

THE CHEMISTRY OF FERROCENE AND RELATED COMPOUNDS

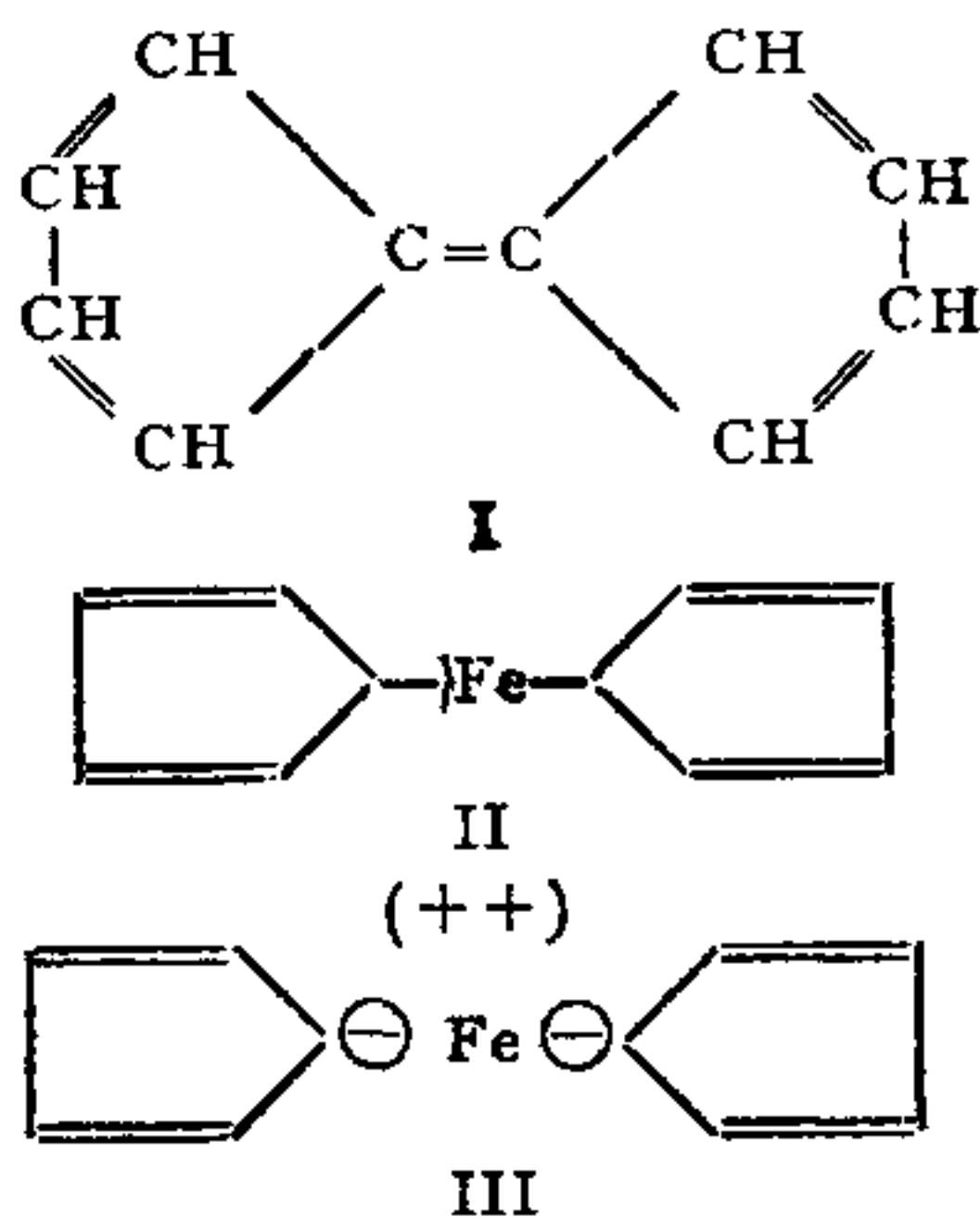
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As a possible route to fulvalene (I), Kealy and Pauson¹ studied the reaction between cyclopentadienylmagnesium bromide and anhydrous ferric chloride but obtained an orange crystalline compound which melted at 173-74° and was analysed for C₁₀H₁₀Fe. This compound was soluble in many organic solvents and in addition, was found to be remarkably stable towards acids and bases in striking contrast to the failure of earlier attempts to prepare compounds containing only carbon, hydrogen and iron. The authors suggested that the compound was formed according to the equation

$$2 R MgBr + FeCl_2 \rightarrow R FeR + MgBr_2 + MgCl_2$$

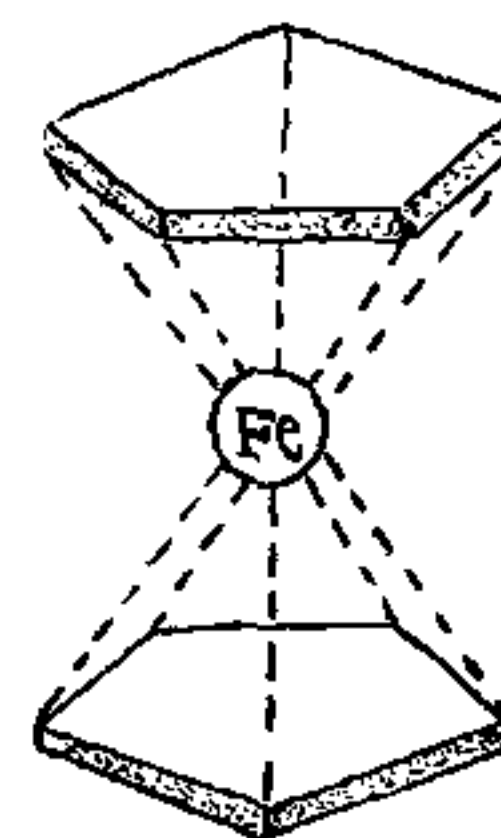
after initial reduction of the ferric salt by the Grignard reagent. They formulated it as biscyclopentadienyliron (II) and attributed the stability of the compound to the tendency of the cyclopentadienyl group to become aromatic by acquisition of a negative charge, resulting in important contributions from the resonance form (III) and intermediate forms:



The isolation of the same compound was reported almost simultaneously by Miller *et al.*² who obtained it by reaction of cyclopentadiene at 300° with reduced iron. Biscyclopentadienyliron has since been prepared in excellent yield by reacting the pyridine complex of ferrous acetylacetonate with cyclopentadienylmagnesium bromide.³

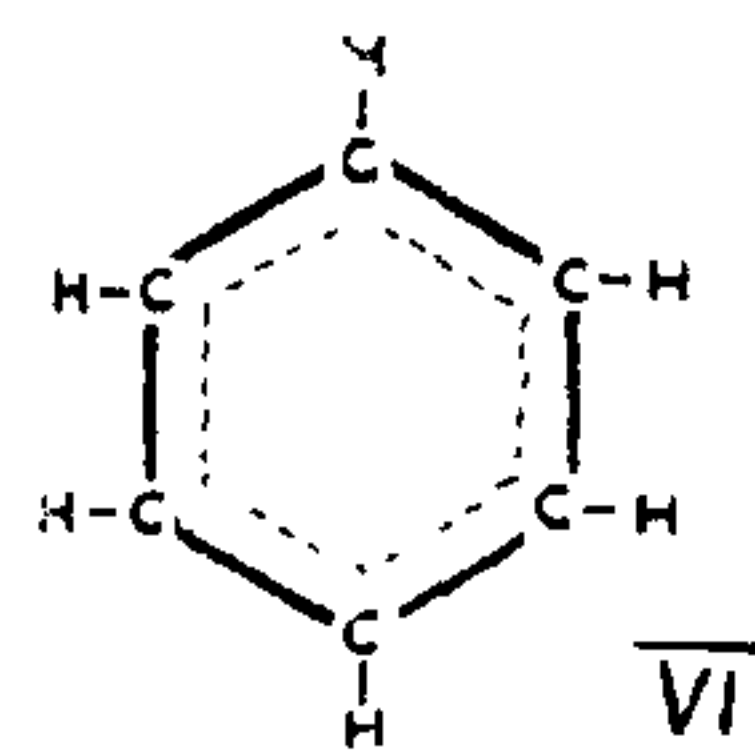
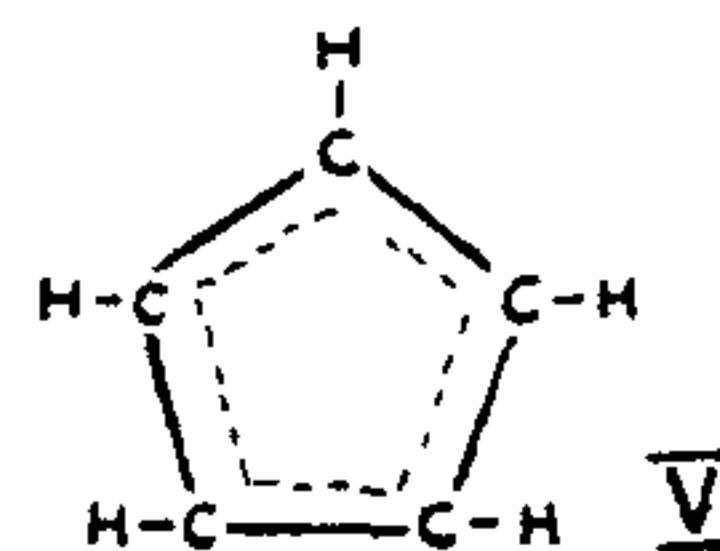
Woodward and co-workers⁴ found that the compound was diamagnetic ($\chi^{25^\circ} = -125 \times 10^{-6}$ C.G.S.U.) and that its infra-red spectrum contained in the 3-4 μ region a single sharp band at 3.25 μ indicative of the presence of C-H bonds of one type only in the molecule. The ultra-violet spectrum showed maxima at

326 m μ and 440 m μ and the dipole moment was almost zero. The compound was easily oxidised to a blue cation [Fe(C₅H₅)₂]⁺ which was isolated in the form of its double salts. In the light of these properties, Woodward *et al.*⁴ preferred structure IV according to which two cyclopentadienyl units are bound covalently and symmetrically to ferrous iron. This structure has since been confirmed by X-ray structural studies.⁵⁻⁷



IV

Woodward *et al.*⁸ while leaving open the question of the electronic structure of biscyclopentadienyliron, thought it likely that the equivalent ring bonds connecting the equivalent C-H₂ groups in the molecule might be of effective order greater than one and might result in a situation as represented in V and similar to what obtains in benzene (VI).



This consideration led them to conclude that biscyclopentadienyliron might behave as an aromatic substance and to study some of its reactions which, indeed, established the aromatic nature of the compound which in consequence was named ferrocene.

Ferrocene does not have any properties typical of unsaturated compounds in spite of its formal unsaturation. It does not undergo a Diels-Alder reaction with maleic anhydride and cannot be hydrogenated. With acetyl chloride, in presence of aluminium chloride, it yields a red diacetyl derivative which gives a dioxime and which can be oxidised to a dicarboxylic acid; with β -chloropropionyl chloride and phthalic anhydride, the reaction is similar. With acetic anhydride in anhydrous hydrogen fluoride, monoacetylferrocene⁹ is obtained. Ferrocene undergoes sulphonation and also condensation with aliphatic and aromatic aldehydes.⁹ Strongly oxidising species such as NO_2^+ , Br^+ effect oxidation to the cation, called ferricinium ion, instead of substitution. The infra-red carbonyl absorption maxima for some ketonic derivatives of ferrocene are almost the same as in the corresponding derivatives of benzene. The first dissociation constant of ferrocene dicarboxylic acid ($\text{pK}_1 3.1 \times 10^{-7}$) is nearly the same as the dissociation constant of benzoic acid ($\text{pK} 2.4 \times 10^{-7}$).

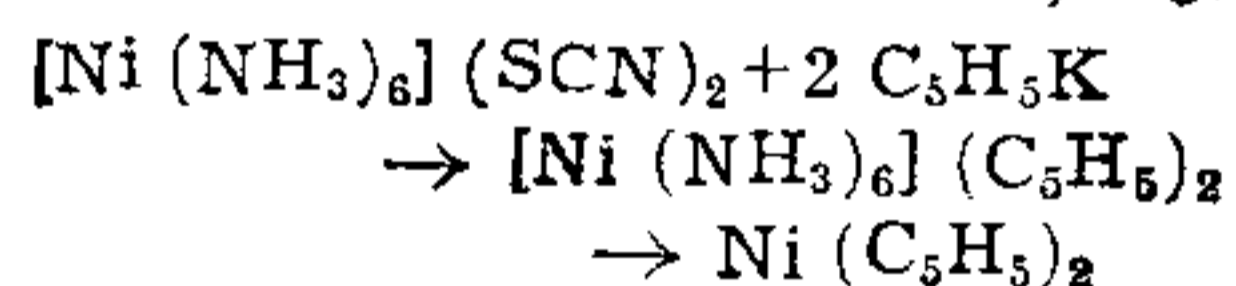
From the vapour pressures and vapour densities, the normal boiling point (249°), molecular weight (186), heats of sublimation (16.8 k. cal./mole) and vaporisation (11.3 k. cal./mole) and the triple point (183°) have been calculated.¹⁰ From the measured heat of combustion of ferrocene, the combined energies of resonance of the five-membered rings and that of C-Fe bonds have been calculated¹¹ to be 113 k. cal. Such a high value accords with the stability of the compound. Accurate bond lengths are not available but the indications⁵⁻⁷ are C-C 1.4 Å and Fe-C 2.0 Å.

Phenylcyclopentadienyl Grignard compounds react similarly to cyclopentadienylmagnesium bromide and a series of ferrocenes substituted by phenyl groups in both rings has been prepared.¹² Monophenylferrocene has been prepared by use of a mixture⁵ of cyclopentadiene and phenylcyclopentadiene. The preparation of dibenzoferrrocene (bisindenyliron) and bisindenyl cobalt salts has also been described.¹³ The preparation of 1, 1'-dibenzhydrylferrocene¹² directly from benzhydrylcyclopentadiene and also starting from diacetyl ferrocene has provided proof that both rings are substituted in the diacetylation of ferrocene. Ferrocene¹⁴ and also ferricinium¹⁵ salts undergo direct arylation when treated with diazonium salts. Both mono- and polyarylated ferrocenes are formed.

The formation of compounds analogous to ferrocene seems to be a general property of transitional elements which have two vacant

or singly occupied *d* orbitals that can be used in bonding. These compounds are of the type $[(\text{C}_5\text{H}_5)_2\text{Mn}]\text{X}_{n-2}$ where *n* represents the oxidation state of the metal M and X is a uni-negative ion. Derivatives of Sc^{16a} , $\text{Ti}^{21,16b}$, $\text{V}^{21,16b,25}$, Cr^{17} , Mn^{18} , $\text{Co}^{3,9,20}$, $\text{Ni}^{3,21,12}$, Y^{16a} , $\text{Zr}^{21,16b}$, Nb^{16b} , Ru^{23} , Rh^{24} , La^{16a} , Ce^{16b} , Ta^{16b} , and Ir^{24} have so far been reported. Two cyclopentadienyl compounds of Mn exist of which one seems to have a sandwich type structure like ferrocene and the other a metal alkyl structure like diethyl zinc. A magnesium derivative¹⁸ of cyclopentadiene is also known and behaves as a metal alkyl.

These compounds are in general prepared either by reacting a metal halide or a metal acetylacetonate with cyclopentadiene magnesium bromide or by the vapour phase reaction of cyclopentadiene with a metal carbonyl. An elegant variation of the former procedure involves the reaction²⁰ in liquid ammonia between an alkali metal salt of cyclopentadiene and the appropriate metal amine salt followed by removal of ammonia *in vacuo*, e.g.,



Another variation¹⁸ of the same method is to react sodium cyclopentadiene with a metal halide in tetrahydrofuran medium.

The similarity of the structures of $\text{Co}(\text{C}_5\text{H}_5)_2$ and $\text{Ni}(\text{C}_5\text{H}_5)_2$ to that of ferrocene has been confirmed²⁰ by X-ray diffraction studies. The infra-red and ultra-violet absorption spectra of the Ru^{23} and Ni^3 compounds are similar to those of ferrocene. The magnetic susceptibilities of the Co and Ni compounds have been measured.³ Many of these compounds are easily oxidised to the corresponding unipositive cations, e.g., $\text{Ni}(\text{C}_5\text{H}_5)_2$ to $[\text{Ni}(\text{C}_5\text{H}_5)_2]^+$. The polarographic behaviour²⁶ of ferrocene and other biscyclopentadienyl compounds has been studied. The mass spectra²⁷ of a series of neutral biscyclopentadienyl compounds have been investigated recently with a view to correlate the spectra with molecular structure. Recently, the first representative of a biscyclopentadienyl metal carbonyl has been reported.²⁸

As regards the electronic structure of ferrocene, a simple ten-bonded structure is excluded since only 18 electrons are available, 5 from each of the two cyclopentadienyl units and 8 from the iron atom. In proposing the structure IV for ferrocene, Woodward *et al.*⁴ suggested that the iron atom could attain the configuration of the inert gas krypton by

utilising these 18 electrons. The filling of vacant metal orbitals in this manner is now regarded unlikely in view of the aromatic character of ferrocene which indicates that the π electrons are not appreciably withdrawn from the rings. Furthermore, the formation of cyclopentadienyl derivatives of transitional elements like Ti, Zr, V, etc., where sufficient electrons are not available for completion of the configuration of krypton, cannot be explained on the basis of such a view. The type of bonding involved in ferrocene and other biscyclopentadienyl compounds has been interpreted by molecular orbital methods by Jaffé,²⁹ Dunitz and Orgel^{6,31} and Moffitt.³⁰ According to Moffitt, the structures of these compounds involve a primary two electron bond between each ring and the metal atom and a mixing and splitting of the $3d_z^2$ and $4s$ orbitals of the metal atom under the influence of the field of the π electrons of the cyclopentadienyl rings. In the compounds there are four d orbitals of the metal atom at approximately the same energy as the unperturbed d orbitals, two of which are used for metal to ring bonding and two ds hybrid orbitals, one below these four d orbitals and one above at about the level of the $4p$ orbitals. The magnetic properties of many of the biscyclopentadienyl compounds have been explained in terms of such structures.

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