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π-CORONENE-π-CYCLOPENTADIENYLIRON CATIONS VIA LIGAND EXCHANGE REACTIONS WITH FERROCENES

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Summary

Ligand exchange reactions of ferrocene and substituted ferrocenes (1,1′-dimethylferrocene, 1,2,3,4,1′,2′,3′,4′-octamethylferrocene and 1,1′-diacetylferrocene) with coronene have been investigated. While octamethylferrocene and diacetylferrocene gave no exchange reactions, ferrocene and 1,1′-dimethylferrocene yielded π-coronene-π-cyclopentadienyliron and π-coronene-π-methylcyclopentadienyliron cations, which were isolated as hexafluorophosphate salts. NMR studies revealed that the CpFe moiety is not coordinated to the inner ring but to an outer ring of coronene. There is also evidence that coronene may be coordinated to more than one CpFe group.

Iterative Extended Hückel Model calculations of the energy contents, bond orders, and charge distributions of four different positions of CpFe-coordination confirm that the CpFe unit is only coordinated to an outer ring.

Introduction

Since the first reports by Nesmeyanov et al. in 1963 [1] many studies have been devoted to ligand-exchange reactions between ferrocene (Cp_2Fe) and arenes in the presence of $AlCl_3$ and Al powder to yield π-arene-π-cyclopentadienyliron cations. It has been demonstrated that not only benzene but also polynuclear aromatic hydrocarbons such as biphenyl, naphthalene or fluorene can be used in these reactions [2].

Further investigations with polynuclear aromatic compounds showed that under suitable conditions more than one aromatic ring of the substrate can coordinate with a CpFe moiety. Thus, fluorene, biphenyl [3], 3,3′,4,4′-tetramethylbiphenyl, diphenylmethane, triphenylmethane, *p*-terphenyl, *β*-phenylnaphthalene, 1,2 : 4,5-dibenzo-1,4-cycloheptadien, 9,10-dihydroanthracene, anthracene, phenantrene, chrysene and 1,2 : 5,6-dibenzanthracene [4] afforded *π*-arenebis(*π*-cyclopentadienyliron) dications. However, attempts to trisubstitute polynuclear aromatic hydrocarbons, such as triphenylmethane, triphenylene and 1,2 : 5,6-dibenzanthracene have been unsuccessful [4]. Only with tetraphenylporphine were products with more than two CpFe groups obtained [4].

One of the most interesting polynuclear aromatic hydrocarbons, coronene, has not previously been used in ligand exchange reactions. In view of its "superaromaticity" it was of great interest to see how coronene would behave in such reactions. We, therefore, investigated ligand exchange reactions of ferrocene and substituted ferrocenes with coronene.

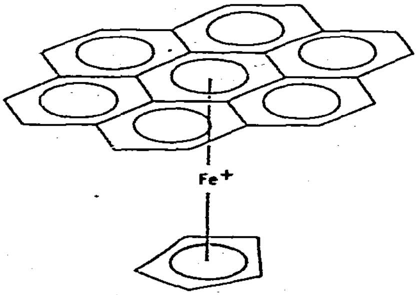
Results and discussion

Following a procedure commonly used for ligand exchange reactions of ferrocenes with arenes [5], coronene and ferrocene were brought into reaction for 5 h in boiling methylcyclohexane in the presence of $AlCl_3$ and Al powder. The molar ratios of coronene, ferrocene, $AlCl_3$ and Al were 1 : 3 : 6 : 3. After the usual work-up of the deep-red reaction mixture, dark red crystals were obtained by precipitation with KPF_6. The elemental analysis confirmed the composition $C_{29}H_{17}F_6FeP$, indicating that only one CpFe group was coordinated to coronene.

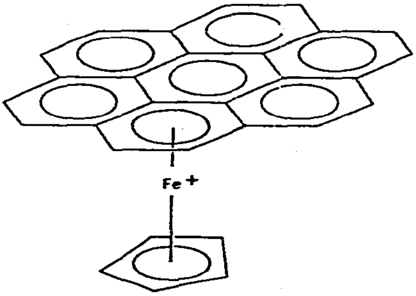
Reduction of the hexafluorophosphate salt with sodium amalgam in THF [6] gave coronene, ferrocene, and iron-containing compounds.

$$C_{29}H_{17}F_6FeP \xrightarrow[\text{THF, 40°C}]{\text{Na/Hg}} \text{coronene} + Cp_2Fe + [Fe]$$

This reaction confirmed that *π*-coronene-*π*-cyclopentadienyliron hexafluorophosphate had been formed via ligand exchange reaction of ferrocene with coronene.



I

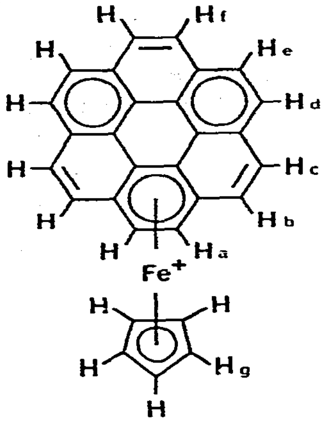


II

The question arose whether the CpFe group was symmetrically coordinated to the inner ring (structure I), or unsymmetrically to an outer ring of coronene (structure II). From the ^1H NMR spectrum which showed more than one signal for the aromatic protons, structure I could be excluded. As shown in Fig. 1 the aromatic protons gave a set of signals indicating two A_2 and two AB systems, as expected for structure II. The chemical shifts and the coupling constants are

TABLE 1

^{1}H MAGNETIC RESONANCE DATA[a]

Structure	Protons	δ (ppm)	*J* (Hz)
	a	6.96	
	b d or c e	7.98 8.32	J_{bc} 9.1
	d b or e c	8.34 8.52	J_{de} 8.4
	f	8.35	
	g	3.17	

[a] 90 MHz spectrum; solvent: CD_3CN.

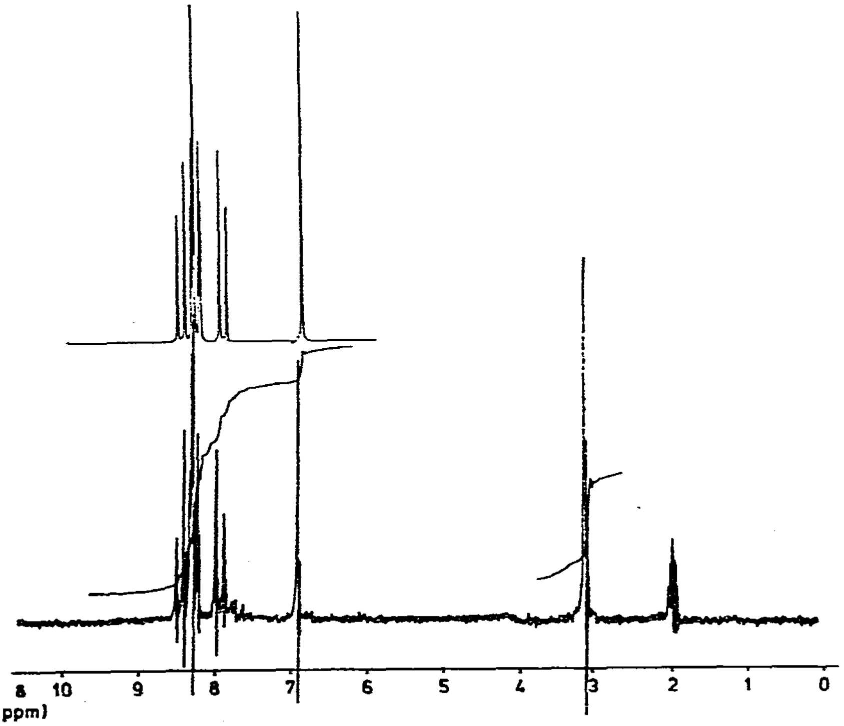


Fig. 1. ^{1}H NMR spectrum of π-coronene-π-cyclopentadienyliron hexafluorophosphate. The inset is the spectrum calculated by the Laokoon program.

given in Table 1. The inset in Fig. 1 is a calculated spectrum using the Laokoon program.

^{13}C NMR data confirmed structure II. The resonances listed in Table 2 were assigned by comparison with the ^{13}C resonances of the uncomplexed coronene (Table 2), on the basis of the calculated charge distribution in structure II (see Fig. 4b) and by analogy with literature data [4].

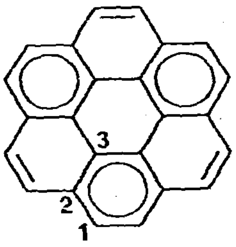
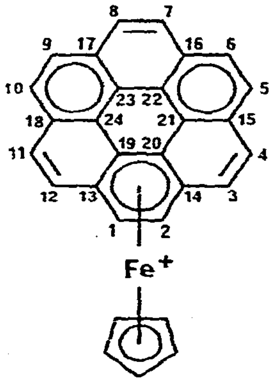
The coordination of the CpFe group with an outer ring and not with the inner ring of coronene is evidently due to the fact that these ring systems differ significantly in electron density. E.g. it has been calculated that the ratio of aromatic ring current intensity is 1.460 for ring A and 1.038 for ring B (see structure III) compared with 1.000 for benzene [7]. Similar differences were found in calculations of the degree of benzene character of the rings A and B. Table 3 shows the results of calculations based on different definitions. Irrespective of the method used, the aromatic character is always greater for the outer rings A than for the inner ring B.

Evidently the coordination of CpFe to coronene occurs at the place of greatest aromaticity.

To study the possibility that the complexed iron could migrate around the various outer rings, which is feasible in view of the "superaromaticity" of the

TABLE 2

CARBON-13 MAGNETIC RESONANCE DATA FOR CORONENE AND π-CORONENE-π-CYCLOPENTADIENYLIRON CATION

Compound	δ (ppm) [a]	Peak assignment
	125.3	C-3
	129.0	C-1
	129.4	C-2
	75.1	C_5H_5 lig.
	82.2	C-1,2
	89.6	C-19,20
	89.9	C-13,14
	124.8	C-15,18,21,24
	126.8	C-16,17,22,23
	128.8	C-5—C-10
	131.5	C-4,11
	133.4	C-3,12

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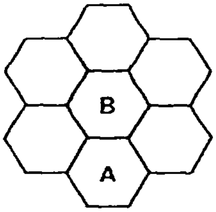
[a] Solvent: acetonitrile; internal standard: TMS; 67.88 MHz.

TABLE 3

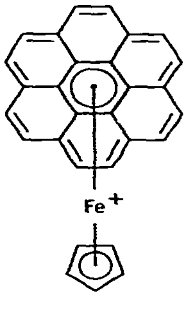
BENZENE CHARACTER OF RING SYSTEMS IN CORONENE [8]

Mode of Calculation	Benzene character	
	Ring A	Ring B
Resonance theory	0.500	0.200
Hückel MO theory	0.837	0.753
Topological index	0.871	0.834

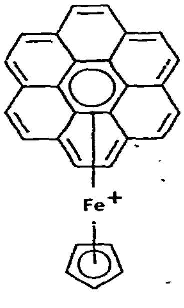


III

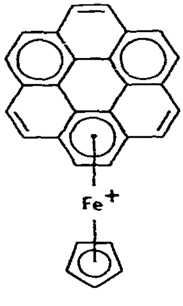
outer ring system, we tried to carry out temperature dependent ^{1}H NMR measurements but these failed because of thermal decomposition of the complex. We thus tried to estimate the rotation barrier by calculations, which were also aimed at determining the stabilities of structures I and II. For this purpose four different coordinations of the CpFe moiety to the coronene molecule were considered, and the Iterative Extended Hückel Model (IEHM) [9] * was used. The system under consideration is a positively charged ion, and the iron atom can be assumed to bear a net positive charge; therefore, the atomic orbitals of Fe^+



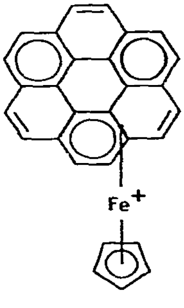
I



Ia



II



IIa

were used in the calculations. The starting configuration was chosen as d^6s.

For this configuration the starting VOIP's (Valence Orbital Ionisation Potentials) of the *s*, *p* and *d* orbitals at the iron atom were calculated using the equation of Mango and Schachtschneider [9] with values of Basch, Viste and Gray [10]:

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* The IEHT program was written by us and checked against results in the literature.

VOIP (*s*) = 7.104 eV
VOIP (*p*) = 3.781 eV
VOIP (*d*) = 8.195 eV

For the iron atom the approximation of the atomic orbitals of the *s*-, *p*- and *d*-type was carried out by linear combinations of STO's (Slater Type Orbitals) [11,12].

The atomic functions for the C and H atoms were chosen according to the literature [13,14].

$\chi(H_{1s}) = 1.0\ (1,0,1.2)$
$\chi(C_{2s}) = 1.0\ (2,0,1.625)$
$\chi(C_{2p}) = 1.0\ (2,1,1.625)$
$\chi(Fe_{3d}) = 0.5505\ (3,2,5.35) + 0.6260\ (3,2,2.0)$
$\chi(Fe_{4s}) = -0.02078\ (1,0,25.38) + 0.07052\ (2,0,9.75) - 0.1744\ (3,0,4.48) + 1.0125\ (4,0,1.40)$
$\chi(Fe_{4p}) = 0.04091\ (2,1,10.60) - 0.14364\ (3,1,4.17) + 1.00932\ (4,1,1.25)$

In these expressions (n, l, ξ) stands for an STO. n is the main quantum number, l the sub-quantum number and ξ the Slater exponent. The non-diagonal elements of the Hamilton matrix were calculated from the equation of Wolfsberg and Helmholtz [15]. For the constant K the value of 1.8 was chosen [9].

The calculations of the coordinates of the system [coronene—Fe—Cp]$^+$ were based on the following structural parameters: 1.07 Å was taken for all C—H distances, 1.40 Å for all C—C distances (c.f. [16]) and 1.65 Å for the distance between Fe and the ring plane of coronene as well as for the distance between Fe and the Cp plane. The coronene molecule was assumed to be planar, and to be parallel to the plane of the Cp ring.

The calculations of the energies of the structures I, Ia, II and IIa allow the conclusion that structure II is the most stable one (Table 4), its energy, corrected according to Schuster [17], being 0.226 eV lower than that of I.

This explains why CpFe coordinates with an outer ring and not with the inner ring of coronene. It can also be seen from Table 4 that the position of CpFe in II must be fixed, because rotation along the outer rings has to overcome an energy barrier of about 1.7 eV ($\Delta E_{\text{II-IIa}}$). Transition from II to I should need an energy of about 1.5 eV.

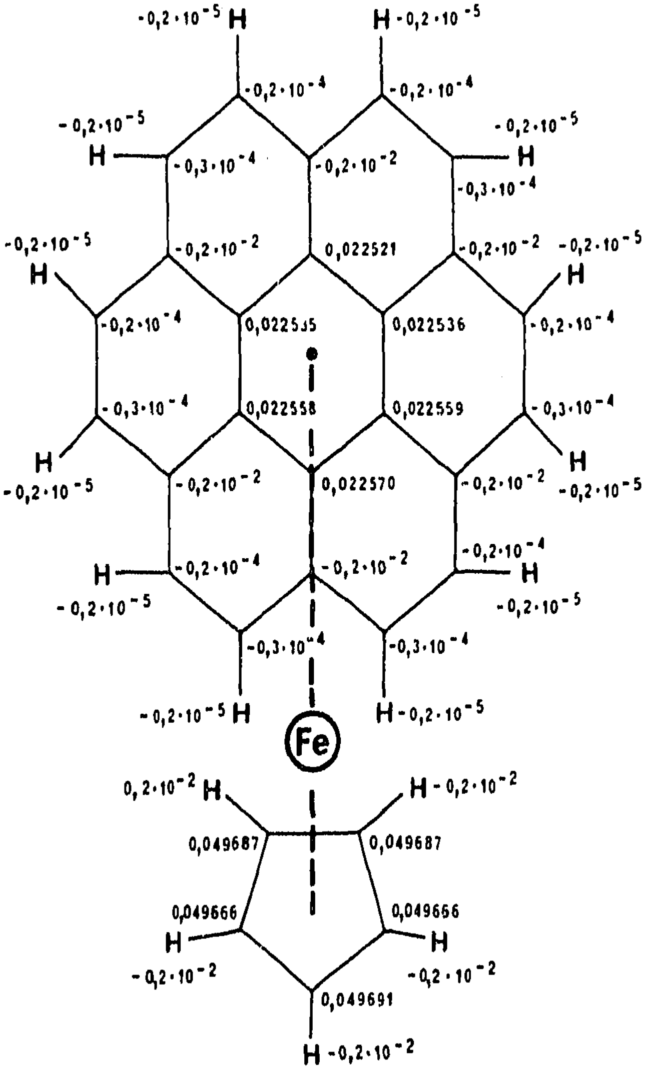
These considerations are supported by the bond-order analysis of the different structures. The bond orders between the iron atom and the carbon and hydro-

(continued on p. 325)

TABLE 4

ENERGY CONTENTS OF DIFFERENT [coronene—Fe—Cp]$^+$ STRUCTURES

Structure	Energy (eV)	
	Calculated with IEHM	Calculated with IEHM and corrected according [17]
I	—2245.705	—2244.116
Ia	—2244.515	—2242.873
II	—2245.872	—2244.342
IIa	—2244.337	—2242.626



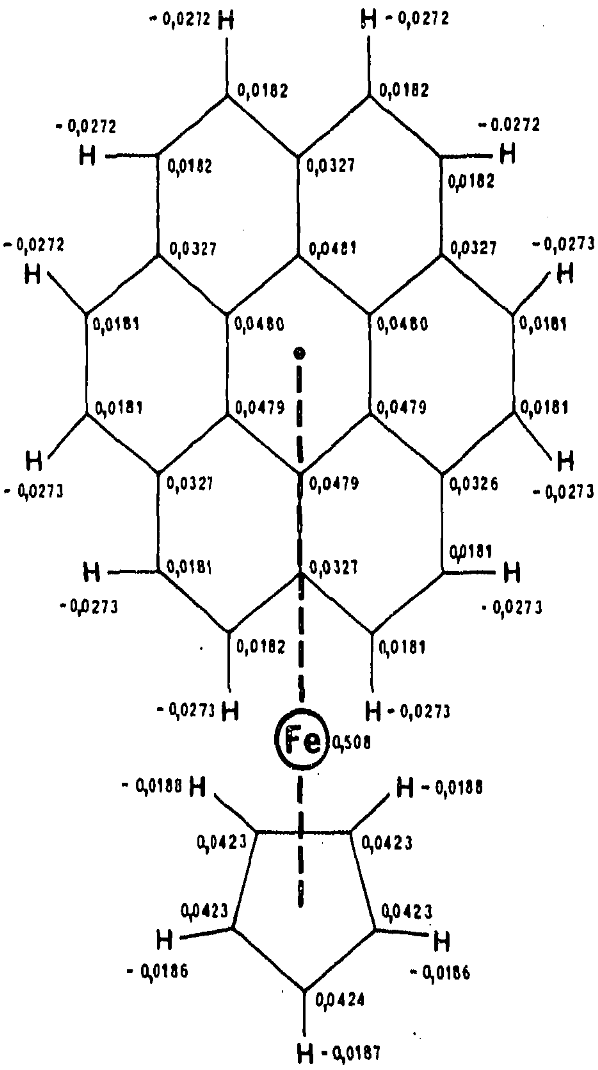
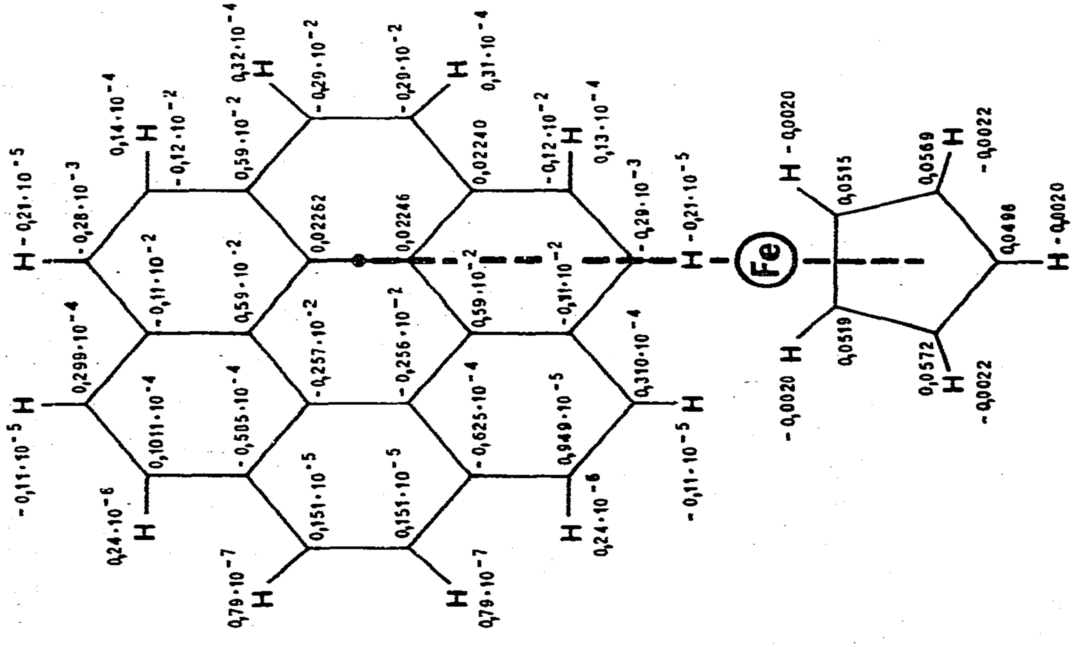


Fig. 2a. Mulliken overlap populations of all C and H atoms with the iron atom in structure I.
Fig. 2b. Charge distributions in structure I (calculated according to Löwdin [19].



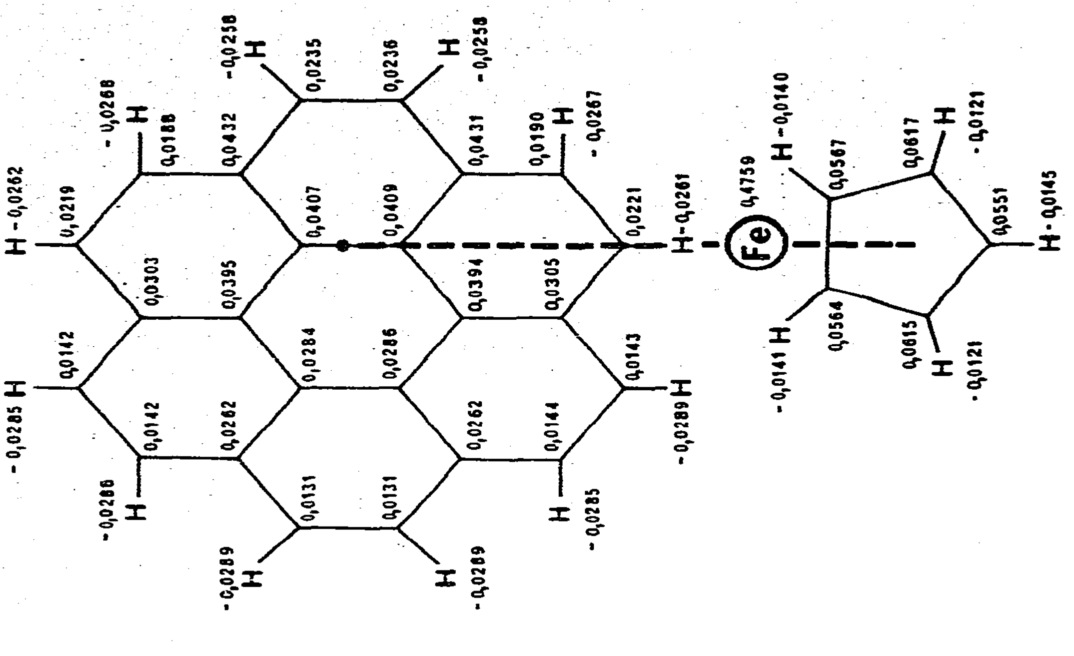


Fig. 3a. Mulliken overlap populations of all C and H atoms with the iron atom in structure Ia.
Fig. 3b. Charge distributions in structure Ia (calculated according to Löwding [19]).

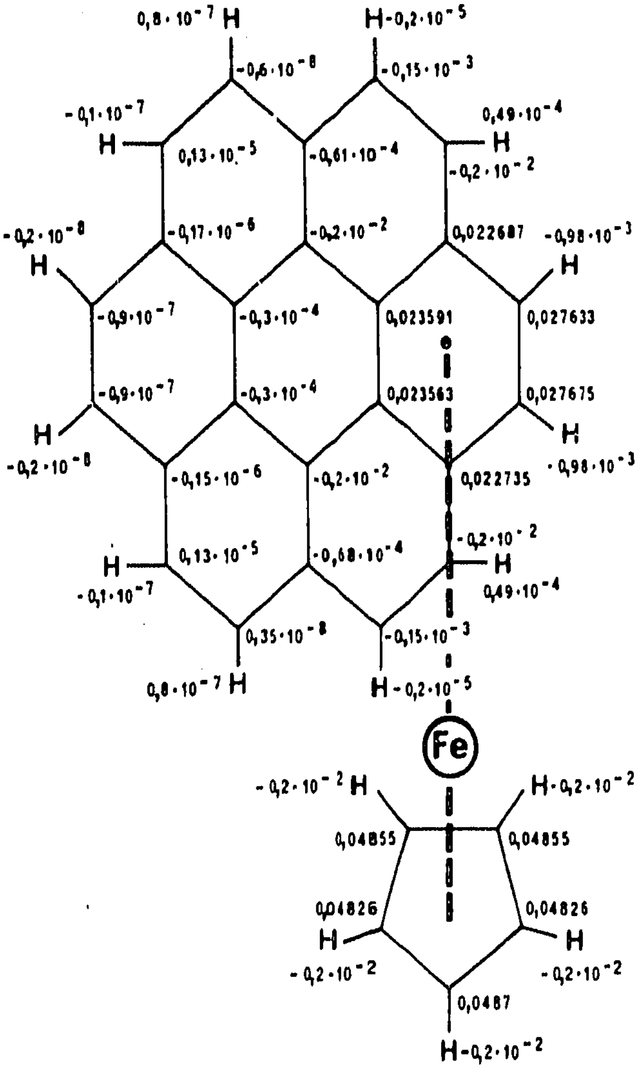


Fig. 4a. Mulliken overlap populations of all C and H atoms with the iron atom in structure II.

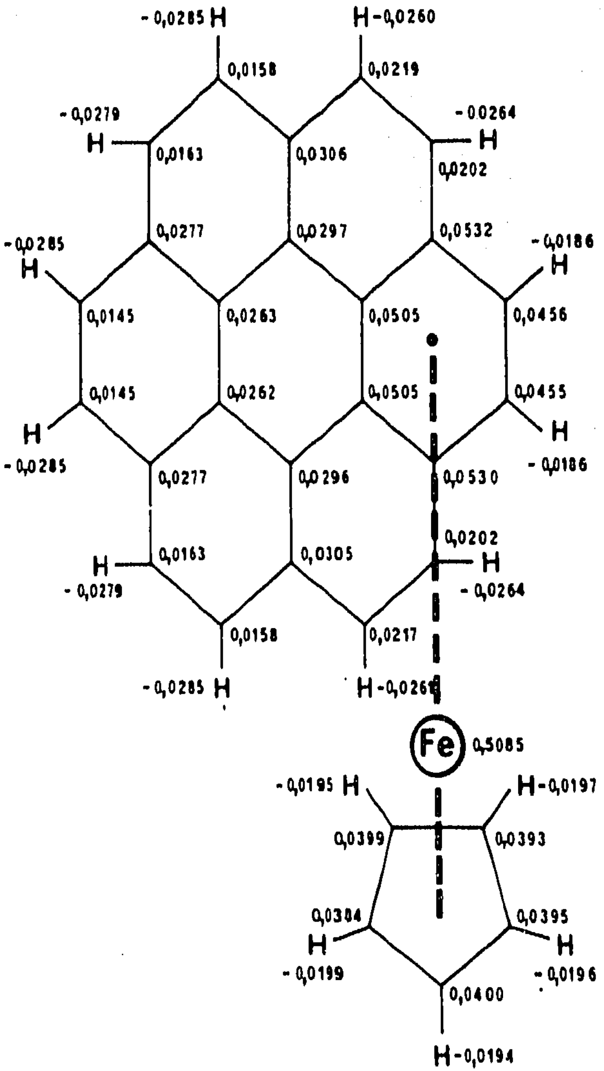
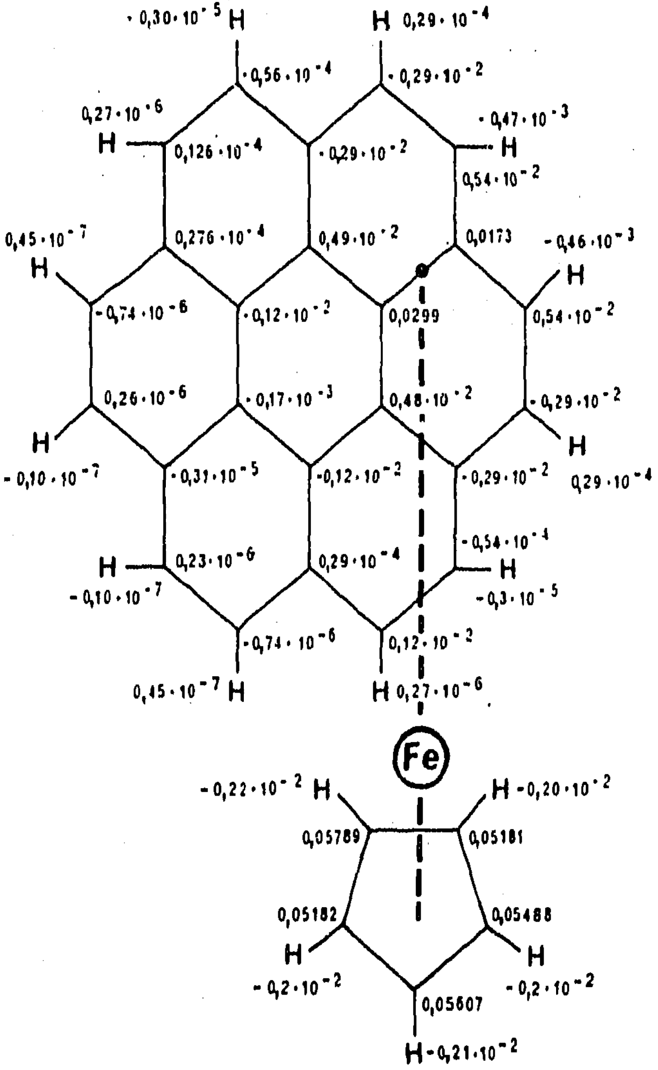


Fig. 4b. Charge distributions in structure II (calculated according to Löwdin [19]).



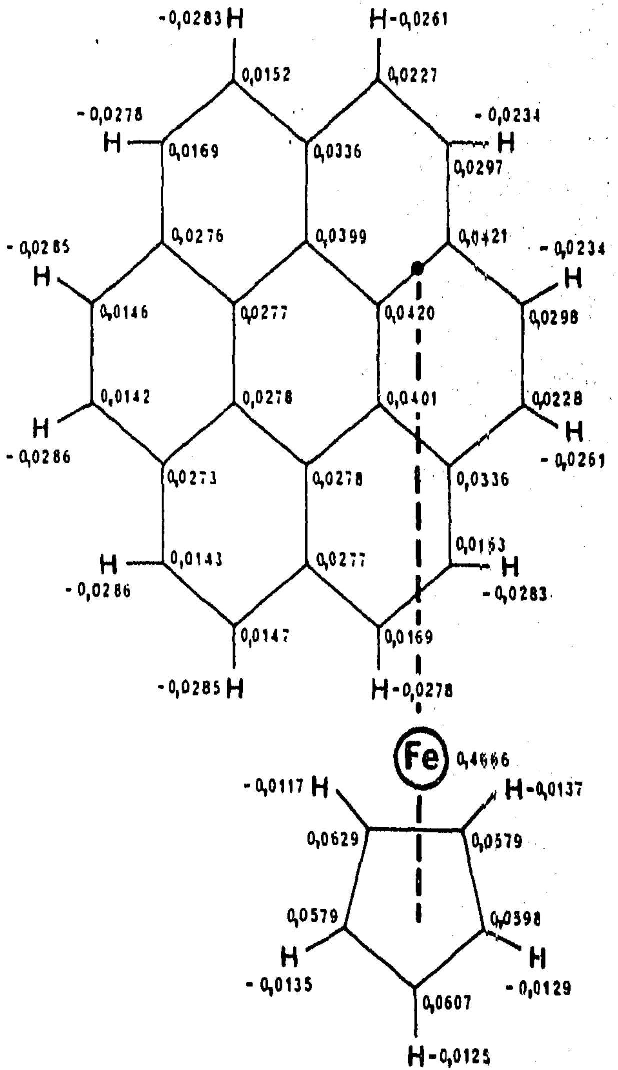


Fig. 5a. Mulliken overlap populations of all C and H atoms with the iron atom in structure IIa.
Fig. 5b. Charge distributions in structure IIa (calculated according to Löwdin [19]).

TABLE 5

OVER-ALL BOND ORDERS

Structure	Fe—coronene	Fe—Cp
I	0.1224	0.248
Ia	0.0690	0.267
II	0.1394	0.242
IIa	0.0547	0.273

gen atoms, calculated by Mulliken population analysis [18], are given in Fig. 2a to 5a, and show that the highest bond orders exist between the iron atom and the carbon atoms of that six-membered ring under which the iron atom is located. Negative values at atoms which are far from the iron atom mean that there is an antibonding interaction between this atom and the iron atom. The sum of the bond orders between the iron atom and all C atoms of coronene and all C atoms of the cyclopentadienyl ring are listed in Table 5. The values demonstrate again that the iron atom has the strongest bonding to the coronene system in structure II.

The charge distribution in all structures are given in Fig. 2b to 5b. In all cases the net charge at the iron atom calculated according to Löwdin [19] is positive (Table 6).

From the values in Table 6 the electrostatic interaction energies can be calculated according to the equation

$$E_{\text{electrost.}} = \sum_{i<j} \frac{q_i \times q_j}{r_{ij}}$$

The results of these calculations are listed in Table 7 and demonstrate that the lowest electrostatic interaction energies are calculated for structure II.

The final configurations of the iron atom in the four calculated structures are given in Table 8.

The numerical values of the calculations reported in this paper, which could possibly be improved by optimisation of structural parameters, e.g. the distances between the iron atom and both ring systems, confirm that structure II should have the greatest stability, thus supporting the spectroscopical results.

To investigate the influence of substituents at ferrocene in this reaction, we treated 1,1′-dimethyl-ferrocene, 1,2,3,4,1′,2′,3′,4′-octamethylferrocene and 1,1′-diacetylferrocene with coronene in methylcyclohexane in the presence of $AlCl_3$

TABLE 6

CHARGE DISTRIBUTIONS IN THE DIFFERENT [coronene—Fe—Cp]$^+$ STRUCTURES

Structure	Charge at		
	Coronene	Fe	Cp
I	0.3744	0.5080	0.1176
Ia	0.2995	0.4759	0.2246
II	0.3925	0.5085	0.0990
IIa	0.2985	0.4666	0.2349

TABLE 7

ELECTROSTATIC INTERACTION ENERGIES

Structure	$E_{\text{electrost.}}$	
	a.u.	eV
I	0.09427	2.565
Ia	0.10116	2.752
II	0.09262	2.520
IIa	0.10231	2.783

TABLE 8

CONFIGURATION OF THE IRON ATOM IN THE DIFFERENT [coronene—Fe—Cp]$^+$ STRUCTURES

Structure	Fe configuration		
	d	*s*	*p*
I	7.4833	0.0002	0.0084
Ia	7.4153	0.1094	0.0003
II	7.4069	0.0082	0.0002
IIa	7.4026	0.1305	0.0003

and Al. Using 1,1'-dimethylferrocene we obtained a 10% yield of π-coronene-π-methylcyclopentadienyliron hexafluorophosphate. Octamethylferrocene and 1,1'-diacetylferrocene did not react at all. Thus the effect of substituents at ferrocene on ligand exchange reactions with coronene show great similarities to the corresponding reactions with benzene [20].

We also tried to coordinate more than one CpFe group to coronene by further ligand exchange. Reactions of [coronene—Fe—Cp]PF_6 with an excess of ferrocene in the presence of $AlCl_3$ and Al powder were unsuccessfull. Neither alteration of the molar ratios of the reactants nor variations in reaction temperature (50—190°C), solvent (cyclohexane, methylcyclohexane, decaline) or reaction time (up to 90 h) yielded products with more than one CpFe group per molecule. However, using the method described for the preparation of [coronene—Fe—Cp]$^+$, but with a prolonged reaction time (16 h), the work-up with KPF_6 gave an orange product. The ^1H NMR showed two different signals for Cp and a different pattern of aromatic proton resonances. Fractional precipitation by adding ether to an acetonitrile solution revealed the presence of at least two species. Unfortunately the products could not be isolated analytically pure. Further attempts to poly-coordinate coronene with CpFe-moieties are in progress.

Experimental

^1H NMR spectra were recorded on a Varian EM 390 spectrometer, while ^{13}C NMR spectra were recorded on a Bruker WH 270 spectrometer. Coronene * was recrystalled twice from toluene (99.5% purity as analyzed by GLC). Ferrocene,

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* The coronene was available in the institute. We will be glad to provide small quantities to other research workers.

aluminium chloride and aluminium powder were used as purchased. 1,1'-dimethylferrocene, 1,2,3,4,1',2',3',4'-octamethylferrocene and 1,1'-diacetylferrocene we prepared as described in the literature [21—23]. Solvents such as cyclohexane, methylcyclohexane and decaline were dried and distilled from sodium under argon just before use.

π-Coronene-π-cyclopentadienyliron hexafluorophosphate. Coronene (3.0 g, 10 mmol), ferrocene (5.6 g, 30 mmol) $AlCl_3$ (0.8 g, 60 mmol) and Al powder (0.81 g, 30 mmol) were refluxed under argon in methylcyclohexane (100 ml) for 5 h. The mixture was cooled and ice (25 g) added. The organic layer was separated and extracted with water (3 × 100 ml). The combined aqueous phase was washed with cyclohexane (2 × 30 ml) and then filtered into a concentrated solution of potassium hexafluorophosphate. The precipitated hexafluorophosphate salt (2.8 g, 49%) was recrystalled from acetone/ether as dark-red needles, m.p. 120°C (dec.). (Found: C, 61.40; H, 3.11; Fe 9.75. $C_{29}H_{17}F_6FeP$ calcd.: C, 61.51; H, 3.03; Fe, 9.86%.) It is soluble in acetone, THF, HMPT and acetonitrile, and slightly soluble in nitrobenzene and ethyl acetate; the solutions are highly light-sensitive.

π-Coronene-π-methylcyclopentadienyliron hexafluorophosphate. The preparation was performed as described above. The yield of the hexafluorophosphate salt (red needles) was 0.58 g (10%), m.p. 124°C (dec.). (Found: C, 62.27; H, 3.42; Fe, 9.50. $C_{30}H_{19}F_6FeP$ calcd.: C, 62.09; H, 3.30; Fe, 9.62%.)

Acknowledgements

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References

1 A.N. Nesmeyanov, N.A. Vol'kenau and I.N. Bolesova, Dokl. Akad. Nauk SSSR, 140 (1963) 615; Tetrahedron Lett., (1963) 1725.
2 A.N. Nesmeyanov, N.A. Vol'kenau and I.N. Bolesova, Dokl. Akad. Nauk SSSR, 166 (1966) 607.
3 C.C. Lee, R.G. Sutherland and B.J. Thomson, J. Chem. Soc., Chem. Commun., (1972) 907.
4 W.H. Morrison, Jr., E.Y. Ho and D.N. Hendrickson, J. Amer. Chem. Soc., 96 (1974) 3603.
5 R.G. Sutherland, S.C. Chen, J. Pannekoek and C.C. Lee, J. Organometal. Chem., 101 (1975) 221.
6 A.N. Nesmeyanov, N.A. Vol'kenau, L.S. Shilovtseva and V.A. Petrakova, J. Organometal. Chem., 61 (1973) 329.
7 N. Jonathan, S. Gordon and B.P. Dailey, J. Chem. Phys., 36 (1962) 2443.
8 E. Clar, The Aromatic Sextet, Wiley Interscience Publ., London, 1972.
9 F.D. Mango and J.H. Schachtschneider, The Catalysis of Symmetry Forbidden Reactions, in B.N. Schrauzer (Ed.), Transition Metals in Homogeneous Catalysis, Marcel Dekker, Inc., New York, 1971.
10 H. Basch, D. Viste and H.B. Gray, J. Chem. Phys., 44 (1966) 10.
11 J.W. Richardson and W.C. Nieuwport, J. Chem. Phys., 36 (1962) 1057.
12 J.W. Richardson, R. Powell and W.C. Nieuwport, J. Chem. Phys., 38 (1963) 796.
13 C. Zerner, Phys. Rev., 36 (1930) 51.
14 J.C. Slater, Phys. Rev., 36 (1930) 57.
15 M. Wolfsberg and L. Helmholtz, J. Chem. Phys., 20 (1952) 837.
16 J.K. Fawcett and J. Trotter, Proc. Roy. Soc. A, 289 (1965) 66.
17 P. Schuster, Monatsh. Chem., 100 (1969) 1033.
18 R.S. Mulliken, J. Chem. Phys., 23 (1955) 1833; 23 (1955) 2338.
19 P.O. Löwdin, J. Chem. Phys., 18 (1950) 365.
20 D. Astruc and R. Dabard, J. Organometal. Chem., 111 (1976) 339; see literature cited.
21 P.L. Pauson, J. Amer. Chem. Soc., 76 (1954) 2187.
22 G. Schmitt and S. Özman, Chem. Z., 100 (1976) 143.
23 M. Rosenblum and R.B. Woodward, J. Amer. Chem. Soc., 80 (1958) 5443.