FERROCENE AND RELATED COMPOUNDS

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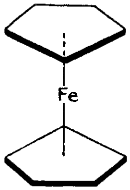
The discovery that iron can react with *cyclo*pentadiene to form an organometallic compound of unusual stability [1, 2] was rapidly followed by the recognition that this di*cyclo*pentadienyliron or "ferrocene" [3] is equally remarkable for its unusual structure [4, 5] and its aromatic character.[3] To the theoretical interest in this novel compound may now be added the practical interest arising from its usefulness in reducing carbon deposition and smoke formation when added to fuel oils.[6]

The structure of ferrocene, $(C_5H_5)_2Fe$, is represented diagrammatically in Fig. 1. It has been described by the American authors as a "sandwich" structure [7] and by the German workers, perhaps more appropriately, as a "Doppelkegelstruktur".[8] Its essential feature is the symmetrical binding of the central metal atom to all five carbon atoms of each ring. Only a single covalent bond however links the metal to each ring so that the structure cannot properly be described in classical valency-bond terminology. A *d*-orbital of the metal must be available for such bonding—a condition satisfied by the transition metals, all of which have now been shown capable of yielding such *cyclo*pentadienyl derivatives. The same geometrical arrangement is, however, also assumed by di*cyclo*pentadienylmagnesium [9] which cannot use *d*-orbitals of the metal and must possess considerable ionic character.



(I)

Fig. 1

There is also known a group of compounds with only one *cyclo*pentadienyl ring linked to a metal atom to which other groups such as CO are also attached. These may be regarded as intermediate between the di*cyclo*pentadienyl derivatives and the metal carbonyls which are, apart from the cyanides, the first known transition-metal compounds having metal–carbon bonds. The *iso*nitrile complexes which have attracted attention in recent years are strictly analogous to the carbonyls. But simple alkyl and aryl derivatives of the metals of Group VIII, other than platinum, are mostly too unstable to be isolated if formed at all. Our present knowledge of such

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[1] Kealy and Pauson, *Nature*, 1951, **168,** 1039.

[2] Miller, Tebboth, and Tremaine, *J.*, 1952, 632.

[3] Woodward, Rosenblum, and Whiting, *J. Amer. Chem. Soc.*, 1952, **74,** 3458.

[4] Wilkinson, Rosenblum, Whiting, and Woodward, *ibid.*, p. 2125.

[5] Fischer and Pfab, *Z. Naturforsch.*, 1952, **7**b, 377.

[6] Arimoto, Corzilius, Lamb, and Melby, Paper read at the 127th Meeting of the American Chemical Society (March, 1955).

[7] Wilkinson, *J. Amer. Chem. Soc.*, 1952, **74,** 6148.

[8] Fischer and Hafner, *Z. Naturforsch.*, 1954, **9**b, 503.

[9] Weiss and Fischer, *Z. anorg. Chem.*, 1955, **278,** 219

compounds is confined to very indirect evidence of the formation of organo-iron compounds at temperatures below $-40°$,[10] even less convincing evidence for nickel compounds,[11] and the more stable, but complex and rather poorly characterised, arylcobalt halides.[12]

The other transition metals form carbon compounds of varying stability and complexity from the monophenyl derivatives of quadrivalent titanium [13] to the polyphenyl-chromium and -molybdenum compounds studied by Hein [14] and the typical alkyl derivatives of bivalent manganese.[15] Whether the aryl-vanadium, -niobium, and -tantalum polyhalides [16] can truly be regarded as organometallic compounds is uncertain.

The di*cyclo*pentadienyl derivative of bivalent manganese is similar in reactivity to its alkyls and its magnetic properties are compatible with an ionic formulation although, like the magnesium compound, it appears to have ferrocene-like geometry.[17] The same may be true of the bivalent titanium and vanadium derivatives which have not yet been described in detail, but remarkably stable *cyclo*pentadienyl derivatives, which must be more closely analogous to ferrocene in bond type, can be formed by these three elements in other valency states.

Other hydrocarbons which, like *cyclo*pentadiene, give rise to stable anions may be expected to yield similar, though perhaps not equally stable, derivatives of the transition metals and indeed the closest analogues of ferrocene known at present are undoubtedly the compounds [18] derived from acetylenes and exemplified by $(C_6H_5C\vdots C)_2Fe(CO)_4$. This compound is, however, in contrast to ferrocene, a typical hexaco-ordinated derivative, presumably having d^2sp^3 bond hybridisation (octahedral structure) and inert-gas configuration of electrons. Other acetylene derivatives of cobalt [19] and iron [18, 20] which are formed without replacement of the acidic hydrogen (*i.e.*, also from disubstituted acetylenes) cannot be regarded as analogous in the same sense; they are more likely to be analogues of the π-bonded olefin complexes which are best known among the platinum metals but include such substances as butadiene iron tricarbonyl reported by Reihlen *et al.*[21] It is not entirely clear at present whether the apparent parallelism between

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[10] Job and Reich, *Compt. rend.*, 1922, **174**, 1358; Champetier, *Bull. Soc. chim. France*, 1930, **47**, 1131.

[11] Schlenk and Weichselfelder, *Ber.*, 1923, **56**, 2230; Weichselfelder, *Annalen*, 1926, **447**, 64; *Ber.*, 1929, **62**, 769.

[12] Ingles and Polya, *J.*, 1949, 2280; Briggs and Polya, *J.*, 1951, 1615.

[13] Herman and Nelson, *J. Amer. Chem. Soc.*, 1952, **74**, 2693; 1953, **75**, 3877, 3882.

[14] Hein, *Z. angew. Chem.*, 1938, **51**, 503. These compounds have recently been re-investigated by Zeiss (paper presented at the 14th Congress of I.U.P.A.C., Zürich, July, 1955).

[15] Jones and Gilman, *Chem. Rev.*, 1954, **54**, 835.

[16] Mertes and Fleck, *Ind. Eng. Chem.*, 1915, **7**, 1037; Funk and Niedlerländer, *Ber.*, 1928, **61**, 1385; Afanasyev, *Chem. and Ind.*, 1940, **59**, 631.

[17] Weiss and Fischer, *Z. Naturforsch.*, 1955, **10**b, 58.

[18] Whiting, Symposium on Organometallic Compounds, Manchester, April, 1955.

[19] Sternberg, Greenfield, Friedel, Wotiz, Markby, and Wender, *J. Amer. Chem. Soc.*, 1954, **76**, 1457.

[20] Reppe and Vetter, *Annalen*, 1953, **582**, 133.

[21] Reihlen, Gruhl, Hessling, and Pfrengle, *ibid.*, 1930, **482**, 161.

this butadiene derivative and the *cyclo*pentadienyl-metal carbonyls should be regarded as entirely fortuitous.

The earliest discovery among the *cyclo*pentadienyl derivatives of the transition metals, that of *cyclo*pentadienylcopper bistripropylphosphine,[22] has been completely neglected. Present interest in these compounds arises from the discovery of ferrocene, and extension to other metals became possible as more and more powerful methods of preparation were evolved.

Preparation

Of the two methods originally used,[1, 2] only the Grignard method is directly adaptable to other cases and most of the improved methods of preparation may be considered as extensions of this approach.

The reaction between *cyclo*pentadienylmagnesium bromide and ferric chloride was first carried out in the hope that the metal salt would oxidise the Grignard reagent to dihydrofulvalene (di*cyclo*pentadienyl) in the manner in which many transition-metal halides effect oxidation ; *e.g.*, phenyl- and benzyl-magnesium halides to diphenyl and dibenzyl respectively :

$$6RMgX + 2FeX_3 = 2Fe + 3R\text{–}R + 6MgX_2$$

The desired product was never isolated although the formation of di*cyclo*pentadienyliron does involve partial reduction of the ferric salt by the Grignard reagent. The production of ferrocene (I), which was discovered thus accidentally, can then be written as involving ferrous chloride :

$$2C_5H_5MgBr + FeCl_2 = \underset{\text{(I)}}{(C_5H_5)_2Fe} + MgBr_2 + MgCl_2$$

No evidence exists however that the reaction may not also or alternatively proceed *via* the ferricinium salt (II) :

$$2C_5H_5MgX + FeX_3 = \underset{\text{(II)}}{(C_5H_5)_2FeX} + 2MgX_2$$

followed by reduction of the salt (II) by excess of Grignard reagent.

The salt (II) can in fact be obtained quite readily by oxidation of ferrocene. The isolation of ionic ferricinium compounds [4, 5] by the precipitation of various salts from aqueous solution demonstrated the stability of such organometallic ions in water and thus led directly to the preparation of the analogous di*cyclo*pentadienylcobalt(III) salts.[5, 7, 23] These are isoelectronic with ferrocene and at least equally stable.

An important factor in the success of the preparation of ferrocene by this method is the solubility of ferric chloride in organic solvents. For the preparation of the cobalticinium salts Wilkinson [7] had recourse to the similarly soluble acetylacetone complex of cobalt(III). The corresponding ruthenium(II) derivative yielded di*cyclo*pentadienylruthenium,[24] and ferrocene itself can be prepared in high yield from the ferrous acetylacetone–

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[22] van Peski and van Melsen, U.S.P. 2,105,349.

[23] Fischer and Jira, *Z. Naturforsch.*, 1953, **8b**, 1.

[24] Wilkinson, *J. Amer. Chem. Soc.*, 1952, **74**, 6146.

dipyridine complex.[25] The disadvantage of this method is the need to employ large quantities of *cyclo*pentadienylmagnesium bromide, part of which is used up by reaction with the chelating agent. On the other hand the insoluble dihalides of iron, cobalt, and nickel react relatively poorly. Nevertheless, Fischer and Pfab [5] secured di*cyclo*pentadienylcobalt(III) salts by reaction of *cyclo*pentadienylmagnesium bromide with cobaltous bromide followed by oxidation with peroxide. Similarly, di*cyclo*pentadienylnickel was first obtained in low yield from nickelous bromide.[26] A considerably higher yield was secured by the use of the acetylacetone complex [25, 27] but no further improvement results in this case by substituting the more reactive potassium salt of *cyclo*pentadiene for the Grignard reagent. However, an important modification based on the use of an alkali-metal derivative of *cyclo*pentadiene in liquid ammonia was developed by Fischer and Jira. They employed hexamminonickel thiocyanate which reacted to give an intermediate regarded as the hexamminonickel salt (III) of *cyclo*pentadiene : [28]

$$2C_5H_5K(\text{or Na or Li}) + Ni(NH_3)_6(SCN)_2 \\ = 2K(\text{or Na or Li})SCN + [Ni(NH_3)_6]^{++}(C_5H_5^-)_2 \quad \text{(III)}$$

When this compound was heated it lost ammonia, giving di*cyclo*pentadienylnickel. The method proved capable of extension to yield for the first time the neutral di*cyclo*pentadienyl derivatives of cobalt, chromium, and manganese.[28, 29, 30]

Before this work *cyclo*pentadienylpotassium had only been obtained in benzene suspension by direct interaction between the metal and *cyclo*pentadiene. Sodium does not react in these conditions or in ether, but reacts in solvents in which the product is more soluble such as methylal, 1 : 2-dimethoxyethane, and tetrahydrofuran. The sodium salt is particularly soluble in the last solvent and its use led to a further improvement in the method of obtaining the transition-metal derivatives and made practicable the use of the insoluble halides of these metals.[31, 32]

It is of theoretical interest that, in place of using a metal salt of *cyclo*pentadiene, one can treat this hydrocarbon with metal halides in presence of an organic base, *e.g.*, triethylamine or pyridine, but the yields by this method are poor.[33]

The Carbonyl Method.—Entirely different methods of preparation are the direct thermal process and the carbonyl method. The original discovery

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[25] Wilkinson, Pauson, and Cotton, *J. Amer. Chem. Soc.*, 1954, **76**, 1970.

[26] Thomas, U.S.P. 2,680,758 (*Chem. Abs.*, 1955, **49**, 4725).

[27] Wilkinson, Pauson, Birmingham, and Cotton, *J. Amer. Chem. Soc.*, 1953, **75**, 1011.

[28] Fischer and Jira, *Z. Naturforsch.*, 1953, **8**b, 217.

[29] *Idem*, *ibid.*, p. 327.

[30] Fischer and Hafner, *ibid.*, p. 444.

[31] Wilkinson and Birmingham, *J. Amer. Chem. Soc.*, 1954, **76**, 4281.

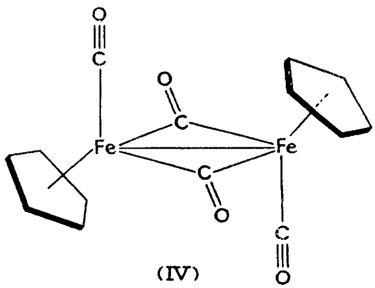
[32] Wilkinson and Cotton, *Chem. and Ind.*, 1954, 307.

[33] Birmingham, Seyferth, and Wilkinson, *J. Amer. Chem. Soc.*, 1954, **76**, 4179.

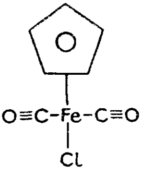
of ferrocene by the former process [2] has not been followed by further developments of the method. The yields were too low compared with those of other methods and although iron in any reactive form could probably react directly with *cyclo*pentadiene, the temperature required (375°) would almost certainly preclude the use of a similar method to obtain the less stable derivatives of other metals.

Perhaps not unrelated to this method, however, is the direct interaction of *cyclo*pentadiene with metal carbonyls. The process was first applied to iron carbonyl in several industrial laboratories and was used by Wilkinson as a flow method [34] to obtain di*cyclo*pentadienylchromium (simultaneously with Fischer and Hafner's preparation of that compound). In this form of the method the mixed vapours of *cyclo*pentadiene and the metal carbonyl are passed through a heated tube in a stream of inert carrier gas, and the products are condensed on a cold-finger condenser. These conditions give the di*cyclo*pentadienyl derivatives of chromium, cobalt, iron, and (in very low yield) nickel directly, although the *cyclo*pentadienylmetal carbonyls are the main products obtained from molybdenum and tungsten carbonyls. At lower temperatures, in the liquid phase, iron, cobalt, and chromium likewise afford intermediate *cyclo*pentadienyl carbonyls which may be converted into the di*cyclo*pentadienyl compounds at higher temperature. The most convenient mode of operation is to heat the metal carbonyl to the appropriate temperature in excess of di*cyclo*pentadiene which will gradually depolymerise. The monomer probably reacts as rapidly as it is formed so that in spite of the monomer's volatility the process is successful at atmospheric pressure.

The first product thus formed [35, 36] from the iron carbonyls is di*cyclo*pentadienyldi-iron tetracarbonyl (IV). This decomposes above 200° to ferrocene, no additional *cyclo*pentadiene being required. *cyclo*Pentadienyliron dicarbonyl chloride (V) obtained by oxidation of (IV) affords ferrocene in the same manner. The mechanism whereby a *cyclo*pentadienyl group becomes transferred from one iron atom to another in these processes is not yet understood.



(IV)



(V)

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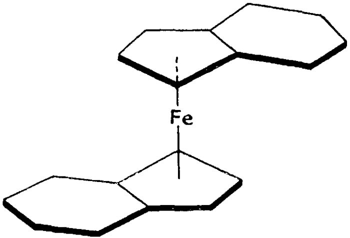
[34] Wilkinson, *J. Amer. Chem. Soc.*, 1954, **76**, 209.

[35] Piper, Cotton, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1955, **1**, 165.

[36] Hallam, Mills, and Pauson, *ibid.*, p. 313.

For the preparation of the di*cyclo*pentadienyl derivatives the carbonyl method appears to offer little advantage now over the other methods. Its superiority in the case of chromium is largely offset by the inaccessibility of the chromium carbonyl required as starting material, so that even here the reaction of *cyclo*pentadienylsodium with either chromic or chromous chloride in tetrahydrofuran is more convenient, at least for small amounts. That indeed is the method of choice in the majority of cases, for both simplicity and yield.

The original Grignard approach is, however, probably superior for the preparation of metal derivatives from substituted *cyclo*pentadienes. These do not react as smoothly with sodium, but readily afford the required reagent when treated with ethylmagnesium bromide. The somewhat more reactive lithium derivatives obtained even more readily from the *cyclo*pentadiene derivative and an alkyl-lithium have been used successfully to afford several polyphenylferrocenes[37] as well as the di-indenyl derivatives of iron(II) (VI) and cobalt(III).[38] The liquid-ammonia method was more successful for the preparation of the cobalt(II) and nickel(II) derivatives.[39] These compounds obtained from indene are much less stable than the corresponding *cyclo*pentadiene derivatives and the failure to obtain similar compounds from fluorene is therefore understandable. The reaction of some highly substituted *cyclo*pentadienyl-lithium derivatives with ferric chloride likewise fails. Here the substituents appear to hinder only the reduction of the ferric ion, as the sodium salt of tetraphenyl*cyclo*pentadiene has been successfully converted into octaphenylferrocene by ferrous chloride in liquid ammonia.[40]



(VI)

Structure

The suggestion that the stability and properties of ferrocene are best explained by the pentagonal antiprism configuration (Fig. 1) already referred to[41] was first published independently by two groups of workers. The American authors[4] adduced only suggestive evidence, *viz.*, the diamagnetic

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[37] Pauson, *J. Amer. Chem. Soc.*, 1954, **76**, 2187.

[38] Pauson and Wilkinson, *ibid.*, p. 2024.

[39] Fischer, Seus, and Jira, *Z. Naturforsch.*, 1953, 8b, 692; Fischer and Seus, *ibid.*, p. 694.

[40] Weinmayr, *J. Amer. Chem. Soc.*, 1955, **77**, 3012.

[41] This structure was suggested to the author in September, 1951, by Dr. W. E. Doering.

nature, single C–H stretching frequency in the infrared region, and non-polar character of the substance ; Fischer and Pfab, however, were further able to support their suggestion very convincingly with X-ray crystallographic data demonstrating the centrosymmetric nature and compactness of the molecule.[5, 42] Somewhat more complete X-ray evidence was secured simultaneously by Eiland and Pepinsky [43] and especially by Dunitz and Orgel.[44] The latter school has recently completed a three-dimensional Fourier analysis.[45] An electron-density map of the complete molecule obtained from this work is shown in Fig. 2. Despite a somewhat large standard deviation (0·024 Å) the mean iron–carbon distance (2·044 Å) is in excellent agreement with values obtained [46, 47] in two electron-diffraction studies (2·06 ± 0·02 and 2·03 ± 0·02 Å). The mean carbon–carbon distance (1·403 Å : standard deviation 0·040 Å) is, however, significantly less than the values [46, 47] (1·44 and 1·43 ± 0·03 Å) obtained by electron-diffraction methods, but by analogy with benzene [48] a difference of this type is to be expected if the X-ray data are uncorrected for anisotropic thermal motion of the rings.

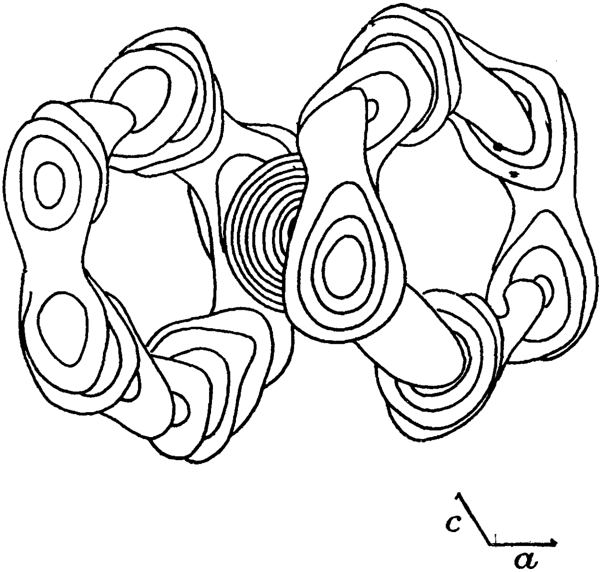

FIG. 2

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[42] Pfab and Fischer, *Z. anorg. Chem.*, 1953, **274**, 317.

[43] Eiland and Pepinsky, *J. Amer. Chem. Soc.*, 1952, **74**, 4971.

[44] Dunitz and Orgel, *Nature*, 1953, **171**, 121.

[45] Dunitz, Orgel, and Rich, unpublished results.

[46] K. Hedberg, Berndt, and Hamilton, unpublished results.

[47] Seibold and Sutton, personal communication.

[48] Cox, Cruickshank, and Smith, *Nature*, 1955, **175**, 766.

It has also been shown by electron diffraction [49] that the carbon–metal distance in di*cyclo*pentadienylnickel is larger than in ferrocene (2·18 Å, a symmetrical model being assumed) as was already suggested by the greater unit cell dimensions [42] and in conformity with the weaker ring–metal binding (see p. 403).

The original suggestions concerning the structure of ferrocene [4, 5] were based on the postulate that all the π-electrons of the *cyclo*pentadiene rings are used in bonding these to the iron atom, so that all its available electronic orbitals are filled to produce the configuration of the inert gas, krypton. Theoretical treatments which have supported this view [50] have been criticised by Moffitt.[51] It is difficult to visualise a geometric arrangement of the carbon orbitals which would permit the use of all the electrons or to justify the accumulation of negative charge on iron which this implies. From the experimental point of view, the aromatic substitution reactions imply a high electron availability at the carbon atoms in ferrocene, while the synthesis of di*cyclo*pentadienyltitanium dibromide [27] provided the first example of a very stable compound of the same class in which the inert-gas configuration was clearly unattainable. Di*cyclo*pentadienylnickel on the other hand has two more electrons than iron; if then an outer orbital had to be used to accommodate these they would be expected to enter the 5*s* orbital and be paired, whereas in practice the substance shows paramagnetism equivalent to two unpaired electrons.*

A more correct picture of the structure, which appears to have gained general acceptance, was first put forward by Dunitz and Orgel,[44] being based on the molecular-orbital treatment. With some corrections this has been amplified by Moffitt [51] who has also presented it in a form understandable to the experimentalist not trained in molecular-orbital theory. Dunitz and Orgel have more recently placed this treatment on a semi-quantitative basis [52] to show that it can account, not only for the magnetic properties, but also for the strength of the metal–ring bonds as calculated from the heats of combustion.

If we consider the five 3*d* orbitals of the metal, which are of three types

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[49] K. Hedberg and L. Hedberg, personal communication.

[50] Jaffé, *J. Chem. Phys.*, 1953, **21**, 156; Simonetta, *Ricerca sci.*, 1953, **23**, 1234 (*Chem. Abs.*, 1954, **48**, 1086).

[51] Moffitt, *J. Amer. Chem. Soc.*, 1954, **76**, 3386.

[52] Dunitz and Orgel, *J. Chem. Phys.*, 1955, **23**, 954.

* Since this account was written, the Reviewer has learnt from Drs. E. Ruch and E. O. Fischer that they have developed their theoretical views in greater detail. They maintain that in its present form their theory overcomes these objections. Dr. Ruch's calculations of the overlap integrals show that the alternative theory described in the following paragraphs neglects important interactions. Only preliminary reports of these views have been published (Ruch and Fischer, *Z. Naturforsch.*, 1952, **7**b, 676; Ruch, *Sitzungsber. bayer. Akad. Wiss., München, math.-naturwiss. Kl.*, 1954, 347; Ruch and Fischer, Internat. Conf. on Co-ordination Chemistry, Amsterdam, April, 1955). Experimental evidence supporting the view that the iron atom in ferrocene attains the inert-gas configuration comes from measurements of the dichroism of ferrocene crystals (Yamada, Nakahara, and Tsuchida, *J. Chem. Phys.*, 1954, **22**, 1620) and more particularly of the *X*-ray absorption edges of various *cyclo*pentadienyl–metal compounds (unpublished work by E. O. Fischer and his collaborators).

according to whether they have magnetic quantum number $m_l = 0$, $m_l = \pm 1$, and $m_l = \pm 2$ respectively and are normally equivalent, the theory shows that only the pair with $m_l = \pm 1$ has both the same transformation properties, and approximately the same energy content, as one of the available orbitals of each *cyclo*pentadiene ring ; this is the condition for strong bonding. One each of these orbitals of the metal will therefore combine with the appropriate orbital of each ring to give a strongly bonding (and of course also an antibonding) molecular orbital. We are considering here the ring as a whole, so that the result will be a single covalent bond from the metal atom to the ring as a whole ; *i.e.*, not to one particular carbon atom but " resonating " equally among all five carbon atoms. Any additional bonding involving other orbitals is regarded as sufficiently weak to be negligible to a first approximation. This highly simplified account of the theory must be supplemented by adding that the orbital with $m_l = 0$, which has the same transformation properties as the $4s$ orbital, is regarded as combining with the latter to produce a pair of hybrid orbitals, one of lower and one (" antibonding ") of higher energy than either. This hybridisation is caused by the Coulombic repulsion of the *cyclo*pentadiene rings and results in only the lower-energy orbital's being occupied, a point which is important in interpreting the magnetic properties. Thus, in the case of ferrocene, we are left with just four electrons to occupy fully the two remaining $3d$ orbitals ($m_l = 2$). The two extra electrons in di*cyclo*pentadienylnickel now have the choice of the above-mentioned antibonding orbitals and the three $4p$ orbitals, any two of which they would be expected to occupy singly, thus accounting readily for the observed paramagnetism. The magnetic properties of these and related compounds have recently been re-investigated by the para-hydrogen method [53] and good agreement with the direct magnetic measurements and with the theory is shown throughout.

Jaffé and Doak [54] have discussed the instability of the alkyls of the transition metals (which we have noted already) in terms of the molecular-orbital theory. They compare all the elements of the first long period and point out that, except in the case of the alkali and alkaline-earth metals, the ionic resonance energies are small because the electronegativity differences between the metals and carbon are small. Hence there can only be small ionic contributions to the structures of such compounds. They therefore calculate the overlap integrals for suitable orbitals of the metal with $2s2p^3$ hybrid atomic orbitals of carbon and show that these are relatively small for the transition metals (with sd^n hybridisation) compared with copper, zinc, and the following elements (which can use sp^n hybrids). It is clear that in the *cyclo*pentadienyl compounds the situation is radically different. Here, after assigning the orbitals used in linking the C_5H_5 ring together, we are left with five π electrons (in the radical). These have available five hybrid orbitals (with different energies and/or transformation properties). It is one of those orbitals, *i.e.*, an orbital of quite different type from those which would be used in simple alkyls, which the molecular-orbital treatment

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[53] Schwab and Voitländer, *Z. phys. Chem.* (*Frankfurt*), 1955, **3**, 341.
[54] Jaffé and Doak, *J. Chem. Phys.*, 1953, **21**, 196.

shows to be capable of overlapping strongly with one of the metal orbitals. Thus the stability of these compounds is amply accounted for. That this is true even in a rough quantitative sense has been demonstrated [52] by an assessment of the ring–metal binding energy. The theoretical values for ferrocene (*ca.* 300 kcal. mole^{-1}) and for di*cyclo*pentadienylnickel (*ca.* 200 kcal. mole^{-1}) are in good agreement with the values deduced from the heats of combustion (see p. 402).

The theory moreover correctly predicted the existence of compounds with only one *cyclo*pentadiene ring linked to a metal atom, amply confirmed by the isolation of the *cyclo*pentadienyl metal carbonyls. Further it predicts " free " rotation of the two rings in ferrocene relative to each other. For this also there is now a considerable amount of confirmatory evidence. It is not to be expected of course that there would not be a small barrier to rotation of the magnitude, say, of the rotational barrier in ethane. In the crystal therefore the rings occupy fixed (and, as the centre of symmetry shows, staggered) positions, yet even here the observed apparent spreading of the carbon atoms along the circumference of the ring [45] is regarded as being possibly due to a fairly large amplitude of hindered rotation. The electron-diffraction results on the vapour at high temperature [47] are, however, best accounted for if the rings are rotating freely under these conditions. In solution also the rings may be rotating quite freely as shown by dipole-moment measurements on diacetylferrocene.[55, 56] By comparison with the measured moment of the monoacetyl derivative the results can be shown to be in good agreement with a freely rotating model. In the solid, on the other hand, it is reasonable to expect that diacetylferrocene would be non-polar like dibenzoferrocene (di-indenyliron) which has been shown by *X*-ray investigation [57] to have the centrosymmetric configuration.

Purely chemical evidence for the rotational freedom can be seen in the fact that no rotational isomers have ever been isolated, either by direct synthesis of polysubstituted ferrocenes from substituted *cyclo*pentadienes, or by polysubstitution reactions from ferrocene itself. In the latter case this negative evidence might appear to find an alternative explanation in a strong directive effect. Thus in the further acetylation of acetylferrocene only one position might be attacked because all others are too strongly deactivated by the first acetyl group. To test whether this or free rotation is responsible, Woodward and Rosenblum [58] carried out the following experiments : Diacetylferrocene (VII) was partially hydrogenated to yield acetylethylferrocene (VIII). Ethylferrocene (IX) (obtained similarly from acetylferrocene) was acetylated, yielding three isomeric acetylethylferrocenes of which one was identical with structure (VIII). These results can only be explained if the rings are free to rotate. For, if fixed, then one ethyl group should activate those positions which an acetyl group deactivates so that the acetylethylferrocenes obtained from it should differ in orientation

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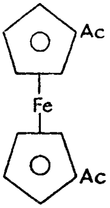
[55] Richmond and Freiser, *J. Amer. Chem. Soc.*, 1955, **77**, 2022.

[56] Similar measurements on di-(*p*-chlorophenyl)ferrocene have been made by Roberts ; see ref. 40.

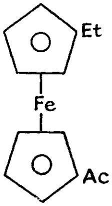
[57] Robertson and Trotter, personal communication.

[58] Robenblum, Thesis, Harvard, 1953.

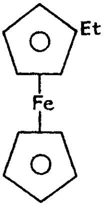
from diacetylferrocene [and hence from structure (VIII)]. Or, if the influence is too weak, then it should yield five isomeric acetyl derivatives. The three actually found correspond to the number expected if there is free rotation, *i.e.*, two with both substituents in the same ring in addition to



(VII)



(VIII)



(IX)

(VIII) as the unique product with both rings substituted. That the other two isomers are in fact the 1 : 2- and 1 : 3-isomers is evident from their infrared spectra which clearly show several bands not present in the compound (VIII) and generally found in all ferrocene derivatives in which at least one ring is unsubstituted, but not found otherwise.

Properties

Ferrocene and its analogues all behave as typical covalent compounds. Thus they are soluble in common organic solvents and readily volatile. Ferrocene sublimes at 100° under atmospheric pressure and may be distilled with steam, a convenient method of purification. Its vapour-pressure curve has been studied [59] up to 400° C and shows the compound to be completely stable up to that temperature. Its normal boiling point deduced from these measurements is 249° C. Similar measurements are lacking for the other compounds, but although they appear less volatile they all readily sublime under reduced pressure. Since they are less stable in air, this is in many cases the preferred method of purification. The similarity in physical properties is strikingly illustrated by the melting points which are all at or within a few degrees of 173° for metals in the same Period as iron, but increase to 196° for the ruthenium and 218—219° for the osmium compound.[60]

It has been shown by Fischer and his collaborators [9, 17, 42] that the di*cyclo*pentadienyl derivatives of iron, cobalt, nickel, chromium, vanadium, and magnesium are all isomorphous, crystallising in the monoclinic system, space group $P2_1/c$, and having very similar unit-cell dimensions. Thus the same geometrical arrangement must apply to all. The vanadium and magnesium compounds have the largest molecular volumes, which accords with the larger metal–ring distance to be expected for their more ionic bond type. The manganese compound appears to form an exception, existing at room temperature in a brown rhombic modification. This however [32, 61]

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[59] Kaplan, Kester, and Katz, *J. Amer. Chem. Soc.*, 1952, **74,** 5531.

[60] Lippincott, personal communication.

[61] Fischer and Jira, *Z. Naturforsch.*, 1954, **9**b, 618.

changes at 158—159° to a colourless modification melting at 172°. The crystal structure of the latter form as well as the nature of the transition are as yet unknown; it appears possible that a change to the usual monoclinic form may be involved. Even in the brown form di*cyclo*pentadienylmanganese has almost the same molecular volume as ferrocene, suggesting a similar molecular structure.[17]

Great similarity is shown also by the infrared spectra of these compounds, as can be seen from the published curves for ferrocene and its nickel [25] and ruthenium [24] analogues. These three spectra and the corresponding Raman spectra have been analysed in detail by Lippincott and Nelson.[62, 63] By including in their study an examination of the deuterium analogue of ferrocene, $C_{10}D_{10}Fe$, they have been able to assign all the bands with the exception of the group of medium-strong bands around 1700 cm.$^{-1}$.

The most striking feature of these spectra is their simplicity, arising from the high symmetry of the molecules. In addition to the C–H stretching frequency at 3075 cm.$^{-1}$, in the region typical for aromatic C–H bonds, there are only four strong bands. Two of these, at 811 and 1002 cm.$^{-1}$ in ferrocene, arise from C–H bending vibrations, one at 1108 cm.$^{-1}$ is an antisymmetrical ring breathing, and one at 1411 cm.$^{-1}$ an antisymmetrical C–C stretching vibration. It has been observed empirically [37, 58] that all these are retained (although with reduced intensity) at very nearly the same positions in all monosubstituted ferrocene derivatives, but all four bands disappear when both rings are substituted. The spectra of the ferricinium ion and of other related ionic species retain these four maxima.[31] By contrast, the ultraviolet spectrum changes radically from ferrocene to the ferricinium ion [58] (or from one metal to another). The spectrum of the ferricinium ion is characterised by a peak at 252 mμ (log ε 4·12) followed by a broad plateau terminating in the peak at 620 mμ (log ε 2·56) which accounts for its blue colour. The orange colour of ferrocene itself finds its source in a broad peak around 440 mμ (log ε 1·96),[58, 59] which is shifted to 455 mμ (log ε 2·63) and 460 mμ (log ε 2·73) respectively in the red mono- and di-acetyl derivatives.[58] The only other peak above 200 mμ in ferrocene is at 325 mμ (log ε 1·71 in ethanol), shifted to 335 mμ (log ε 3·05) in the acyl derivatives. The general red-shift noted in these acylated compounds reveals two further low-wavelength maxima, which appear at 268 (log ε 3·73) and 225 mμ (log ε 4·16) in the case of acetylferrocene.

The thermodynamic stability of the di*cyclo*pentadienyl-metal compounds has been assessed for the iron and nickel compounds by measurements of their heats of combustion.[25, 64] From them, the heats of formation from the elements in their standard states, ΔH_{298°, are deduced to be 33·8 and 62·8 kcal. mole^{-1} respectively. From the vibrational spectra values of 57·5 and 79·6 kcal. mole^{-1} have been deduced [63] for the gaseous molecules which, when corrected for the heat of sublimation [59] (16·8 kcal. mole^{-1}), give values + 40·7 kcal. mole^{-1} for ferrocene and + 62·8 kcal. mole^{-1} for

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[62] Lippincott and Nelson, *J. Chem. Phys.*, 1953, **21**, 1307.

[63] *Idem*, *J. Amer. Chem. Soc.*, 1955, **77**, 4990.

[64] Cotton and Wilkinson, *ibid.*, 1952, **74**, 5764.

di*cyclo*pentadienylnickel, in good agreement with the above values. Similar analysis of the spectrum of di*cyclo*pentadienylruthenium shows that it is more stable thermodynamically than ferrocene. To obtain estimates of the ring-to-metal bonding energies the heats of formation from *cyclo*pentadienyl radicals and gaseous metal have been estimated from the above combustion data. These are $-$ 147 kcal. mole^{-1} for $C_{10}H_{10}Fe$ and $-$ 123 kcal. mole^{-1} for $C_{10}H_{10}Ni$, indicating a difference of 24 kcal. mole^{-1} in the stabilities of these two compounds. It has recently been pointed out however that this treatment neglects the energy required to promote the metals to their valency states. As this energy is small for nickel (*ca.* 28 kcal. mole^{-1}) but large for iron (*ca.* 125 kcal. mole^{-1}) the ring–metal bonding energies on this new basis differ by approximately 120 kcal. mole^{-1}.[52]

This large difference in stability is reflected in the significantly longer metal–carbon distance of the nickel compound already mentioned. It results moreover in much greater chemical reactivity of this compound. This is illustrated by the action of reagents like carbon monoxide[8] and nitric oxide[35, 61] which displace one or both of the *cyclo*pentadiene rings.

The thermodynamic stability of the compounds of other metals is unknown, but it is reasonable to assume, both on theoretical grounds and from the *X*-ray data,[42] that the cobalt compound is intermediate between iron and nickel. Undoubtedly the much greater difficulties encountered in its isolation and handling result not from instability in this sense, but from its powerful reducing action. The polarographically determined oxidation–reduction potentials of a number of di*cyclo*pentadienyl metal compounds are shown in Table 1. They indicate that the behaviour of most of these

TABLE 1

Reaction studied[a]	Oxidation potential in water (v)[b]	Oxidation potential in 90% ethanol (v)	Ref.
$C_{10}H_{10}Fe \rightarrow C_{10}H_{10}Fe^{+}$		$+$ 0·31	65
$C_{10}H_{10}Fe^{+} \rightarrow C_{10}H_{10}Fe$	$+$ 0·16	$+$ 0·30	65
$C_{10}H_{10}Ru \rightarrow C_{10}H_{10}Ru^{+}$		$+$ 0·26	65
$C_{10}H_{10}Ru^{+} \rightarrow C_{10}H_{10}Ru$	$+$ 0·11	$+$ 0·22	65
$C_{10}H_{10}Co^{+} \rightarrow$?[c]	$-$ 1·16		65
$C_{10}H_{10}Rh^{+} \rightarrow$?[c]	$-$ 1·53		66
$C_{10}H_{10}Ni \rightarrow C_{10}H_{10}Ni^{+}$		$-$ 0·08	25
$C_{10}H_{10}Ni^{+} \rightarrow C_{10}H_{10}Ni$	$-$ 0·21		25
$C_{10}H_{10}Ti^{++} \rightleftarrows C_{10}H_{10}Ti^{+}$	$-$ 0·44		31
$C_{10}H_{10}V^{++} \rightleftarrows C_{10}H_{10}V^{+}$	$-$ 0·32		31
$C_{10}H_{10}Nb^{+++} \rightarrow$?[c]	$-$ 0·44 $-$ 0·71		31
$C_{18}H_{14}Co^{+}$[d] $\rightarrow$?[c]	$-$ 0·60		38

[a] All ionic species as perchlorate.
[b] *Versus* the saturated calomel electrode (American sign convention).
[c] Irreversible reductions.
[d] $C_{18}H_{14} = 2 \times$ indenyl.

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[65] Page and Wilkinson, *J. Amer. Chem. Soc.*, 1952, **74,** 6149.

[66] Cotton, Whipple, and Wilkinson, *ibid.*, 1953, **75,** 3586.

compounds is not unlike that of the corresponding metal ions or related complex ions in the same oxidation state. Thus the ferrocene–ferricinium system has an oxidation–reduction potential close to that of the ferrocyanide–ferricyanide system and, although the di*cyclo*pentadienylcobalt(III) ion is greatly favoured over the neutral bivalent compound, an isoelectronic di*cyclo*pentadienylnickel(IV) ion cannot be obtained by further oxidation of the tervalent ion. The increased stability of higher oxidation states of elements of higher atomic weight is clearly evident from a comparison of the potentials of the pairs iron and ruthenium, cobalt and rhodium, or vanadium and niobium. While the titanium and vanadium compounds are sufficiently stable in the tervalent state to be reduced to that state by means of a Jones reductor, the zirconium compound cannot be so reduced and the niobium and tantalum compounds are known only in the quinquevalent state ; although the niobium compound could be reduced, isolation of the lower (IV or III) valency states was not achieved.[31]

Another similarity to the behaviour of the simple salts of the corresponding metals may be seen in the ease of hydrolysis of, *e.g.*, di*cyclo*pentadienylniobium(V) bromide to the corresponding hydroxydibromide or di*cyclo*pentadienyltitanium(IV) bromide to the hydroxybromide.[31] The halogen atoms in the titanium compound have also been shown to be replaceable by organic anions. Thus aryl-lithium compounds convert di*cyclo*pentadienyltitanium dichloride into diaryldi*cyclo*pentadienyltitanium compounds, of which the diphenyl compound [67] is moderately stable and can be kept in the solid state for many months. The di-(*p*-dimethylaminophenyl) derivative was found to be appreciably less stable.[67] Sodium phenylacetylide reacts similarly with the dichloride, to yield di*cyclo*pentadienyldi(phenylethynyl)-titanium [68] which is likewise stable in the solid state, but rapidly destroyed by hydroxylic solvents. These products are of course entirely covalent in character. The di*cyclo*pentadienyltitanium dihalides from which they are derived themselves show [like titanium(IV) halides] considerable covalent character, being volatile and soluble in many organic solvents but only very sparingly so in water. The fluoride is much more soluble in water and aqueous solutions of true salts such as the perchlorate can readily be prepared with the aid of anion-exchange resins.[31]

By contrast, anhydrous ferricinium chloride is completely insoluble in such solvents as ether. It is exceedingly soluble in water and has not yet been obtained pure. The aqueous solutions of the ferricinium ion yield precipitates of such salts as the tri-iodide,[58] reineckate,[5] tetraphenylborate,[23] tetrachlorogallate,[4] silicotungstate, etc. Sparingly soluble salts are also obtained with the picrate and related organic anions. These are conveniently prepared by oxidation of ferrocene in benzene or other organic solvents with benzoquinone in presence of picric acid. The precipitated salt may then be purified by crystallisation from water. Related cations such as the di*cyclo*pentadienyl-cobalt(III), -nickel(III), -rhodium(III), etc., ions give insoluble salts with the same reagents. The cobalt compound is con-

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[67] Summers and Uloth, *J. Amer. Chem. Soc.*, 1954, **76**, 2278.
[68] Hallam and Pauson, unpublished results.

veniently precipitated as the tribromide, $C_{10}H_{10}Co^+ Br_3^-$, and is so stable that this salt may be dissolved in hot hydrobromic acid and evaporated to dryness (finally in a desiccator) to yield the very hygroscopic simple bromide $C_{10}H_{10}CoBr$.

As would be expected of a chromous compound, di*cyclo*pentadienylchromium is, like its cobalt analogue, extremely readily oxidised and dissolves in dilute acid with evolution of hydrogen to give a blue solution.[34] This does not give the above precipitation reactions but undoubtedly contains the $C_{10}H_{10}Cr^+$ ion which has recently been described by Fischer and Hafner in another connection.[69]

When larger organic residues are attached to the metal atom the solubility of the salts in water decreases and that in organic solvents increases such that, *e.g.*, di-indenylcobalt(III) perchlorate is sparingly soluble in water and readily crystallised from that solvent, but is readily soluble in acetone.[38]

*cyclo*Pentadienyl metal carbonyls and related compounds

To obtain *cyclo*pentadienylmetal carbonyls one may start either from the di*cyclo*pentadienyl derivatives or from the metal carbonyls. The latter method has already been outlined in the section on preparation. Thus, when the mixed vapours of *cyclo*pentadiene and molybdenum or tungsten carbonyl are passed through a tube heated to 250—300° (or when the carbonyls are refluxed in di*cyclo*pentadiene), they react as follows :[34]

$$2C_5H_6 + 2W(CO)_6 \longrightarrow \underset{(X)}{(C_5H_5)_2W_2(CO)_6} + \text{gaseous products}$$

The structure of the product (X) has not yet been established. At the high temperatures originally used, chromium carbonyl was converted directly into di*cyclo*pentadienylchromium. The intermediate di*cyclo*pentadienyldichromium hexacarbonyl (XIII) may be isolated under milder conditions,[70] but was first obtained by the reverse process from di*cyclo*pentadienylchromium.[71]

This has now been shown [69] to proceed through the following stages :

(1) $(C_5H_5)_2Cr + CO \longrightarrow C_5H_5Cr(CO)_3\cdot$ (XI)

(2) $(C_5H_5)_2Cr + C_5H_5Cr(CO)_3\cdot \longrightarrow (C_5H_5)_2Cr^+[C_5H_5Cr(CO)_3]^-$ (XII)

(3) $(C_5H_5)_3Cr_2(CO)_3 + CO \longrightarrow [C_5H_5Cr(CO)_3]_2$ (XIII)

(4) $[C_5H_5Cr(CO)_3]_2 + CO \longrightarrow Cr(CO)_6$

If the reaction is carried out at 100—110° (100 atmospheres' pressure of carbon monoxide) the salt (XII) is the main product, while at 150—170° the blue-green binuclear di*cyclo*pentadienyldichromium hexacarbonyl (XIII) results either from the former product or by direct dimerisation of the radicals (XI) formed in the first step. The final step occurs at 250° under these conditions.

The anion of the salt (XII) is also obtained *via* the corresponding free

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[69] Fischer and Hafner, *Z. Naturforsch.*, 1955, **10**b, 140 ; Fischer, personal communication.

[70] Cotton and Wilkinson, *ibid.*, 1954, **9**b, 417.

[71] Schwab, Fischer, and Voitländer, *Naturwiss.*, 1954, **41**, 228.

acid (XIV), formed when hydrogen is added to the reaction so that the intermediate (XI) reacts according to:

$$(5)\ 2C_5H_5Cr(CO)_3{\cdot} + H_2 = 2C_5H_5Cr(CO)_3H \qquad (XIV)$$

The acid (XIV) is obtained as a yellow crystalline solid which evolves hydrogen at its melting point (58°) and decomposes by the reverse reaction (5) to yield the hexacarbonyl (XIII). This *cyclo*pentadienylchromium tricarbonyl hydride (XIV) is analogous to the simple metal carbonyl hydrides such as $Co(CO)_4H$ and dissolves in alkali to give the anion. From the resultant aqueous solutions the covalent mercury derivative may be precipitated:

$$2[C_5H_5Cr(CO)_3]Na + Hg(CN)_2 = 2NaCN + Hg[C_5H_5Cr(CO)_3]_2$$

The latter is soluble in organic solvents and with the di*cyclo*pentadienylchromium(III) ion, $C_{10}H_{10}Cr^+$, precipitates the violet-brown salt (XII), which, while showing the solubility characteristic of a salt, is also volatile and must therefore possess at least partial covalent character. A crystalline methyl ester has been obtained from *cyclo*pentadienyltungsten tricarbonyl hydride by treatment with diazomethane. It and the analogous carbonyl hydride of molybdenum have been obtained by reaction of the metal carbonyl with *cyclo*pentadienyl-lithium:

$$C_5H_5Li + M(CO)_6 = [C_5H_5M(CO)_3]Li + 3CO \text{ (where M = Mo or W)}$$

followed by acidification.[69] This represents a third method for obtaining the *cyclo*pentadienyl-metal carbonyls.

The method employing the di*cyclo*pentadienyl derivatives as starting materials has its most important application in the preparation of the vanadium and manganese carbonyls. The solutions obtained from the metal halides and *cyclo*pentadienylsodium may be used directly for the reaction with carbon monoxide without isolating the very unstable intermediate di*cyclo*pentadienyl compounds which are converted in this way [8] into the orange *cyclo*pentadienylvanadium tetracarbonyl, $C_5H_5V(CO)_4$, and the yellow [35, 61] *cyclo*pentadienylmanganese tricarbonyl, $C_5H_5Mn(CO)_3$, respectively. By contrast with the intermediates, the former is moderately and the latter completely stable to water.

The same method may be employed to obtain the *cyclo*pentadienylcobalt dicarbonyl, but this is prepared more conveniently from cobalt carbonyl, which reacts exothermally with *cyclo*pentadiene at room temperature.[35] Nickel carbonyl on the other hand has not yielded a comparable product while di*cyclo*pentadienylnickel gave only nickel carbonyl on treatment with carbon monoxide.[8]

Finally, any of the three iron carbonyls (but preferably the pentacarbonyl) reacts with di*cyclo*pentadiene on being heated to yield the binuclear derivative, $(C_5H_5)_2Fe_2(CO)_4$ (IV), already mentioned. Its structure has been elucidated by *X*-ray crystallographic methods.[36] The most notable feature is the presence of the iron–iron bond, in agreement with the diamagnetic nature of the molecule. Its length is found to be the same as that in iron enneacarbonyl. There are two bridging carbonyl groups [in conformity with the carbonyl absorption at 1760 cm.$^{-1}$ (in KBr)] and two non-bridging carbonyl groups (infrared absorption at 1936 and 1982 cm.$^{-1}$) roughly at right angles to the former. The *cyclo*pentadiene rings are not perpendicular to the iron–iron bond but are inclined away from the non-bridging carbonyl groups as indicated in formula (IV).[72] By aerial oxidation in acidic medium the binuclear derivative (IV) is converted into the cation $C_5H_5Fe(CO)_2{}^+$. The crystalline chloride, $C_5H_5Fe(CO)_2Cl$ (V),[35] or the corresponding bromide [36] is readily isolated from the products of this reaction. Thus there exists the following series of mononuclear *cyclo*pentadienylmetal carbonyls, tabulated together with some of their properties in Table 2.

TABLE 2

Compound	M.p.	Colour	Effect of heat
$C_5H_5V(CO)_4$.	138°	Pale orange	Loses CO above 110° *in vacuo*.
$C_5H_5Cr(CO)_3H$.	57—58	Yellow	Loses H_2 at m.p.
$C_5H_5Mn(CO)_3$.	77	Pale yellow	Sublimes unchanged in air above 60°.
$C_5H_5Fe(CO)_2Cl$.	— *	Red	Yields some ferrocene on strong heating.
$C_5H_5Co(CO)_2$.	— †	Dark red	Loses CO *in vacuo*.

* Decomp. at 87°. † B.p. 75°/22 mm.

All the compounds in Table 2 are diamagnetic and, assuming that in each case the *cyclo*pentadiene ring is linked to the metal atom by what may be regarded as a single covalent link and that each carbonyl group donates two electrons to the metal atom, we have in each case fourteen outer orbital electrons associated with the metal atom. The alternative view still held by Fischer [69] is that all the π-electrons of the *cyclo*pentadiene ring are utilised, resulting in eighteen outer orbital electrons (krypton configuration) in each case. These rules cannot apply to the ion $C_5H_5Fe(CO)_2{}^+$ which has two fewer electrons in its truly ionic salts, *e.g.*, the reineckate. The chloride (V) and the bromide are somewhat soluble in water but are completely extracted by chloroform and must be regarded as largely covalent. The sulphate and perchlorate have been prepared only in aqueous solution. When the former is treated with barium chloride, a solution of an ionic species, possibly $[C_5H_5Fe(CO)_2OH_2]^+Cl^-$, is obtained which is not immediately extractable by chloroform but changes to the normal chloride (V) on being kept.[68] The essentially covalent character of this chloride is also apparent from its slow reaction with silver nitrate.[35] The bromide reacts much faster, and the iodide (readily obtained by the action of alkali-metal iodides on the chloride in acetone or ether) even more so.[68] Prolonged treatment with potassium cyanide converts the chloride (V) into the corresponding cyanide, $C_5H_5Fe(CO)_2CN$.[35]

Rapid replacement of halogen occurs when the chloride (V) (or bromide) is treated with *cyclo*pentadienylsodium and di*cyclo*pentadienyliron dicarbonyl

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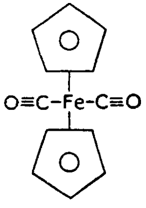
[72] Mills, unpublished results.

(XV) is formed.[73] By a side-reaction the binuclear carbonyl (IV) is also formed, presumably *via* the radical $C_5H_5Fe(CO)_2\cdot$ which is also a likely intermediate in its formation from iron carbonyl. This carbonyl (IV) becomes the sole recognisable product when the chloride (V) is treated with sodium phenylacetylide.

The carbonyl groups are quite strongly held in these *cyclo*pentadienyliron carbonyls. Even di*cyclo*pentadienyliron dicarbonyl (XV), which decomposes rapidly at 80°, is only partially converted into ferrocene by loss of carbon monoxide, while part decomposes to di*cyclo*pentadienyldi-iron tetracarbonyl (IV), presumably by the splitting off of a *cyclo*pentadienyl radical.[68] In *cyclo*pentadienylcobalt dicarbonyl on the other hand the carbonyl groups have been shown to be replaceable by phosphorus trichloride and related reagents although no pure product was isolated.[35] In the case of the manganese compound replacement by nitric oxide was demonstrated and the resultant ion, $[C_5H_5Mn(CO)_2NO]^+$, isolated as its chloroplatinate.[35] The isoelectronic $C_5H_5Cr(CO)_2NO$ and its molybdenum and tungsten analogues have recently been obtained as orange crystals.[69]


(XV)

The related *cyclo*pentadienylnickel nitrosyl, C_5H_5NiNO, was obtained both by Fischer and Jira [61] and by Piper, Cotton, and Wilkinson [35] by direct replacement of one *cyclo*pentadiene group of di*cyclo*pentadienylnickel by nitric oxide. It is a dark red volatile diamagnetic liquid of considerable stability.

Aromatic Character

The remarkable similarity in behaviour of the C_5H_5 ring of ferrocene to that of a benzene ring was first demonstrated by Woodward, Rosenblum, and Whiting.[3] In the first place, they were able to demonstrate that ferrocene does not undergo addition reactions, either with maleic anhydride or even with hydrogen in the presence of Adams's platinum oxide catalyst. As benzene rings are attacked under these conditions, we may indeed consider ferrocene even more aromatic in this sense. This has received striking confirmation by the hydrogenation of di-indenyliron in which the benzene rings are reduced to yield di(tetrahydroindenyl)iron.[74] Bromine in carbon tetrachloride (or as *N*-bromosuccinimide in acetic acid) [75] does add to the rings, but only after oxidising the compound to the much less stable ferricinium ion. The reaction is accompanied by complete rupture of the molecule to yield pentabromo*cyclo*pentane.[76]

More important, Woodward and his collaborators were able to demonstrate that ferrocene undergoes typical aromatic substitution reactions,

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[73] Hallam and Pauson, *Chem. and Ind.*, 1955, 653.

[74] Fischer and Seus, *Z. Naturforsch.*, 1954, **9**b, 386.

[75] Woodward and Csendes, personal communication.

[76] Nesmeyanov, Perevalova, and Nesmeyanova, *Doklady Akad. Nauk S.S.S.R.*, 1955, **100**, 1099.

notably Friedel–Crafts acylation.[3] With acyl halides and aluminium chloride as catalyst, mixtures of mono- and di-acyl derivatives were obtained. These could be separated very readily both from each other and from any unchanged ferrocene by chromatography on activated alumina.[58]

Careful separation of the acetylation products reveals the presence of a very small amount of a second diacetyl derivative in which both groups are attached to the same ring, probably 1 : 3-diacetylferrocene. [Evidence that the main disubstitution products are symmetrical (*i.e.*, substituted in each ring) is discussed on p. 412.] This compound resisted further acetylation,[58] giving the first suggestion that substituents in the first ring significantly affect further substitution in the second ring. It was subsequently observed that one acetyl group suffices to hinder substitution in the second ring quite significantly. Thus, if the amount of aluminium chloride used does not exceed one molecule (as $AlCl_3$) per molecule of acyl halide high yields of monoacyl derivative are obtained.[75] Under these conditions, virtually no disubstitution occurs even when two equivalents of the acetyl chloride–aluminium chloride complex are added per mole of ferrocene.[77] Similarly, when acetic anhydride is used with hydrogen fluoride,[78] boron trifluoride,[77] or stannic chloride [79] as catalysts, almost exclusive monosubstitution results. The success of the reaction with the last two catalysts under mild conditions suggests that ferrocene is more reactive than benzene. This has been amply confirmed in competitive experiments between the two substances and between ferrocene and various benzene derivatives. Thus when one molecule of ferrocene and ten molecules of anisole were allowed to compete in chloroform solution for a limited amount of acetyl chloride–aluminium chloride complex in the same solvent, acetylferrocene was formed to the exclusion of any detectable amount of methoxyacetophenone.

The same ease of substitution is evident in other reactions. Thus Nesmeyanov *et al.* have shown that mercuration succeeds readily under very mild conditions [79] while an earlier attempt to effect this reaction under the conditions necessary to mercurate benzene led only to the formation of mercury-containing polymers.[80] Similarly, attempted chloromethylation has hitherto yielded only poly(methyleneferrocene).[80]

Ferrocene has also been shown to condense with aldehydes in anhydrous hydrogen fluoride to yield diferrocenylmethane derivatives : [78, 81]

$$2C_{10}H_{10}Fe + R{\cdot}CHO \xrightarrow{HF} (C_{10}H_9Fe)_2CHR$$

It is perhaps surprising therefore that simple alkylations fail when attempted under the same conditions. Only a " self-alkylation " is then observed, which also occurs when ferrocene is dissolved in hydrofluoric acid in the

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[77] Broadhead and Pauson, unpublished results.

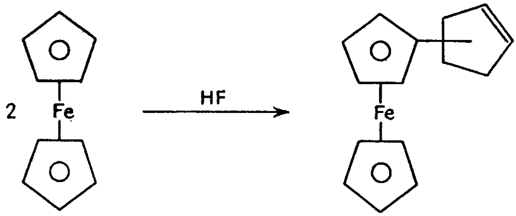
[78] Weinmayr, *J. Amer. Chem. Soc.*, 1955, **77**, 3009.

[79] Nesmeyanov, Perevalova, Golovnya, and Nesmeyanova, *Doklady Akad. Nauk S.S.S.R.*, 1954, **97**, 459.

[80] Pauson, unpublished results.

[81] Weinmayr, U.S.P. 2,694,721.

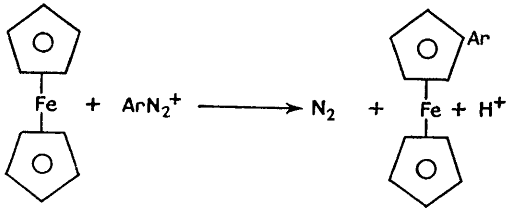
absence of other reactants and must involve disruption of part of the ferrocene used : [78]



Other substitution reactions such as halogenation, nitration, and sulphonation are complicated by the ease of oxidation of ferrocene. This results in the formation of the positively charged ferricinium ion and therefore makes electrophilic substitution virtually impossible. In the case of sulphonation the difficulty has been overcome by working in acetic anhydride as solvent.[78] On a hundred-gram scale this is reported to result in an exothermic reaction when 100% sulphuric acid is used as the sulphonating agent, but on a smaller scale the use of oleum appears to be necessary.[77] The yellow disulphonic acid thus formed separates directly from the reaction mixture. The monosulphonic acid was isolated when much less sulphuric acid was used.[78]

Another useful substitution is the metallation of ferrocene with *n*-butyllithium.[79, 82] Though rather slow and incomplete, it yields ferrocenyllithium accompanied by some of the dilithium derivative from which a variety of other substitution products may be derived.

Arylation with diazonium salts occurs with great ease with ferrocene.[79, 83, 84] In view of the analogy of this process to the Gomberg reaction of benzenoid compounds and of the fact that the reaction succeeds equally well with the positively charged ferricinium ion [40] as with ferrocene, it must be regarded as of free-radical type and thus different in nature from the above electrophilic substitutions. The reaction may also be carried out with nitrosoacetanilide as the source of the aryl radicals,[84] and Nesmeyanov and his colleagues [79, 83] have employed diazoacetates under the usual Gomberg conditions ; but when the reaction is carried out in strongly acidic media [40, 84] the mechanism must differ. The overall reaction may then be written as :



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[82] Benkeser, Goggin, and Schroll, *J. Amer. Chem. Soc.*, 1954, **76**, 4025.

[83] Nesmeyanov, Perevalova, and Golovnya, *Doklady Akad. Nauk S.S.S.R.*, 1954, **99**, 539.

[84] Broadhead and Pauson, *J.*, 1955, 367.

This must involve an oxidation–reduction step by which the aryl radicals are generated, most probably the electron-transfer reaction:

$$C_{10}H_{10}Fe + ArN_2^+ = C_{10}H_{10}Fe^+ + ArN_2\cdot$$

which is followed (or accompanied) by rapid decomposition of the aryldiazonium radical to nitrogen and the aryl radical. This may be followed by:

$$C_{10}H_{10}Fe + Ar\cdot = C_{10}H_9ArFe + H\cdot$$

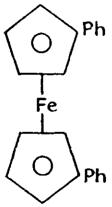
in which case the overall reaction could be completed by:

$$H\cdot + C_{10}H_{10}Fe^+ = H^+ + C_{10}H_{10}Fe$$

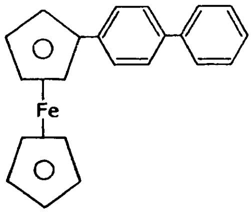
although other modes of reaction are clearly open to the hydrogen atom.

It is noteworthy that the reaction with nitrosoacetanilide as the source of phenyl radicals can be carried out in *cyclo*hexane, a solvent from which these radicals might ordinarily be expected to abstract hydrogen. The demonstration provided by the careful work of Hey and others [85] that widely different partial rate factors can be obtained in such arylations for different aromatic substrates (as well as for different positions in the ring) proves that such aryl radicals are fairly selective reagents (and hence by inference that they are reagents of only moderate reactivity). The ability of ferrocene to compete with a good hydrogen donor therefore merely demonstrates its very high reactivity towards free radicals, which is comparable to its high reactivity towards electrophilic reagents.

This reactivity must be reduced by an aryl substituent to account for the predominant attack on the unsubstituted ring in the further phenylation of phenylferrocene.[84] That the only disubstitution product which could be isolated from this reaction is indeed the symmetrical diphenylferrocene (XVI) was proved by its identity with the product previously synthesised from phenyl*cyclo*pentadiene.[37] That the ferricinium ion is much less reactive towards aryl radicals is suggested by the fact that in this case two other disubstitution products may be isolated,[77] one of which has been identified as compound (XVII) by direct comparison with a specimen prepared from ferrocene and *p*-phenylbenzenediazonium sulphate. It has further been found that the reaction with the ferricinium salt proceeds only if some free ferrocene is also present, and is inhibited completely if this is removed by extraction of the aqueous ferricinium salt solution with ether. It appears



(XVI)



(XVII)

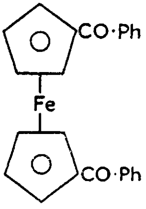
[85] Cadogan, Hey, and Williams, *J.*, 1955, 1425, where references to earlier papers are given.

reasonable to assume that the ferrocene is required to generate the free radicals by the above electron-transfer process.

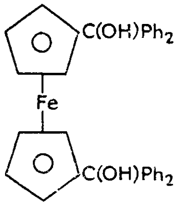
Miscellaneous ferrocene derivatives

By the substitutions described in the previous section, and particularly by further transformations of the products so obtained, a wide variety of ferrocene derivatives becomes accessible. Only a few of the possibilities opened up in this way have been explored hitherto.

The acylferrocenes may not only be reduced to the corresponding alkyl derivatives,[58] but the acyl groups stabilise the ferrocene nucleus sufficiently towards oxidation to make selective oxidation of the side chain possible.[3, 86] In this way, acetylferrocene is readily converted by hypohalite into ferrocenecarboxylic acid, and diacetylferrocene similarly into the dicarboxylic acid. The dissociation constants (K_a) of these acids have been found to be $1{\cdot}8 \times 10^{-7}$ for the mono-[58] and $3{\cdot}1 \times 10^{-7}$ and $2{\cdot}7 \times 10^{-8}$ for the dicarboxylic acid.[3] The proximity of these values to the constant for benzoic acid under the same conditions ($2{\cdot}4 \times 10^{-7}$) constitutes further evidence for the aromatic nature of ferrocene. Moreover, the small difference between the first and the second ionisation constant of the dicarboxylic acid is a clear indication of the fact that the two carboxyl groups (and hence the acetyl groups in the parent compound) are attached to different rings.[3] Direct proof for this was obtained in the case of dibenzoylferrocene (XVIII) which is readily formed from ferrocene and benzoyl chloride in presence of aluminium chloride. It reacts in the usual manner with phenylmagnesium bromide to yield the tertiary alcohol (XIX). Reduction of this alcohol with titanous sulphate converts it into bisdiphenylmethylferrocene (XX) [75] and this proved to be identical with a sample prepared from diphenylmethyl*cyclo*pentadiene (XXI) by treatment with phenyl-lithium followed by ferric



(XVIII)



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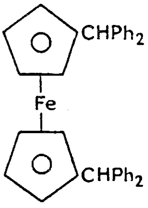

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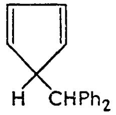
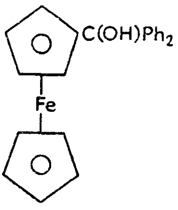


(XXI)



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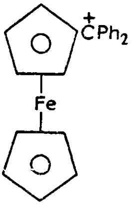
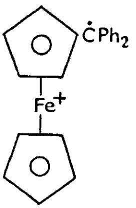


(XXIII)



(XXIV)

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[86] Weinmayr, U.S.P. 2,683,157.

chloride.[37] The alcohol (XXII), prepared from monobenzoylferrocene with phenylmagnesium bromide, readily reacts with anhydrous hydrochloric or other acids to yield blue salts. Magnetic measurements suggest however that these are salts of the carbonium ion (XXIII) and not (as the colour might suggest) of the ferricinium radical ion (XXIV). Attempts to convert the alcohol (XXII) into the ferrocenyldiphenylmethyl radical, analogous to the triphenylmethyl radical, proved unsuccessful.[75]

Whereas an attempt to prepare ferrocenecarboxylic acid by a direct Friedel–Crafts reaction using carbonyl chloride yielded only a trace of the desired compound, the main product being diferrocenyl ketone (XXV), the *N*-methylamide of the acid was readily prepared with methylcarbamoyl chloride, $CH_3{\cdot}NH{\cdot}COCl$.[75] Other derivatives of the acid such as the simple esters [58, 82] and amide [77] may be obtained by conventional methods. The thiomorpholide of the homologous ferrocenylacetic acid is formed from acetylferrocene by the Willgerodt reaction.[80] Woodward and Rosenblum [58] have applied the Curtius rearrangement to the diazide (prepared from the dicarboxylic acid *via* the diester and dihydrazide) and have thus obtained the urethanes (XXVI; $R = Et$ and $R = CH_2Ph$), which are the first compounds having nitrogen directly linked to the ferrocene nucleus.

Friedel–Crafts acylation also succeeds with the half-ester acid chlorides $Cl{\cdot}CO{\cdot}[CH_2]_n{\cdot}CO_2Et$ ($n = 0$, 1, or 2).[58] Hydrolysis followed by catalytic hydrogenation converts these into the acids $C_5H_5FeC_5H_4{\cdot}[CH_2]_{n+1}{\cdot}CO_2H$ ($n = 1$ or 2). The ferrocenylpropionic acid so obtained is cyclised by trifluoroacetic anhydride to a ketone which is most probably (XXVII) in which the two rings are bridged.[75]

The halogen derivatives of ferrocene, which cannot be obtained by direct halogenation, have very recently become available through the mercuration products. Both the mono- and di-chloromercury derivatives of ferrocene react with iodine and with bromine to yield mono- and di-iodo- and mono- and di-bromo-ferrocene respectively.[76]

The lithium derivatives also offer many possibilities for further synthesis. Apart from yielding the acids (more easily prepared by the above method) on carboxylation, they have been used to obtain mono- and di-(triphenylsilyl)-ferrocene.[82] A more important use has been found by Nesmeyanov, who has shown that ferrocenyl-lithium undergoes the Kocheshkov reaction [87] with *O*-benzylhydroxylamine, $NH_2{\cdot}O{\cdot}CH_2Ph$, to yield the interesting aminoferrocene $C_5H_5FeC_5H_4{\cdot}NH_2$, the ferrocene analogue of aniline.[88]

With increasing numbers of substituted ferrocene derivatives becoming available in these ways it may be appropriate to conclude by considering very briefly the stereochemical situation which arises in the unsymmetrical polysubstitution products. Inspection of formula (XXVIII) shows that it is not superimposable on its mirror image and should therefore be resolvable into its optical antipodes (this applies also if A and B are non-adjacent and

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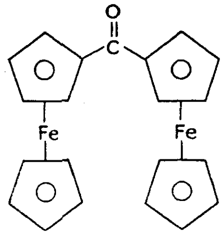
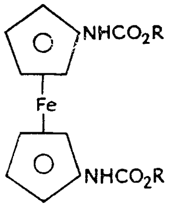
[87] Sheverdina and Kocheshkov, *J. Gen. Chem. (U.S.S.R.)*, 1938, **8**, 1825 (*Chem. Abs.*, 1939, **33**, 5804); *Bull. Acad. Sci. U.S.S.R., Classe sci. chim.*, 1941, 75 (*Chem. Abs.*, 1943, **37**, 3066); cf. also Coleman, Hermanson, and Johnson, *J. Amer. Chem. Soc.*, 1937, **59**, 1896.

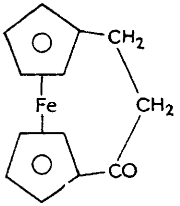
[88] Nesmeyanov, personal communication.



(XXV)

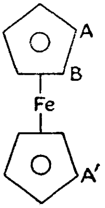


(XXVI)



(XXVII)

if A′ = A or H). Although such compounds are known, resolution has not yet been attempted. Tetrasubstitution products of the type (XXIX) are the simplest cases of geometrical isomerism and exist in the forms XXIX*a* and XXIX*b*. The first example of this type (XXIX ; A = Me, B = Ph) has now been prepared.[80] It should prove possible to distinguish between isomers of this type since the *cis*-isomer (XXIX*a*) is a " *meso* "-form, whereas the *trans*-isomer (XXIX*b*) is a racemate.



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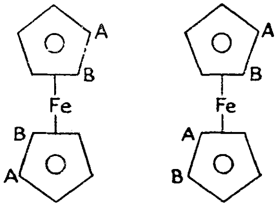

(*a*) (*b*)

(XXIX)