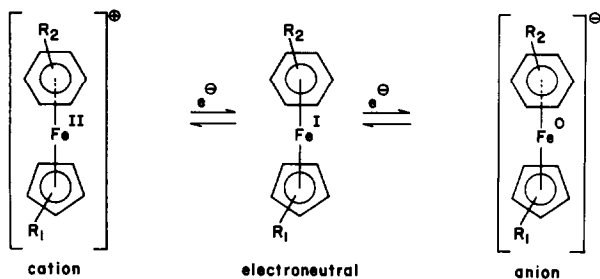
Such anions are unstable and Nesmeyanov et al. [94] proposed that they may be intermediates in the Na/Hg reduction of cations but react immediately with unreacted cation to give the observed electroneutral complex. El Murr [115] trapped anions by reaction with electrophilic reagents obtaining (cyclohexadienyl)(Cp)iron(II) complexes; the same product being obtained in reaction of electroneutral complexes III (after 1st-monoelectronic cathodic wave) with the same electrophilic reagents along with additionally starting cation. These (cyclohexadienyl)(Cp)iron(II) complexes are oxidized electrochemically to corresponding cations of (cyclohexadienyl)(Cp)iron(III), isoelectronic with ferricinium cations.

4. (η^5-Cyclohexadienyl)(η^5-cyclopentadienyl) iron (II) complexes

4.1. Synthesis

The method of synthesis of (cyclohexadienyl)(Cp)iron complex used depends on its structure. For complexes IIa (Fig.1), the most common method is the addition of nucleophile to a complexed arene ring. Many complexes have been obtained by addition of hydride [44,45,56,57,59,92-95] or carboanions [50,60] to benzene or substituted benzene rings. Other routes involve oxidation of electroneutral complexes (type III) by air or oxygen [12,38,48,54,104,108,116] dimerization of electroneutral complexes [12,13,26,106,107,117,118] during the reduction of cations (type I) with Na/Hg [94,107] and the dimerization of radicals obtained during the electroreduction of cations in various media [43,94,112]. Synthesis of cyclohexadienyl complexes (type IIa) were achieved during high vacuum, low temperature co-condensation of iron atoms and arenes followed by addition of cyclopentadiene [119,120]. Complexes bearing -XH$_n$ group bounded to complexed arene ring deprotonate easily (X = C,N,O,S) giving species which can be described as possessing exocyclic double bond C=X (structure IIb) or "zwitterionic" structure IIc (section 2). Deprotonation studies of complexes with X=carbon [8,9,10,13,29,48,49,52,53,104,109],

nitrogen [29,33,38,39,53,54], oxygen or sulphur [33] have been reported.

Proton abstraction has been achieved by potassium peroxide, potassium

t-butoxide, sodium amide, cyanomethylsodium, bis(trimethylsilyl)amide or

potassium carbonate as a base. Hydride addition to (methyl benzoate)(Cp)iron

cation has been studied by McGreer and Watts [56]; it was observed that the

ortho position is preferred site of addition. Similar studies on addition of

$[CH(CH_3)CN]^-$ anion to (spiroindenepyran)(Cp)iron cation (scheme 13) gave the

following ratio of isomeric products in 49% overall yield:

Scheme 13

pos. 4 – 43%
pos. 5 – 14%
pos. 6 – 41%
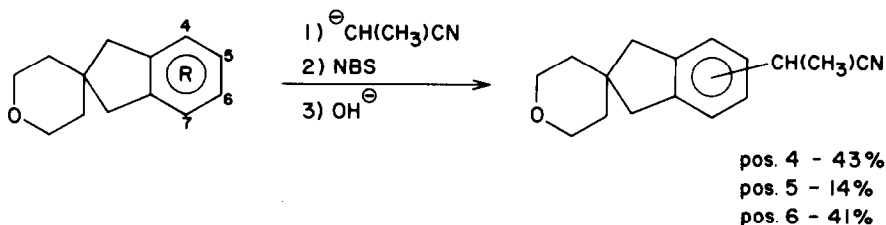
The (exo-R-cyclohexadienyl)(Cp)iron complexes (R-isobutyronitrile or

pinacolone) were obtained by addition of isobutyronitrile or pinacolone anions

to (benzene)(Cp)iron cation [60].

4.2. Spectroscopy

Visible spectra of dimeric compounds IIa were reported by Solodovnikov et

al. [87] and the visible spectra of cyclohexadienyl complexes bearing

exocyclic double bond (type IIb) have also been studied [109]. They

interpreted an intense band ($\epsilon \approx 104, \lambda = 345-375$ nm) and number of weaker bands

in range 400–600 nm as absorption due to d – d rather than $\pi - \pi$ transition

(compare ref. [1]). Studies by Astruc et al. [48] suggested that d – d

transitions in visible and near UV regions are strongly perturbed by the

exocyclic double bond. Photoelectron spectra of cyclohexadienyl complexes

types IIa and IIb-IIc have been investigated by Green et al. [27] who proposed

an MO diagram for those complexes and gave the values of ionisation energies

and ligand field parameters. Nesmeyanov et al. [92] have discussed the IR

spectra of cyclohexadienyl complexes.

^{1}H and ^{13}C NMR data are usually given as a part of the characteristics of complexes. Proton spectra of complexes IIb – IIc show upfield shift for Cp protons signals (ca 0.5 ppm) and cyclohexadienyl protons (0.5 – 1.0 ppm), compared to the starting cations. Protons bonded to exocyclic carbon appéar in range 5–6 ppm (vinylic) for type IIb and for type IIa in the aliphatic range 1.2 – 3.0 ppm. Carbon-13 spectra show significant upfield shift of the exocyclic carbon atom signal (type IIb – IIc)as do the quaternary carbons in complexed rings. Koridze et al. [89,93] discussed the ^{13}C spectra of cyclohexadienyl complexes of type IIa, enriched in [57]Fe while Nesmeyanov et al. [92] compared ^{13}C spectra of cyclohexadienyl rings complexed by Fe(Cp) and Fe(CO)$_3$ moieties.

4.3. Reactivity

The (cyclohexadienyl)(Cp)iron complexes (II) are very reactive species and many reports on their reactivity appeared recently. Complexes type IIa bearing hydroxyalkyl substituent on either Cp or cyclohexadienyl ring treated with CF_3CO_2H undergo hydride transfer connected with loss of the hydroxy group [57,59]. Examples of reactions causing reoxidation to the cation have been observed with trityl cation [9,44,45,48,106,112],acids [9,116], NBS [50,60,94,107,118], O$_2$ [106,107,109,117,118], or I$_2$ [38,109,117,118] while excess of NBS [50,60] or Ce(IV) [60] decompose the complexes with liberation of the arene. The pyrolysis of cyclohexadienyl complexes [106,116,118] leads to formation of ferrocene and arene. Reactivity of complexes type IIa have been examined for dimers of cyclohexadienyl [118], phenylcyclohexadienyl [106], chlorocyclohexadienyl [107] and the dimeric peroxide of cyclohexadienyl [116]. The first and the last of these react with organic halides [116,118] or acetone [116] giving mono- or dimeric (acetone) cyclohexadienyl complexes with exo – R substituent. LAH reduction of the peroxide also gives cyclohexadienyl complex [116]. The peroxide reacts with water, ethanol and acids at room temperature evolving oxygen with formation of the cation [116].

With acids at -78°C oxygen, peroxide and cation is formed [116]. Thiophenol, benzoyl chloride and carbon tetrachloride transform peroxide to cation related with partial decomposition [116]. Reactivity of complexes of type IIb or IIc attracted more interest and their reactions with electrophiles have been extensively studied. Complexes IIb or IIc have been generated in situ from cations (I) by action of bases on alkyl - or aralkyl benzenes [10,49,52,53,104], aminobenzenes [33,39], toluidines [54], heterocycles [53], phenol and thiophenol [33] complexed by (Cp) Fe(II) moiety. Complexes of the type IIb - IIc were isolated by the action of oxygen on electroneutral $(C_6 (CH_3)_5 NH_2)$ (Cp)iron(I) [38], (n-alkylbenzene) (Cp)iron(I) [12,13,48,104,108] or by action of bases on alkylbenzene complexes [48,104] (scheme 14).

Scheme 14.
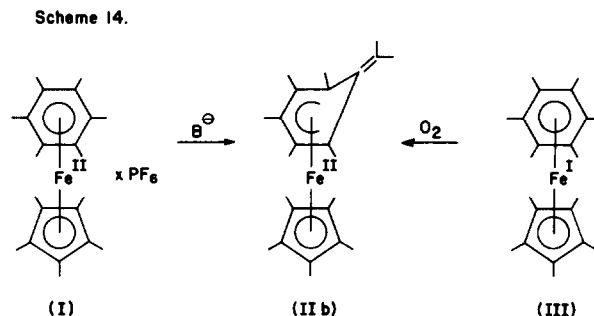
These complexes react with various electrophiles to form: C-C bonds [9,10,12,13,48,52,53,104,108], C-N bonds [49], O-C and S-C bonds [33], N-C bonds [33,38,39,53,54], C-Si and C-P bonds [12,48]. Astruc & coworkers [12,48] also reported the nucleophilic addition of IIb to the chlorobenzene cation, dimerization in the presence of I_2 leading to 1,2-diphenylethane dication, formation of complex with TCNQ and reactions with metal carbonyls (scheme 15).

Lee et al. [54] have shown that when both carbon and nitrogen are present, deprotonation occurs exclusively on nitrogen. Permethylation of the arene ring stablize the complexes type IIb - IIc [10,48]. Reactions of IIb with RX (halogens) in the presence of excess of the base lead to polyalkylated

Scheme 15.
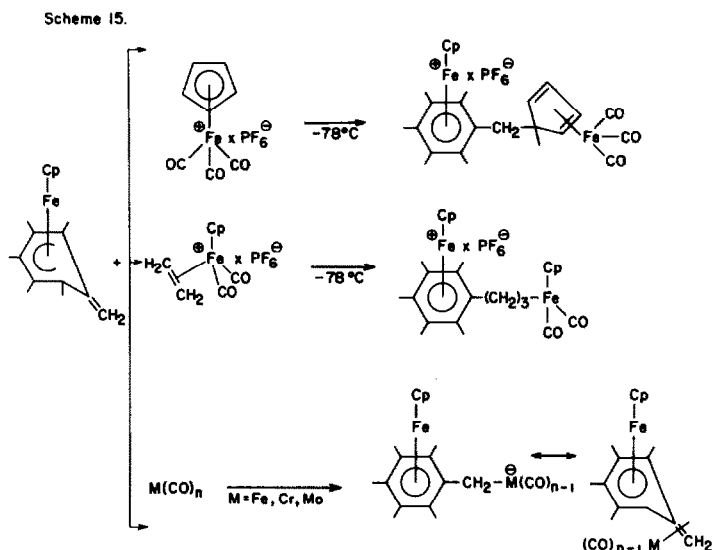
products [10,33] (also observed for reactions with CO_2 of CS_2 [53,54]); in the case of hindered alkylbenzenes (C_6Me_6) only monoalkylation takes place while $C_6H_3Me_4$ or $C_6H_4Me_2$ give bisalkylated or trisalkylated products [10]; with $(C_5Me_5)Fe(C_6Me_6)PF_6$ rings alkylaton of both Cp and benzene rings were observed; this was not observed for $(C_5Me_5)Fe(C_6H_6)PF_6$ [10]. Compounds IIb can be hydrogenated easily in the presence of Pd/C catalyst [12,48,78] giving cyclohexadienyl complex IIa, the fluorenyl complex (type IIc) gives only 5% of hydrogenation product [9]. Reaction of complexes (IIc — IIb) type with sodium ammalgam leads to electroneutral (arene)(Cp)iron(I) complexes [109].

5. (η^6-Arene) (η^5-Cyclopentadienyl) iron (I) complexes

5.1.Synthesis

The simplest route to the electroneutral (type III) complexes is Na/Hg reduction of the cations (I) and it has been used frequently [13,24,26,27,38,48,94,106-108,118]. Complexes (III) are available also by electroreduction of complexes (I) [43,94,112,113,115], hydrogenation of cyclohexadienyl complexes (IIc) (first step; second leads to complex type IIa)

[78] and addition of hydride from LAH to cations (I) (only at -60°C; at room temperature addition leads to cyclohexadienyl complex IIa) [95]. Electroneutral complexes are very unstable and in many cases their dimerization products are formed. Permethylation of the arene ring stabilizes electroneutral complex while permethylation of Cp ring leads to dimerizaton [26,43,48,112].

5.2. Spectroscopy

Electronic spectra of electroneutral complexes (III) have been examined [25,26,87]. Nesmeyanov et al. found that d-d bands transitions are shifted to longer wavelengths compared to these bands in related cations (I). Hamon et al. [26] examined the spectra of permethylated species and found that the broad, low intensity band in range 700 nm (corresponding to dark green colour of the d^7 complexes) should be attributed to spin-forbidden metal $\longrightarrow$ ligand $e^*_1 \longrightarrow e^*_2$ (arene) transition. Green et al. [27] have examined photoelectron spectra of some d^7 electroneutral complexes, and gave ligand field parameters for them. They established the first ionizaton energies, which were very low and close to those of heavier alkali metals. This could explain the extreme reactivity of d^7 complexes. IR spectrum of (benzene)(Cp) iron complex has been examined and data for frequencies of non-planar C-H vibrations of both arene and Cp ring given [110]. MS spectra of d^7 complexes have been used to confirm the structure of these complexes and the presence of the molecular peak of ferrocene was observed in all spectra [111]. Mössbauer spectroscopy provide the best way of investigating the structure of d^7 complexes (III) [13,26,48,121]. The parameters observed differ considerably from those found for related cations (I - IS = 0.3; QS = 1.5 mm/s; d^7 = III - IS = 0.73 - 0.75; QS = 0.5 - 0.6 mm/s) and are temperature dependent. Hamon et al. estimated 65-75% of metal character for the antibonding HOMO e^*_{1g} orbital occupied by the 19th electron [13,26]. This technique has also been applied to control the aerobic oxidation of (Cp) Fe(I) (C_6H_6) in the solid state [48]. EPR

spectra of electroneutral complexes (III) have been studied extensively [13,21,24,26,109,110,122] and parameters (g in range 2.01 - 1.30) for number of d^7 complexes given. Dynamic Jahn-Teller effect have been examined [13,21,122] because of observed degeneration of electronic ground state in d^7 complexes. A detailed examination of results by Rajasekharan et al. [21] questioned data reported earlier and suggested that the 19th electron is placed in metal orbitals. Magnetic susceptibility and paramagnetic NMR have also been employed for investigation of the structure of d^7 complexes [26].

5.3. Chemical properties

Electroneutral complexes (III) exhibit extreme reactivity both in solution and in the solid state. Dimerization of III leads to bis(cyclohexadienyl) complexes (IIa) [12,13,26,106,107,117,118]; similar products were observed by reaction of air or oxygen with them [12,38,48,54,104,108,116] but if no benzylic protons are available oxidative dimerizaton leads to dimeric peroxides of (IIa) [108,116]. Action of oxygen on (III) in the presence of $NaBF_4$ or $NH_4 PF_6$ and H_2O leads to cationic complexes (I) [12,13,24,26,38,48,78,104,106,108,110,111]. The same reaction was observed with I_2 [24,110,111] or Ph_3CCl [110]. In the absence of $NaBF_4$ or $NH_4 PF_6$ and water, oxygen transforms electroneutral complexes into cyclohexadienyl complexes bearing exocyclic double bond with carbon [12,13,48,78,104,108] or nitrogen [38] and the formation of H_2O_2. All neutral complexes decompose; ferrocene and arene were found amongst the decomposition products [24]. Alkylation of arene ring was found to increase stability while alkylation of the Cp ring destabilizes electroneutral complexes [13,26]. Water, methanol,acids, thiophenol and acetylacetone convert electroneutral complexes into corresponding cations (I) with H_2 evolution [111,123]. Arene ligand in electroneutral complex can be replaced by other two- or six-electron donors [106]. Complexes (III) were found to be intermediates in two-step reduction of cations (I) to cyclohexadienyl complexes (IIa) by LAH [95] and by H_2 on

Pd/C catalyst [78]. Polarograpic studies [43,113] have been described; processes accompanying electroreduction of cations (I) to neutral complexes (III) and influences of structural factors on stability of complexes (III) have been studied [112].

6. Applications of complexes

The chemistry of (arene) (Cp) iron (II) salts and related cyclohexadienyl and electroneutral complexes including transformations between those groups is rich and varied. Both methods of synthesis and liberation of complexed arene ligand have been established. Synthesis of arenes otherwise difficult to prepare - for example, so far unknown 2-methylthianthrene [99], o,o'-disubstituted benzophenones [96], cis-9,10-dihydro-9,10-dimethyl - anthracene [65,66], multialkyl or multiaralkyl benzenes [10], partially hydrogenated polycyclic aromatics [66,70,80] have been achieved by modification of complexed arenes in reactions which do not occur in the free arene.

In another application the (arene) (Cp) iron cation has been used as a catalyst for the electroreduction of nitrate ion to ammonia in solution [42]. Neutral complexes have been proposed as a modelic "electron" or "hydrogen reservoirs" for biological systems interacting with oxygen anion radicals. Initial reports on the applications of these compounds for environmental studies have appeared. Crude oil samples from spillage in delta areas in Nigeria have been analyzed for evaluation of types of aromatics present in oil. Aromatic compounds were complexed by (Cp) iron moiety and analyzed by TLC technique [31,32].

7. Acknowledgment

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