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CONTRIBUTION TO THE STUDY OF METALLOCENES

XXIV *. ON THE MECHANISM OF LIGAND EXCHANGE AND COMPLEXATION BY ALUMINIUM CHLORIDE OF FERROCENE AND ITS ALKYLATED AND ACYLATED DERIVATIVES

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Summary

A mechanism of ligand exchange between ferrocene and arenes catalysed by $AlCl_3$ is presented. It is shown how the attacking sites of $AlCl_3$ depend on the electronic effect of substituents on the ferrocene rings. In ferrocene and its alkyl derivatives, two types of complexation occur and compete with each other: complexation of a ring reversibly leads to cleavage; irreversible complexation of the metal, possible only in the absence of electron-withdrawing substituents, inhibits metal—ligand cleavage.

Introduction

In spite of the great number of reports concerning electrophilic reactions on ferrocene and its derivatives [1], the site of electrophilic attack is still the subject of much controversy [2—9]. An example is the cleavage reaction of ferrocene by $AlCl_3$, for which no mechanistic study has been reported [10—12]. The possibility of trapping the intermediate $[(\pi\text{-}C_5H_5)Fe]^+$ by an arene molecule, first reported by Nesmeyanov et al. [13] and then extended [14—22] leads to the $[(\pi\text{-}C_5H_5)(\pi\text{-arene})Fe]^+$ cation. The remarkable stability of these cations allows the easy determination of the amount of cleaved ferrocene derivatives. However, we have shown that the nature of the ligand exchange reactions between ferrocene and arene derivatives depends to a large extent on the substituents of the ferrocene rings [23]. For instance, with symmetrically hetero-disubstituted ferrocenes, refluxing in mesitylene results in exchange of either one or two

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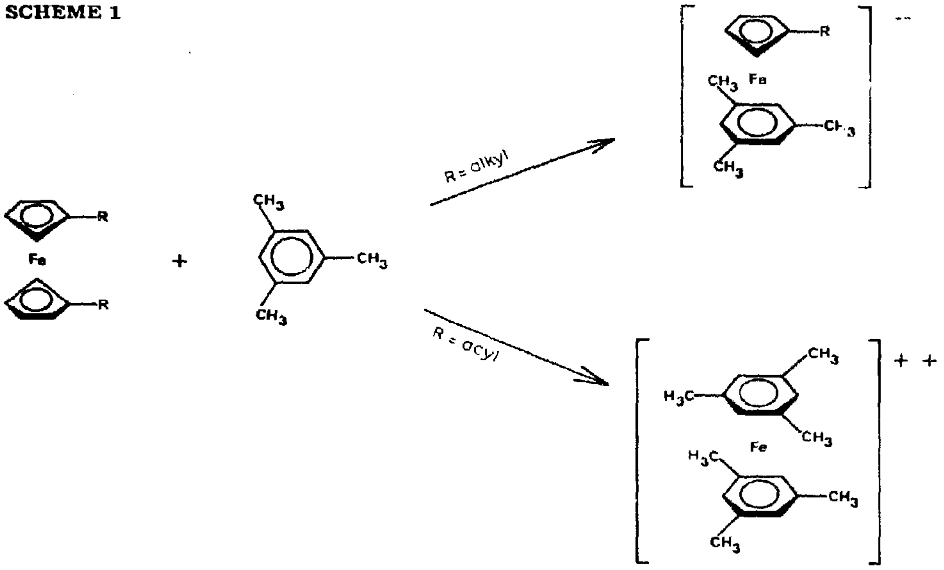
* For part XXIII see ref. 24.

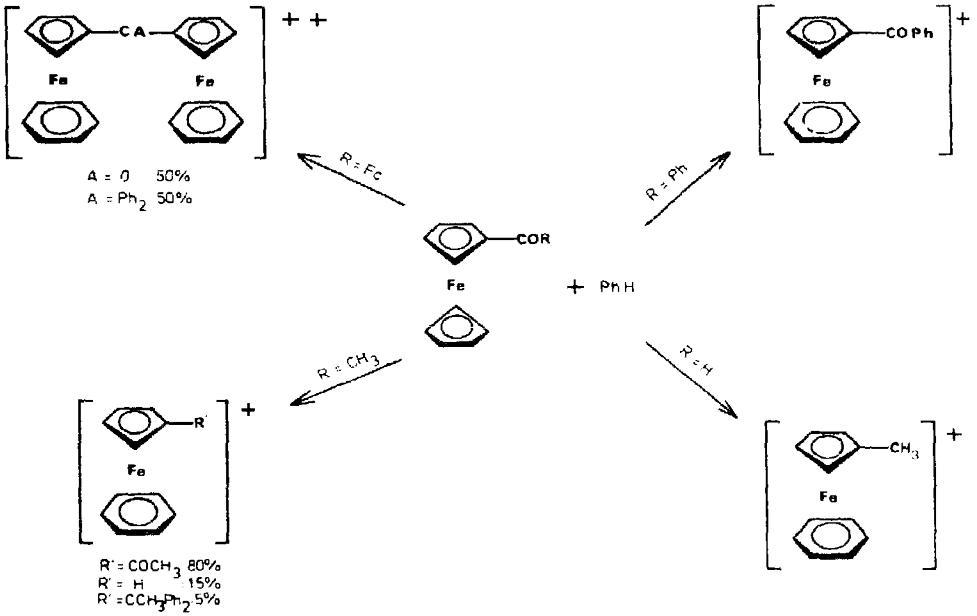
rings, depending on whether the substituents are alkyl or acyl groups (Scheme 1).

SCHEME 1



However if benzene is used, 1,1′-diacylferrocenes do not react at all, while 1,1′-dialkylferrocenes react in the same manner as in mesitylene (only one ring exchange [21]). Remarkably, monoacyl ferrocenes are much more reactive than 1,1′-diacylferrocenes or 1,1′-dialkylferrocenes in benzene at 80°C [21]). Generally selective and quantitative exchange of the unsubstituted ring is observed [24] (Scheme 2).

SCHEME 2



Taking into account the substituent effects described above and the results reported in our earlier publications [21,22,24] it is possible to suggest a mechanism for these reactions.

Results and discussion *

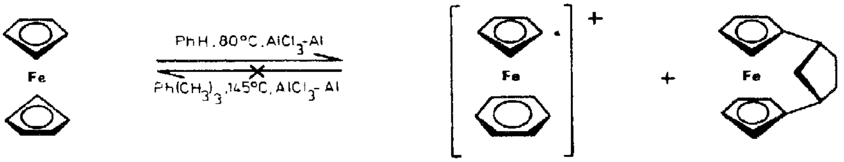
The ligand exchange reactions are not quantitative

Whatever be the temperature and the arene used, a large amount of the starting material is always recovered after hydrolysis of the reaction mixture (50% after 5 h of reaction in benzene at 80°C and 20% after the same time of reaction in mesitylene at 145°C). However, before hydrolysis, the arene solution does not contain any ferrocene, even though ferrocene is very soluble in benzene and mesitylene (the viscous oil also obtained does not contain free ferrocene, but consists only of the $AlCl_3$ complex of ferrocene and the product of ring exchange).

Irreversibility

The cleaved cyclopentadienyl rings protonate and act as electrophiles in the Friedel—Crafts alkylation of the alkyl ferrocenes and arenes [25,26]. The resulting products are present in the organic layer after hydrolysis, while the organometallic cations are in the aqueous layer. The irreversibility of the reaction may be demonstrated by the fact that the two main products yield no ferrocene when heated together under the exchange conditions (145°C, 5 h, mesitylene, $AlCl_3$, Al) (Scheme 3).

SCHEME 3



Reaction of ferrocene with $AlCl_3$ in the absence of arene

The presence of arene is not necessary for ring cleavage of ferrocene derivatives to occur [26—32]. The reaction of ferrocene with $AlCl_3$ in refluxing heptane leads to the same ferrocenophanes as were obtained in the presence of arenes [21,33]: 1,1'-cyclopentyleneferrocene (20%) and the bis(1,1')(3,3')cyclopentyleneferrocenes (1%). As in the presence of arene, part of the starting ferrocene is recovered after hydrolysis. Before hydrolysis, the upper heptane layer is colorless, thus demonstrating the complexation of ferrocene and the alkylferrocene derivatives formed in the reaction.

Formation of ferrocenophanes

The transformation of the cleaved cyclopentadienyl rings into the C_5H_8 cyclopentylene group requires three protons; however, the stoichiometry of the reaction can provide only two. According to Goldberg [34], the source of the mis-

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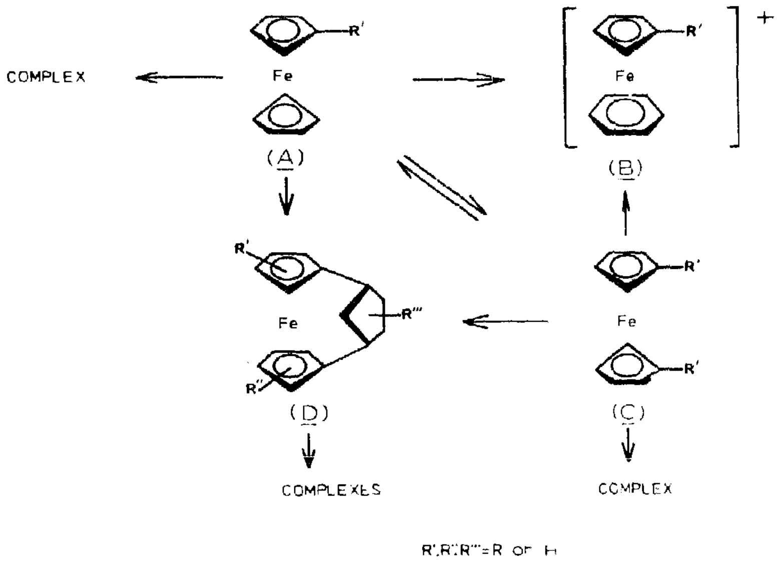
* The problem of cleavage of acylated rings in mono- and 1,1'-diacylferrocenes is discussed in ref. 24.

sing proton is traces of water present in the medium. However, after eliminating traces of water very carefully, we observed no diminution in yield of products containing cyclopentylene bridges. Similarly, if D_2O is added at the start of the reaction with benzene in the ratio 1 mol D_2O : 1 mol ferrocene : 3 mol $AlCl_3$, the mass spectrum of the principal product formed 1,1′-cyclopentyleneferrocene) shows only 50% of the product to contain an atom of deuterium. If the reaction is carried out in C_6D_6, an identical result is obtained. Finally, it can be shown that not the hydrolysis stage explains the source of the proton. The mass spectrum of 1,1′-cyclopentyleneferrocene obtained from a reaction hydrolysed with D_2O shows that the compound does not contain any deuterium in the bridging ring. These experiments show that the proton missing from the reaction stoichiometry arises not only from traces of water, but also from the arene.

Alkyl substitution of a ring

Alkyl substitution does not modify the nature of the ligand exchange [21]. In general, the substituted ring is a little more reactive with respect to exchange than is the unsubstituted ring [14,21]. Bublitz has shown that, in refluxing CH_2Cl_2, alkylferrocenes undergo a reversible disproportionation into ferrocene and the corresponding 1,1′-dialkylferrocene [35]. We have also observed this result under the experimental conditions necessary for the formation of $[(\pi\text{-}C_5H_4R)(\pi\text{-arene})Fe]^+$ cations. The cleaved rings may also recombine with the alkylferrocenes (Scheme 4, Table 1).

SCHEME 4



These results show that if the reaction is totally irreversible, the first stage i.e., the cleavage of the cyclopentadienyl ring, is reversible. In the absence of arene, the reaction follows a similar course to give ferrocene (8%), 1,1′-diethylferrocene (8%) and 1,1′-cyclopentylenealkylferrocene derivatives (30%), while some ethylferrocene (15%) is recovered.

TABLE 1

YIELDS (%) IN REACTION PRODUCTS STARTING FROM FcR

FcR, R	A	B	C	D
H [21]	50	20	—	15
Me	15	30	15	20
Et	15	30	15	20
CH_2Ph [22]	20	22	15	20

Complexation of ferrocene derivatives by $AlCl_3$

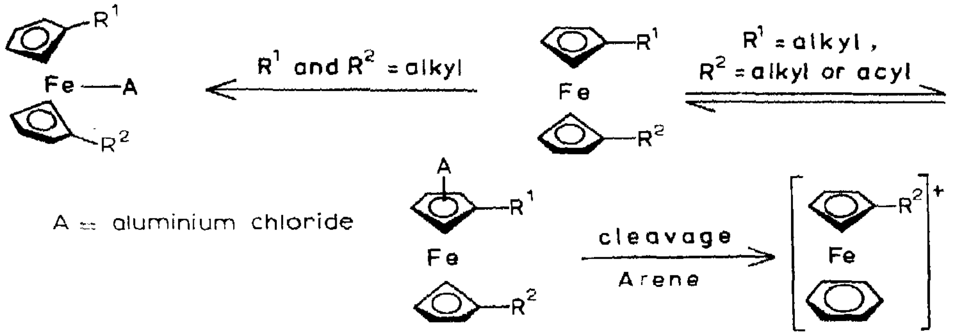
Cleavage of ferrocene derivatives by $AlCl_3$ has been observed under a variety of conditions [25—38], notably in the absence of arene. The presence of complexed ferrocene and alkylferrocenes before hydrolysis in inert solvents (heptane as well as aromatic solvents) shows that $AlCl_3$ must be responsible for the complexation. A charge-transfer complexation between ferrocene and the $[(\pi\text{-}C_5H_5)(\pi\text{-}C_6H_6)Fe]^+$ cation cannot be excluded, since such complexes between ferrocene and the $[(\pi\text{-arene})_2Fe]^{2+}$ cation are known [39]. However, this type of reversible complexation does not modify the general mechanism, and is excluded in any case for those reactions carried out in the absence of arene.

Thus $AlCl_3$ takes part in the reaction in two ways: cleavage of ferrocene and complexation of ferrocene and its alkyl derivatives. This latter complexation does not lead to cleavage, since no increase in the yield of cleavage products is noted after long reaction periods. The irreversibility of the ligand exchange and recombination of the cleaved rings shows that the ferrocene derivatives obtained after hydrolysis were complexed differently in respect of those which underwent cleavage. Two types of complexation of alkylferrocenes by $AlCl_3$ may thus be envisaged: one which enhances ligand exchange and another which inhibits it. In support of this hypothesis, it may be noted that 2 mol of $AlCl_3$ per mol of ferrocene are necessary to obtain maximum yield.

The comparison of the degrees of cleavage which we have observed with ferrocene (20%), monoacetylferrocene (100%) and 1,1′-diacetylferrocene (0%) at 80°C are particularly interesting with respect to the determination of the site(s) of attack by $AlCl_3$. The only explanation for the great difference in reactivity between the mono- and di-acetyl derivatives is that cleavage occurs via an intermediate involving complexation of the non-acylated ring. The insensitivity of the metal to electrophilic attack (in contrast to ferrocene, acetylferrocene is stable to air in solution in the presence of excess $AlCl_3$) and the quantitative yield of the product of ligand exchange in the case of monoacetylferrocene shows that inhibition of the ligand exchange reaction in the case of ferrocene is due to complexation of the metal. Similarly, inhibition of acylation of ferrocene was suggested by Rosenblum et al. to be due to protonation of the metal by $HAlCl_4$ [4,9,41]. Our reaction conditions are quite different from those used for the acylation and it is difficult to determine in what form the $AlCl_3$ acts as a complexing agent. It may be in the form of a Lewis acid, or in a protonated form, with the reaction medium acting as a source of protons. Finally, from an energetic point of view, it would appear to us that complexation of the ferrocene ring is more likely to lead to destabilisation of the metal—ligand bond than is complexation to the metal. The former type of complexation will result in significant diminution of electron density in the iron—ring bond, while in contrast the latter type of complexation will require the use of the 3*d* metal non-bonding orbitals and consequently, little perturbation of the energy of the molecule will occur, even if the cyclopentadienyl rings are now found at a significant angle to one another: according to Dahl and Ballhausen [40], the two rings may form an angle of 45° or less, without the loss of a significant amount of energy in the metal—ligand bonds.

The complexation of ferrocene by $AlCl_3$ may thus be represented as in Scheme 5.

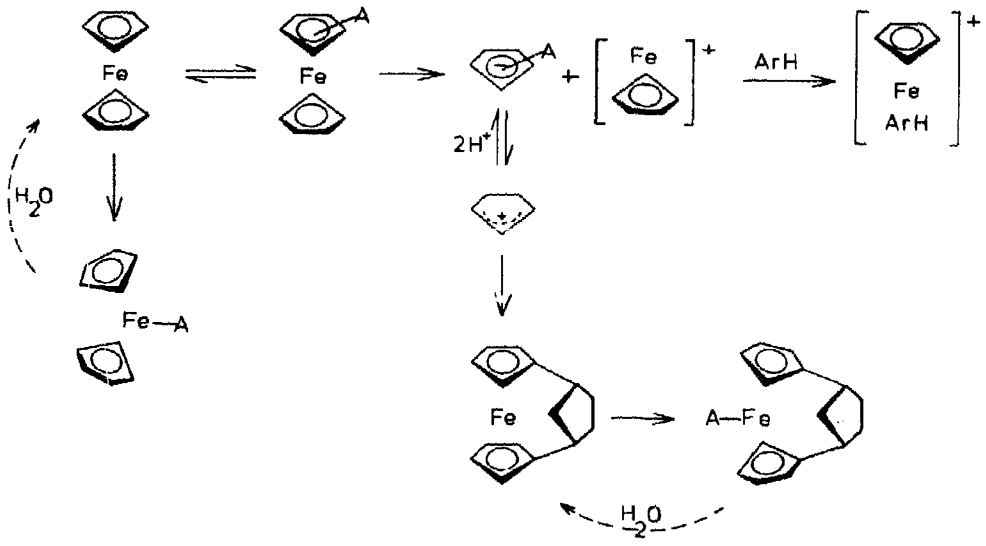
SCHEME 5



Since the formation of $[(\pi\text{-}C_5H_5)(\pi\text{-}C_6H_6)Fe]^+$ and of ferrocenophane is irreversible, complexation of ferrocene derivatives by $AlCl_3$ at the iron atom must also be irreversible. The observation that the presence of electron-donating methyl groups on the arene increases the yield of salt for the same reaction temperature [20,21] confirms the existence of a competition between the two types of $AlCl_3$ complexation.

The general mechanism of the exchange reaction between ferrocene and arenes can be represented as in Scheme 6.

SCHEME 6



Experimental

IR spectra were recorded using a Beckman IR 33 spectrophotometer. NMR spectra were recorded on a Varian EM 360 spectrometer, while mass spectra were obtained on a Varian MAT 311 instrument at the Regional Centre for Physical Measurements (Rennes). All new compounds gave correct analyses for C and H. References relative to the preparation of known ferrocene derivatives may be found in Organic Syntheses (Vol. 2). Benzene was dried and distilled from sodium under an inert atmosphere just before use. The methods used for the ligand exchange reactions are described in ref. 13, 21 and 24. The reactions were conducted under an atmosphere of nitrogen or argon dried with calcium chloride, Mesitylene, aluminium powder, and aluminium chloride were used as purchased.

Analytical chromatography was performed using thin layer silica gel plates (0.3 mm). Preparative chromatography was performed using silicic acid columns or thick layer silica gel plates (1 mm). Previously dried and distilled hexane was used as eluant.

Examination of the reaction medium before and after hydrolysis

(a) Reactions in the presence of arene. At the end of the reaction, the reaction mixture is cooled to 0° C and the red-brown arene layer is decanted off. Thin layer chromatography of this solution does not reveal the presence of any ferrocene derivative. The $AlCl_3$/arene charge-transfer complex is destroyed by hydrolysis, resulting in arene and aqueous layers which are both uncoloured. Extraction with pentane of the oily residue remaining after decantation does not remove any ferrocene derivative. After hydrolysis of this residue with ice-water, the resulting green aqueous phase may be shown to contain aluminium chloride and organometallic salts [21]. The organic phase, washed with sodium bicarbonate and water and dried with $MgSO_4$, contains alkylferrocene derivatives, which may be detected using thin layer chromatography and separated using column chromatography followed by thick layer chromatography on silica gel plates [21].

(b) Reaction in the absence of arene (heptane). The same method is used when the aromatic solvent is replaced by heptane [22]. The heptane solution decanted at the end of the reaction is colourless. The residue remaining after decantation is analysed in the same fashion and gives similar results to those observed in the presence of arene. The 1,1'-cyclopentyleneferrocene and the mixture of bis-(1,1')(3,3')cyclopentyleneferrocenes were identified using authentic specimens [21] by comparison of the chromatographic retention times (hexane solvent), melting point (for 1,1'-cyclopentyleneferrocene only), and IR and ^1H NMR spectroscopy. In addition, a complex mixture of other ferrocenic hydrocarbons containing cyclopentylene bridges (detected in the NMR spectra by comparison with known compounds) is isolated in a yield of 30%. The ratio Fc : C_5H_8 is around 1 : 1.

(c) Irreversibility. The same reaction conditions as used in the ligand exchange reactions were applied to a 1 : 1 equimolar mixture of 1,1'-cyclopentyleneferrocene and $[(\pi\text{-}C_5H_5)(\pi\text{-}C_6H_6)Fe]^+ BF_4^-$ in excess mesitylene in the presence of 1 mol of Al powder and 4 mol of $AlCl_3$ per mol of ferrocene derivative. After 5 h of reaction at 145° C, the organometallic cation present as the tetrafluorobo-

rate in the aqueous phase was precipitated and isolated as the hexafluorophosphate by addition of an aqueous solution of $NaPF_6$, following a method previously described [21]. The yield of recovered cation was 100%. 95% of the ferrocene derivative may be recovered from the organic phase, along with traces of ferrocenic hydrocarbons which migrate more slowly than 1,1'-cyclopentyleneferrocene on the TLC plate (hexane as eluant). If only 1,1'-cyclopentyleneferrocene is subjected to the ligand exchange reaction conditions, traces of salts (2%) are obtained. The NMR spectrum (CD_3COCD_3 solvent, TMS as reference) shows signals at δ(ppm) 6.15 (π-Ar), 5.15 (π-Cp), 2.45 (CH_3) and 1—2, indicating a structure of the type $[(\pi\text{-}RC_5H_4)(\pi\text{-mesitylene})Fe]^+$ where R is a hydrocarbon group (or a mixture). No trace of ferrocene was detected in these reactions using TLC and development with iodine.

Formation of deuterated ferrocenophanes

The proportion of deuterated ferrocenophane was determined by mass spectroscopy using the ratio of the height of the molecular ion $(M + 1)^+$ for the deuterated product to the height of the molecular ion of 1,1'-cyclopentyleneferrocene : 252. This was done for both the reactions where D_2O was added at the start of the reaction, and in the case where the reaction was performed in C_6D_6.

In the reaction hydrolysed with D_2O, the ferrocenophane formed contains up to 8 atoms of deuterium per molecule and follows a Gaussian distribution *. If the 1,1'-cyclopentyleneferrocene formed is placed in an acid medium, no additional deuterium is incorporated. This shows that the cyclopentylene bridge is formed before hydrolysis.

Alkyl substitution of a ring

The ligand exchange reactions were conducted according to the general method described [21,22]. The alkylferrocenes obtained were isolated by thick layer chromatography on silica gel or by use of a method similar to that described by Bublitz [35], and were identified using classical procedures [1,35]. Among the numerous theoretical possibilities for compounds of type D, only the compound with R' = R'' = R''' = H was isolated. The other fractions isolated were mixtures; the fraction R''' = alkyl was characterised by the presence of NMR signals due to the cyclopentylene bridge and the alkyl substituent of the ferrocene ring [1] (4 racemic isomers are possible, with the isomer having the alkyl group β to the bridge being the most predominant). Finally, the last fraction was a complex mixture; the NMR spectrum is in accord with the general formula D.

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* In acid media, H/D exchange is rapid in the case of ferrocene [44].

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