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MONO- AND DI-CATIONS FROM LIGAND EXCHANGE REACTIONS BETWEEN FERROCENE AND SOME HETEROCYCLIC SYSTEMS

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Summary

Ligand exchange reactions between ferrocene (FcH) and dibenzodioxin (IIIA), phenoxathiin (IIIB), thianthrene (IIIC) or phenoxazine (IIID) were carried out to give η^6-heterocycle-η^5-cyclopentadienyliron cations for comparison with previous preparations of such cations from nucleophilic substitution reactions of the η^6-*o*-dichlorobenzene-η^5-cyclopentadienyliron cation with two nucelophilic groups located in the 1,2-positions of a benzene ring [1]. Using a large excess of FcH, ligand exchanges with these heterocyclic systems also gave rise to the η^6,η^6-heterocycle-di-η^5-cyclopentadienyliron dications. The *trans*-orientation for the two $CpFe^+$ groups was found for the dications from IIIA and IIID, while both *cis*- and *trans*-dications were formed from IIIB and IIIC. A possible explanation for this difference, based on the planar or folded shape for the heterocyclic molecule, was proposed.

Introduction

Recently, we have shown that η^6-*o*-dichlorobenzene-η^5-cyclopentadienyliron hexafluorophosphate could undergo nucleophilic substitution reactions with two nucleophilic groups (OH, SH and/or NH_2) located in the 1,2-positions of a benzene ring to give a cyclopentadienyliron complexed heterocycle related to 9,10-dihydroanthracene, with two heteratoms at the 9,10-positions. Upon pyrolytic sublimation of the complex, the free heterocyclic compound was obtained, thus providing a method of synthesis of such heterocyclic systems [1]. The compounds prepared in this way are IIIA–IIIE [1].

Direct ligand exchanges between heterocycles and ferrocene, effected in the presence of $AlCl_3/Al$, have also been studied in this laboratory [2]. Among the complexed heterocycles obtained from such ligand exchanges were the monocations

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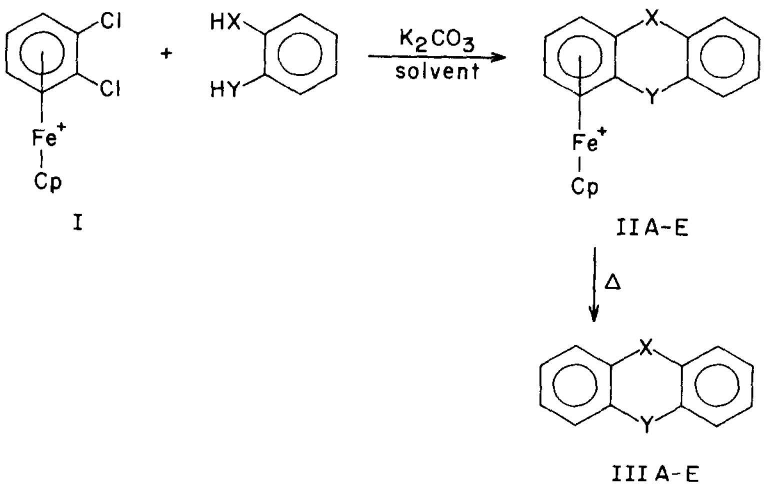
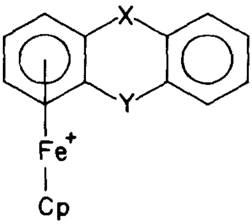
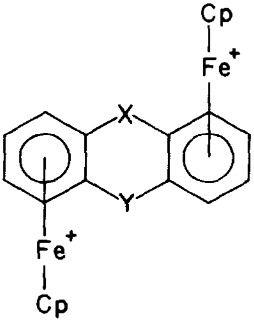


(IIIA: $X = Y = O$, Dibenzodioxin; IIIB: $X = S$, $Y = O$, Phenoxathiin; IIIC: $X = Y = S$, Thianthrene (the compound prepared was IIIC′, 2-methylthianthrene); IIID: $X = NH$, $Y = O$, Phenoxazine; IIIE: $X = NH$, $Y = S$, Phenothiazine)

IIE–IIG and the corresponding dications IVE–IVG. It may be noted that only



II E-G



IV E-G

(E: $X = NH$, $Y = S$; F: $X = CH_2$, $Y = O$; G: $X = CH_2$, $Y = S$)

η^6-phenothiazine-η^5-cyclopentadienyliron cation IIE has been prepared both by nucleophilic substitution with I [1] and by ligand exchange [2]. In the present work, ligand exchange studies have been extended to include investigations on the reaction of ferrocene with dibenzodioxin (IIIA), phenoxathiin (IIIB), thianthrene (IIIC) and phenoxazine (IIID).

Results and discussion

The mono- or di-cations similar to II or IV were prepared from ligand exchanges between ferrocene (FcH) and IIIA, IIIB, IIIC or IIID under the same conditions previously described for such ligand exchanges with other heterocyclic systems [2]. Reaction between equimolar quantities of FcH and IIIA, IIIB or IIID gave, respectively, the cyclopentadienyliron complexed monocation of dibenzodioxin (IIA), phenoxathiin (IIB) or phenoxazine (IID), identical with IIA, IIB, or IID obtained from the nucleophilic substitution reaction with I [1]. The yields of IIA, IIB and IID, obtained from ligand exchange in the present work, were 20, 24 and 14%, respectively, and these values are considerably lower than the analogous yields of 78, 76 and 45%, respectively, for IIA, IIB and IID obtained from the corresponding nucleophilic substitution reactions [1]. Similarly, the ligand exchange between FcH and IIIC gave a 28% yield of the η^6-thianthrene-η^5-cyclopentadienyliron cation (IIC) in contrast to an 82% yield of the η^6-2-methylthianthrene-η^5-cyclopentadienyliron cation (IIC′) obtained from the reaction of I with 3,4-dimercaptotoluene [1]. Thus in all of these cases, a substitution reaction between I and two nucleophilic groups in the 1,2-positions of a benzene ring is capable of giving a higher yield of the complexed heterocycle than a direct ligand exchange reaction. The analytical and spectral data for IIC, which has not been prepared previously, are given in Tables 1 and 2, together with similar data for the dications.

Using a large excess of FcH and under conditions previously described [2], di-η^5-cyclopentadienyliron complexed dications of heterocyclic compounds IIIA, IIIB, IIIC and IIID were prepared. The analytical and spectral data for these dications are summarized in Tables 1 and 2. In previous preparations of dications in which an arene was complexed to two cyclopentadienyliron groups, only a single product was formed in each case, and when *cis*- and *trans*-orientations for the $CpFe^+$ groups were possible, the dication was assigned the *trans*-structure [2–5]. On steric grounds, the *trans*-structure, such as IV, would be preferable to the *cis*-analog.

TABLE 1

YIELDS AND ANALYTICAL DATA

Complex [a]	Yield (%)	Analysis (Found (calcd.)(%))		
		C	H	N
IIC	28	42.42 (42.34)	2.74 (2.72)	–
IVA	36	36.83 (36.91)	2.71 (2.53)	–
IVB	53 [b]	36.12 (36.10)	2.71 (2.48)	–
VB	9 [b]	36.30 [c] (36.10)	2.70 [c] (2.48)	–
IVC	46 [b]	35.07 [d] (35.32)	2.51 [d] (2.43)	–
VC	20 [b]	35.45 [e] (35.32)	2.42 [e] (2.43)	–
IVD	50	36.85 (36.96)	2.71 (2.68)	2.05 (1.96)

[a] Isolated as the mono- or di-hexafluorophosphate salts. IIC is the η^6-thianthrene-η^5-cyclopentadienyliron cation; dications IV and V, respectively, are the *trans*- and *cis*-di-η^5-cyclopentadienyliron complexes, with A, B, C and D, respectively, designating dibenzodioxin, phenoxathiin, thianthrene and phenoxazine as the heterocyclic ligands. [b] Estimated from the integration of the Cp signals in the ^{1}H NMR spectra. [c] For a 5/1 mixture of VB/IVB. [d] For a 5/2 mixture of IVC/VC. [e] For a 5/2 mixture of VC/IVC.

TABLE 2

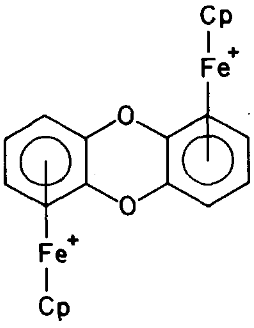
^{1}H AND ^{13}C NMR DATA

Complex	^{1}H NMR (δ, ppm)[a]			^{13}C NMR (δ, ppm)[b]		
	Cp	Complexed aromatic	Others	Cp	Complexed aromatic	Others
IIC	4.93(s,5H)	6.50(m,2H); 6.91(m,2H)	7.66(m,4H) (uncomplexed arom.)	77.5	85.6; 87.6; 104.0*	128.9; 131.7* (uncomplexed arom.)
IVA	5.26(s,10H)	6.40(m,4H) 6.72(m,4H)		79.0	76.2; 84.8; 115.0*	
IVB	5.16(s,10H)	6.42(m,4H) 6.67(m,4H)		79.4	77.9; 84.0; 86.0; 89.4*, 121.0*	
VB[c]	5.33(s,10H)	6.42(m,4H) 6.67(m,4H)		79.7	76.3; 82.1; 86.0; 90.3*, 123.6*	
IVC[d]	5.05(s,10H)	6.54(m,4H) 6.95(m,4H)		80.3	86.4; 86.6; 103.3*	
VC[e]	5.28(s,10H)	6.54(m,4H) 6.95(m,4H)		79.5	87.0; 88.2; 101.2*	
IVD	5.21(s,10H)	6.28(m,4H) 6.44(m,4H)	7.60(s,1H)(NH)[f]			

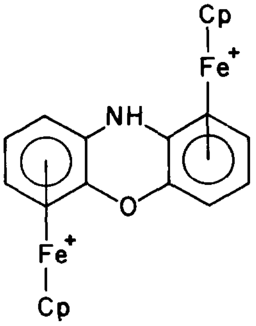
[a] Recorded in a 3/1 mixture of DMSO-d_6/acetone-d_6; [b] Recorded in DMSO-d_6 except that the ^{13}C NMR spectrum of IIC was recorded in acetone-d_6; asterisks indicating quaternary carbons. [c] From the spectrum of a 5/1 mixture of VB/IVB. [d] From the spectrum of a 5/2 mixture of IVC/VC. [e] From the spectrum of a 5/2 mixture of VC:IVC. [f] Recorded in CD_3CN.

Moreover, in some cases, the NMR data were also compatible with the *trans*-assignment. For example, in the dication IVF or IVG, the protons of the methylene group in the C(9) position of the heterocyclic ligand, xanthene or thioxanthene, appeared as a singlet in the ^{1}H NMR spectrum, consistent with a *trans*-configuration for the two CpFe$^+$ groups [2]. If the configuration were *cis*, the methylene protons would not be equivalent and its ^{1}H NMR absorption would not be a singlet.

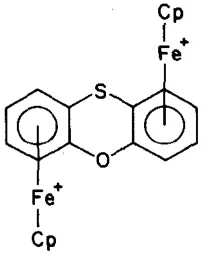
In the present work, a single product was obtained as the dication derived from dibenzodioxin (IIIA) or phenoxazine (IIID), and these were assigned the *trans*-structure, the η^6,η^6-dibenzodioxin-*trans*-di-η^5-cyclopentadienyliron dication IVA and the η^6,η^6-phenoxazine-*trans*-di-η^5-cyclopentadienyliron dication IVD. Interestingly, from either phenoxathiin (IIIB) or thianthrene (IIIC), a mixture of both the *trans*- as well as the *cis*-dications, IVB and VB or IVC and VC, were obtained. The relative amounts of IVB/VB and IVC/VC, based on the integration of the Cp signals in the ^{1}H NMR spectra, were about 6/1 and 7/3, respectively. The major component was assigned the *trans*-structure as discussed later in this paper. Pure IVB was separated from the product mixture of IVB and VB by column chromatography. However, VB,



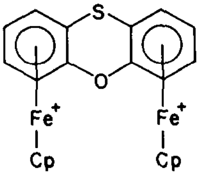
IV A



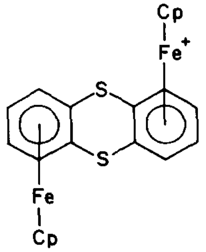
IV D



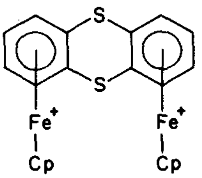
IV B



V B



IV C

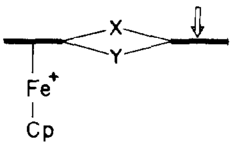


V C

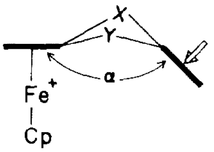
IVC and VC were isolated only as enriched mixtures of 5/1 VB/IVB, 5/2 IVC/VC and 5/2 VC/IVC.

The question arises as to why phenoxathiin (IIIB) and thianthrene (IIIC) could give rise to both *cis*- and *trans*-dications, while the dication from dibenzodioxin (IIIA) or phenoxazine (IIID) and other dications already reported in the literature showed only the *trans*-configuration. An explanation may lie in the shapes of the heterocyclic molecules. From a consideration of the data accumulated in the literature, Hosoya [6] has shown that for heterocyclic compounds related to anthracene with the heteroatoms at C-9 and/or C-10, the molecules are planar if the atoms in the 9,10-positions are any of C, N or O. On the other hand, if at least one of the atoms at the 9,10-positions is S, the molecule is folded. On this basis, IIIA and IIID are planar and IIIB and IIIC are folded. Similar conclusions regarding the planarity or non-planarity of heterocycles have also been obtained from high resolution NMR data [7,8].

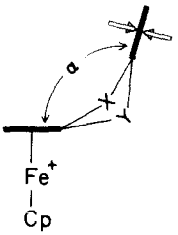
In previous preparations of di-η^5-cyclopentadienyliron complexed dications, it was shown that such dications could be prepared in a stepwise way from the corresponding monocation [3,4]. Such a stepwise process was also demonstrated in the present work by the conversion of monocation IIC to dications IVC and VC. With a planar heterocycle, the monocation could be depicted as VI, with the darker solid lines representing the benzene rings. Incorporation of the second CpFe$^+$ group as indicated by the arrow would give rise to the *trans*-di-cyclopentadienyliron dication. With a folded molecule, two comformations, VIIA and VIIB, would be possible. Incorporation of the second CpFe$^+$ groups in VIIA would also give the *trans*-dication, while with VIIB, both *trans*- and *cis*-dications would be formed. Since the *trans*-dication could arise from both VIIA and VIIB while only VIIB could give the *cis*-dication, the *trans*-structure was tentatively assigned to the major component in the *cis*/*trans* mixture. For the folded structure depicted in VIIB, one might anticipate that the greater the deviation from planarity, i.e. small the angle α, the greater would be the proportion of *cis*-dication formation. The angle α has been estimated from dipole moment measurements to be 150–160° and 135–140°, respectively, for IIIB and IIIC [9], and one would thus expect a relatively greater extent of *cis*-dication formation from IIIC. The presently observed *trans*/*cis* ratios for the dications IVB/VB and IVC/VC, respectively, are about 6/1 and 7/3, in agreement with expectation.



VI

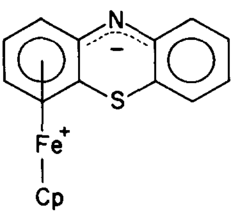


VII A

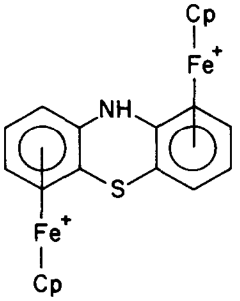


VII B

It is of interest to point out that phenothiazine (IIIE) is folded [6], and accordingly one might expect the formation of both the *cis*- and *trans*-dications from IIIE. In our earlier ligand exchange studies [2], IIIE was found to give only the *trans*-dication IVE. In the present work, the reaction with IIIE was repeated and the formation of only the *trans*-dication was confirmed. A possible explanation that no *cis*-dication was formed from IIIE may be due to the ready loss of a proton from N in such complexed N-containing heterocycles. Preliminary observations in this laboratory indicated that mono- or di-cations such as II or IV, with the heterocyclic ligand containing at least one NH group at the 9,10-positions, could in the presence of a base easily lose the proton from the N heteroatom. An indication of such a deprotonation is found in the entry for IVD in Table 2. In the ^{1}H NMR spectrum of IVD, the proton absorption for the NH group was observed only when the spectrum was recorded in CD_3CN. When the solvent was the more basic DMSO-d_6/acetone-d_6, the NH absorption was absent presumably because of deprotonation. A deprotonated species from the monocation derived from IIIE possibly might be depicted as VIII, which probably would not be folded and would eventually lead to the formation of only the *trans*-dication IVE.



VIII



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Experimental

The heterocyclic compounds, dibenzodioxin (IIIA), phenoxathiin (IIIB), thianthrene (IIIC) and phenoxazine (IIID) were prepared using procedures described in the literature [10–13]. The ligand exchange reactions between FcH and these heterocycles were carried out as previously described [2] to give the monocations IIA, IIB, IIC and IID and the dications IVA, IVB, VB, IVC, VC and IVD, with the yields and relevant analytical and spectral data summarized in Tables 1 and 2. An illustration of a typical preparation of a dication is given below.

Preparation of the dications

A mixture of ferrocene (9.30 g, 50 mmol), $AlCl_3$ (18.65 g, 140 mmol), Al powder (0.27 g, 10 mmol) and dibenzodioxin (IIIA) (1.84 g, 10 mmol) in 40 ml of decalin was heated with stirring at 135–145°C for 4 h. After cooling to about 70°C, the mixture was poured into about 150 ml of ice-water. Any residual solid was removed by filtration and the aqueous layer was washed with ether (2 × 50 ml) before being treated with 3.25 g (20 mmol) of NH_4PF_6. After stirring for 30 minutes, the product that precipitated was collected by filtration, washed with a 9/1 mixture of ether/methanol and then air dried to give 2.57 g (36%) of the dihexafluorophosphate salt of the η^6,η^6-dibenzodioxin-*trans*-di-η^5-cyclopentadienyliron dication (IVA).

In a similar way, the yields of dications obtained from IIIB, IIIC and IIID were 62, 66, and 50%, respectively. The presence of two Cp absorptions for the products from IIIB or IIIC indicated the formation of a mixture of *trans*- and *cis*-dications IVB and VB, or IVC and VC, respectively. From the integrated intensities of these Cp absorptions, the ratio for IVB/VB or IVC/VC, respectively, was estimated to be about 6/1 (53%:9%) or about 7/3 (46%/20%). Pure IVB was obtained from the mixture of IVB and VB by elution with acetone through a 25 cm × 2 cm diameter alumina column (Alcoa Chemicals F20 alumina deactivated by exposure to air for 48 hours). A 5/1 mixture of VB/IVB was then obtained as a second fraction by elution with a 5/1 mixture of acetone/nitromethane. From the mixture of IVC and VC, similar treatment through the alumina column gave a 5/2 mixture of IVC/VC from elution with acetone and a 5/2 mixture of VC/IVC from elution with acetone/nitromethane. Further attempts to separate the mixed products using column chromatography or fractional crystallization failed to improve the 5/1 or 5/2 enrichments.

Conversion of monocation IIC to dications IVC and VC

The procedure adopted is similar to that already described in the literature [4]. A mixture of ferrocene (1.24 g, 6.7 mmol), the hexafluorophosphate salt of IIC (1.61 g, 3.3 mmol), $AlCl_3$ (1.33 g, 1.0 mmol) and Al powder (0.18 g, 6.7 mmol) in 60 ml of methylcyclohexane under N_2 was heated under reflux for 20 h. After the usual work-up as described above in the preparation of dication IVA, the mixture of the dihexafluorophosphate salts of the *trans*- and *cis*-dications IVC and VC was obtained. The product was purified by passage through the alumina column, any unreacted hexafluorophosphate salt of IIC being removed by elution with a 9/1 mixture of methylene chloride/ether. The dicationic products were recovered in 11% yield by elution with a 4/1 mixture of acetone-nitromethane, the ratio of IVC/VC, as estimated by the Cp absorptions in the ^1H NMR spectrum, was about 8/7.

Acknowledgement

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