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RING OPENING REACTIONS OF SOME η^6-HETEROCYCLE-η^5-CYCLOPENTADIENYLIRON HEXAFLUOROPHOSPHATES

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Summary

Ring opening upon reaction with a nucleophile for heterocyclic ligands complexed to cyclopentadienyliron has been studied. The ligands investigated included those related to fluorene with an O, S or NH at C(9) or those related to 9,10-dihydroanthracene again with O, S or NH at the C(9) or C(9) and C(10) positions. Upon treatment with pyrrolidine as the nucleophile, it was found that ring opening occurred only at the site of an O heteroatom. For example, such a reaction with the cyclopentadienyliron complex of dibenzofuran or dibenzodioxin gave, respectively, the cyclopentadienyliron complex of *o*-*N*-pyrrolidinyl-*o'*-hydroxybiphenyl or *o*-*N*-pyrrolidinyl-*o'*-hydroxydiphenyl ether. No ring cleavage was observed at the site of a S or NH as the heteroatom; for example, no reaction took place when the cyclopentadienyliron complex of dibenzothiophene or carbazole was treated with pyrrolidine. A mechanism for the formation of the ring opening products based on the activation of the complexed ring towards nucleophilic aromatic substitution is discussed.

Introduction

Nesmeyanov and coworkers [1,2] have reported that the chlorine atom in η^6-chlorobenzene-η^5-cyclopentadienyliron tetrafluoroborate could be readily replaced by a number of nucleophiles and the reactivity of such a complexed chlorobenzene for nucleophilic substitution was similar to that of 2,4-dinitrochlorobenzene [2]. We have utilized such an activation of chloroarenes towards aromatic nucleophilic substitution in synthetic applications. Thus 20 η^6-*N*-substituted aminobenzene-η^5-cyclopentadienyliron cations were synthesized from reactions of 4 complexed chloro-

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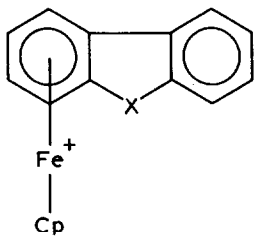
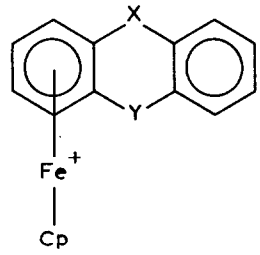
arenes (chlorobenzene and *o*-, *m*- or *p*-chlorotoluene complexed to $CpFe^+$) with 5 different amines [3]. Similarly, reactions of η^6-*o*-dichlorobenzene-η^5-cyclopentadienyliron hexafluorophosphate with two nucleophilic groups (OH, SH and/or NH_2) located in the 1,2-positions of a benzene ring gave rise to cyclopentadienyliron complexed heterocycles related to 9,10-dihydroanthracene with two heteroatoms at the 9,10-positions [4]. In some complexed heterocyclic systems, we have found that reactions with a nucleophilic reagent could lead to a ring opening at the site of a heteroatom, presumably via an aromatic nucleophilic substitution reaction. The present paper describes such ring opening reactions.

Results and discussion

The complexed heterocyclic systems investigated were those related to fluorene, namely, the cyclopentadienyliron complex of dibenzofuran (Ia), dibenzothiophene (Ib), or carbazole (Ic), and those related to 9,10-dihydroanthracene, namely, the cyclopentadienyliron complex of xanthene (IIa), thioxanthene (IIb), dibenzodioxin (IIc), phenoxathiin (IId), phenoxazine (IIe), thianthrene (IIf), or phenothiazine (IIg).





(Ia, X = O;
Ib, X = S;
Ic, X = NH)

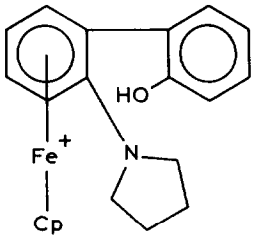
(IIa, X = CH_2, Y = O;
IIb, X = CH_2, Y = S;
IIc, X = Y = O;
IId, X = S, Y = O

IIe, X = NH, Y = O;
IIf, X = Y = S;
IIg, X = NH, Y = S)

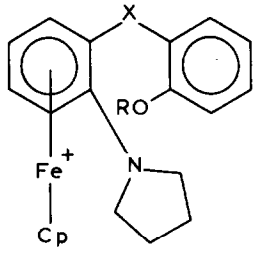
These complexes were obtained either from a direct ligand exchange between ferrocene and the heterocyclic compound [5–7] or from nucleophilic substitution reactions with η^6-*o*-dichlorobenzene-η^5-cyclopentadienyliron hexafluorophosphate [4]. One nucleophilic reagent was used to react with each of Ia–Ic and IIa–IIg in order to give a survey of the reactivity of these complexed heterocycles towards ring opening by a nucleophile.

Pyrrolidine, one of the amines previously employed in nucleophilic substitution reactions with the complexed chloroarenes [3], was chosen as the nucleophile since the presence of an *N*-pyrrolidinyl group as a substituent in the ring cleavage products would be easily detected in the alicyclic region of the NMR spectra without presenting any complicating absorptions in the aromatic region of these spectra. Upon treatment of Ia, Ib or Ic with pyrrolidine in CH_2Cl_2, only Ia gave a ring opening product, the cyclopentadienyliron complex of *o*-*N*-pyrrolidinyl-*o'*-hydroxybiphenyl (III), isolated as the hexafluorophosphate, while Ib or Ic was largely recovered unchanged. Similarly, upon reaction with pyrrolidine, IIa, IIc and IId gave, respectively, the cyclopentadienyliron complex of *o*-*N*-pyrrolidinyl-*o'*-hydroxydiphenylmethane, *o*-*N*-pyrrolidinyl-*o'*-hydroxydiphenyl ether, and *o*-*N*-pyrrolidinyl-

o'-methoxydiphenyl thioether (IV, V and VI, respectively), VI being obtained after the initially formed phenolic ring cleavage product was methylated with diazomethane to facilitate the isolation of its hexafluorophosphate as a solid. The other complexed heterocycles, IIb, IIe, IIf and IIg, did not give ring cleavage on treatment with pyrrolidine. The yields and the analytical and spectral data for the hexafluorophosphate salts of complexed cations III, IV, V and VI are summarized in Tables 1–3.



(III)

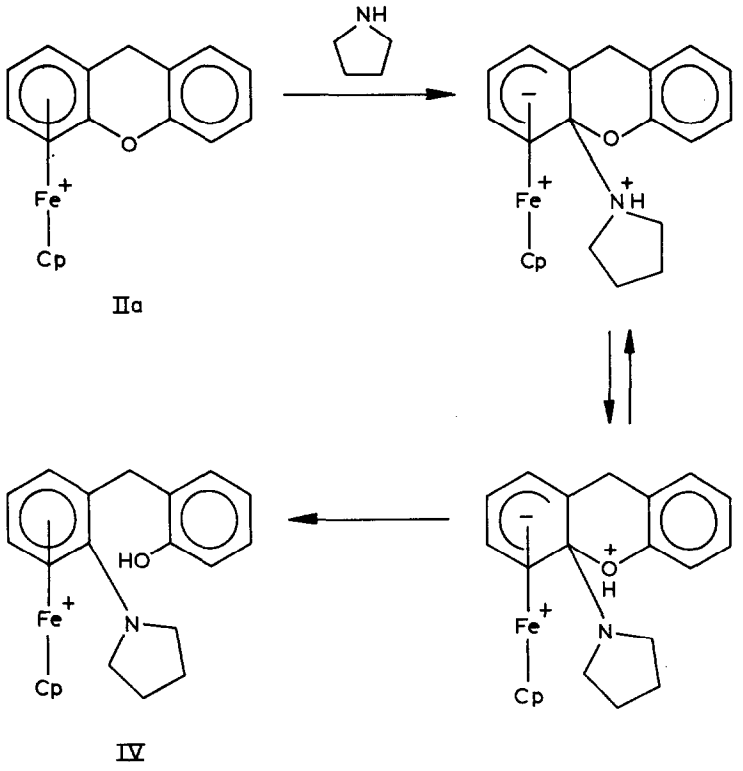


(IV, X = CH_2, R = H;
V, X = 0, R = H;
VI, X = S, R = CH_3)

From the above results, it is seen that ring opening took place only at the site of an O heteroatom, and no cleavage was observed at the S and NH sites. It may be of interest to point out that since ring opening took place with the complexed dibenzodioxin (IIc), possibly, complexation to cyclopentadienyliron followed by treatment with a nucleophile may provide a method for destroying environmentally persistent poisons related to dibenzodioxin. It may also be noted that for the phenoxathiin complex IId, cleavage occurred at the O site, with the S heteroatom unaffected. On the other hand, in the phenoxazine complex IIe with both O and NH present, no cleavage took place even at the O heteroatom. To account for these different behaviors, the mechanism responsible for the ring opening reaction must be considered.

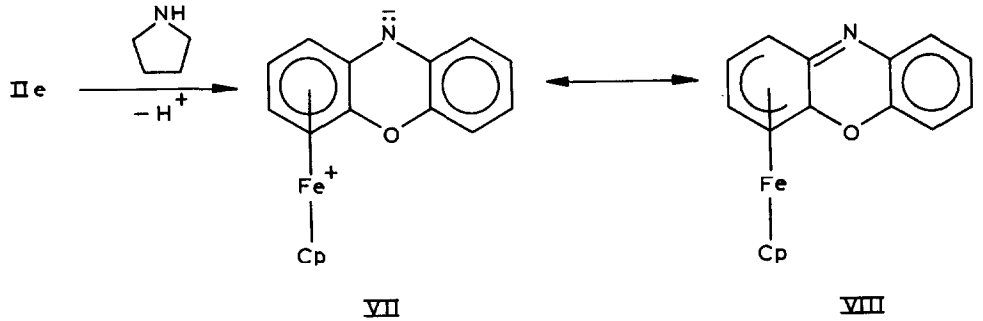
In the ordinary heterocyclic compounds similar to the heterocyclic ligands studied in the present work, ring cleavage took place with reagents such as Li metal to give organolithium compounds. For example, dibenzodioxin when treated with Li in tetrahydrofuran followed by carbonation gave 2-hydroxy-2'-carboxydiphenyl ether [8]. No ring cleavage by nucleophiles analogous to those observed in the present study is known for the uncomplexed heterocyclic compounds. Thus complexation to the $CpFe^+$ moiety likely provided the activation for nucleophilic aromatic substitution [1–4] which led to ring opening, as illustrated in Scheme 1 for the reaction with the η^6-xanthene-η^5-cyclopentadienyliron cation (IIa).

It is well known that weaker bases are better leaving groups in nucleophilic substitutions and an oxonium ion is a better leaving group than a sulfonium ion [9,10]. This order of reactivity could probably account for the finding that ring cleavage as outlined in Scheme 1 would occur at the site of an O heteroatom, but not at the site of a S heteroatom. When the complexed heterocycle has an NH group such as the η^6-phenoxazine-η^5-cyclopentadienyliron cation (IIe), ready deprotonation in the presence of a base would give rise to zwitterion VII which could also be formulated as the cyclohexadienyl complex VIII. The complexed ring in such a



SCHEME 1

species would be rich in electron and would not undergo any nucleophilic substitution reaction, thus no complexed heterocycle containing an NH group could give rise to ring opening via the processes outlined in Scheme 1. Spectroscopic evidence for the formation of species such as VII/VIII from deprotonation has been obtained in this laboratory and will be reported in a subsequent communication.



Experimental

General procedure for the ring opening reaction

To a solution of 1.0 mmol of η^6-heterocycle-η^5-cyclopentadienyliron

hexafluorophosphate in 25 ml of dry CH_2Cl_2 0.15 ml (0.17 g, 1.2 mmol) of pyrrolidine was introduced through a syringe. The mixture was stirred at room temperature under N_2 for 4–5 h and the resulting red solution was shaken with 50 ml of H_2O. The organic layer containing the reaction product was separated and washed successively with 5% HCl (3 × 10 ml), with a solution of 167 mg (1.0 mmol)

TABLE 1

YIELDS AND ANALYTICAL AND IR DATA FOR THE HEXAFLUOROPHOSPHATE SALTS OF RING OPENING PRODUCTS FROM REACTIONS BETWEEN PYRROLIDINE AND SOME COMPLEXED HETEROCYCLIC SYSTEMS

Product [a]	Yield (%)	Analysis (found (calcd.) (%))			IR ν(OH) (cm^{-1})
		C	H	N	
III	70	49.43 (49.92)	3.96 (4.39)	2.49 (2.77)	3550
IV	79	50.98 (50.89)	4.84 (4.66)	2.84 (2.70)	3545
V	72	48.03 (48.39)	4.60 (4.25)	2.59 (2.69)	3540
VI	79	47.56 (47.93)	4.37 (4.39)	2.75 (2.54)	–

[a] Cations III, IV, V and VI were isolated as their hexafluorophosphate salts and were derived from ring opening reactions between pyrrolidine and the cyclopentadienyliron complex of dibenzofuran, xanthene, dibenzodioxin and phenoxathiin, respectively.

TABLE 2

^{1}H NMR DATA (δ(acetone-d_6) ppm)

Product	Cp	Complexed aromatic	Uncomplexed aromatic	Pyrrolidinyl	Other
III	5.10 (s, 5H)	5.85–6.30 (m, 4H)	6.50–7.85 (m, 4H)	1.84 (m, 4H) 3.15 (m, 4H)	
IV	5.01 (s, 5H)	5.90–6.30 (m, 4H)	6.60–7.40 (m, 4H)	2.10 (m, 4H) 3.64 (m, 4H)	4.20 (m, 2H, CH_2)
V	5.02 (s, 5H)	5.83 (broad s, 4H)	6.75–7.25 (m, 4H)	2.04 (m, 4H) 3.76 (m, 4H)	
VI	5.10 (s, 5H)	5.70–6.50 (m, 4H)	6.65–7.65 (m, 4H)	2.06 (m, 4H) 3.83 (m, 4H)	3.96 (s, 3H, OCH_3)

TABLE 3

^{13}C NMR DATA (δ(acetone-d_6) ppm)

Product	Cp	Complexed aromatic [a]	Uncomplexed aromatic [a]	Pyrrolidinyl	Other
III	74.4	68.4; 78.7; 84.5; 89.5; 102.8*; 123.3*	114.6; 118.8; 129.6; 131.3; 124.7*, 154.6*	24.2; 49.7	
IV	74.5	68.1; 80.1; 84.0; 88.1; 84.7*; 124.9*	114.2; 119.0; 127.3; 128.3; 125.8*; 153.6*	24.2; 49.8	32.9 (CH_2)
V	74.6	69.2; 75.3; 77.0; 81.5; 115.3*; 125.8*	116.8; 119.8; 120.4; 125.8; 140.9*; 147.5*	24.1; 49.5	
VI	75.6	67.5; 81.5; 84.8; 92.0; 78.9*; 123.3*	110.7; 120.9; 128.3; 129.2; 127.4*; 155.8*	24.3; 50.2	54.6 (OCH_3)

[a] Quaternary carbons are marked by asterisks.

of NH_4PF_6 in 15 ml of H_2O, and with H_2O (3 × 10 ml). After drying over $MgSO_4$, the hexafluorophosphate salt of the ring opening product was precipitated from the CH_2Cl_2 solution by the addition of diethyl ether.

From the reaction with Ia, IIa or IIc, the product obtained was the hexafluorophosphate salt of III, IV or V, respectively. In the case of the reaction with the phenoxathiin complex IId, the washed and dried CH_2Cl_2 solution of the product was treated with about 7.0 mmol of CH_2N_2 in ether before the methylated product VI was precipitated with an excess of ether. The yields and analytical and spectral data for the hexafluorophosphates of III, IV, V and VI are summarized in Tables 1–3.

When the same procedure was tried with the complex Ib, Ic, IIb, IIe, IIf or IIg, no ring opening reaction took place and 60–80% of the complexed heterocyclic compound was recovered unchanged. With these complexes, raising the reaction temperature to that of refluxing CH_2Cl_2 or refluxing tetrahydrofuran also did not give the ring opening reaction.

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