COMPOUNDS OF AROMATIC RING SYSTEMS AND METALS

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  D. Physicochemical and Crystallographic Properties of Pure Metal Cyclopentadienyl Compounds

I. Introduction

Until 1951, the year in which dicyclopentadienyl iron, $Fe(C_5H_5)_2$, was discovered, the chemistry of complexes formed by metals and hydrocarbons constituted only a small part of either organic chemistry or the chemistry of inorganic complex compounds. Most of the work on organometallic compounds was devoted to alkyl and aryl compounds of metals of the main groups, such as cacodyl (the first organometallic compound known), the Grignard reagents, Gilman's metallic derivatives of organic compounds, and the metal carbonyls.

Unsaturated hydrocarbons were, however, known to be able to form complexes with the halides of some of the platinum metals and with those of copper, silver, and mercury. In such compounds the bonding of the organic residue was sometimes taken to be purely coordinative, as in $(PtCl_2 \cdot C_2H_4)_2$, and sometimes σ-bonding between the metal and carbon, as in CuC_6H_5 or $Pt(CH_3)_4$ was assumed.

Only a few examples of complexes involving aromatic nuclei were then known. Menschutkin's complexes of benzene and its homologues with antimony halides had been discovered and thoroughly investigated; and in these, in the complexes such as $Al_2Br_6 \cdot C_6H_3(CH_3)_3$ isolated by Norris and Ingraham, and in compounds such as $C_6H_6 \cdot AgClO_4$, the essential participation of π-electrons of the aromatic ring in bond formation is now recognized. Coordination compounds in the Sidgwick sense, i.e., with the making up of the electronic structure of the metal atom to an inert gas configuration, were, however, unknown, and the isolation of ferrocene provided the first instance of a substance in which the presence of this type of bonding can be regarded as well established. Since the field of metal complexes containing aromatic rings has in the meantime expanded so extraordinarily, it seems best to discuss the known experimental facts and results in terms of the size of the aromatic ligands. Summaries of five-membered ring metal compounds have been published in 1955 (*42, 150a*).

II. Complex Formation by Five-Membered Ring Systems

Metal derivatives, all largely ionic in character, of the five-membered ring compounds cyclopentadiene, indene, and fluorene have long been known, but there was, until now, no corresponding well-defined organometallic compound of iron. It was therefore a really remarkable event when, in 1951, Miller *et al.* (*130*) and, independently, Kealy and Pauson (*114*), reported the existence of an iron compound $Fe(C_5H_5)_2$ containing two cyclopentadienyl groups attached to one metal atom.

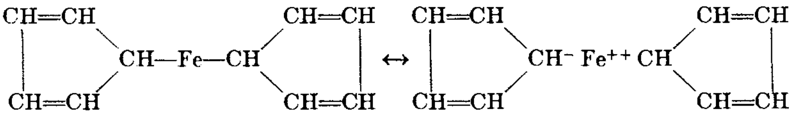
A. DICYCLOPENTADIENYL IRON

The first group of workers observed the formation of this compound by the action of cyclopentadiene on reduced iron at 300°. The latter group described an entirely different approach: it was expected that a coupling reaction of a solution of cyclopentadienyl magnesium bromide containing ferric chloride would yield the (unknown) hydrocarbon "fulvalene," $C_{10}H_8$; instead, the reaction

$$FeCl_2 + 2C_5H_5MgBr \rightarrow Fe(C_5H_5)_2 + 2MgBrCl \qquad (1)$$

took place, with the formation of dicyclopentadienyl iron. Because of the similarity of its reactions to those of benzene, it was christened by R. B. Woodward "ferrocene," by which name it is now usually known.

Ferrocene, $Fe(C_5H_5)_2$, forms orange needles, mp 173-174°; it is insoluble in water, but is readily soluble in all organic solvents. It is stable in air, sublimes readily above 100°, and is thermally stable up to 470°. By suitable oxidizing agents, such as ferric or silver salts, it is converted into the blue dichroic cation $[Fe(C_5H_5)_2]^+$; this process is easily reversible. While ferrocene itself is diamagnetic—its susceptibility $\chi^{25}_{\text{mole}} = -125 \times 10^{-6}$ cm³/mole—the cation has a moment corresponding to the presence of one unpaired electron (*219*). Polarographic studies show the standard potential for the change to be −0.56 v (*149, 219*). Kaplan *et al.* (*112*) investigated the thermodynamic properties of ferrocene and found the heat of sublimation to be 16.81 kcal/mole, the heat of vaporization of the liquid 11.3 kcal/mole, and the heat of fusion 5.5 kcal/mole; the triple point was found to be 183° and the boiling point under normal pressure 249°. The heat of formation from the elements (only hydrogen being in the gaseous state) was found by Wilkinson, from the heat of combustion of ferrocene, to be 33.8 kcal/mole (*21*). Studies of the vibrational spectrum led, after taking into account the heat of sublimation (*112*), to a value of 40.7 kcal/mole (*123*). Infrared and Raman spectra were measured by several workers, and values corresponding to aromatic C-H and C-C bonds were found (*21, 112, 124*); the dichroism of ferrocene crystals was examined by Yamada *et al.* (*225*). All the results of the physicochemical researches on ferrocene may be correlated. X-ray analysis, like the properties mentioned above, soon showed that the original formulation by the discoverers (*114*) as



with partially ionic bonding and localized σ-bonding of the iron to the methylenic carbon atom, was untenable. A new structure was therefore suggested independently by Wilkinson, Woodward, and their co-workers (*219*), and by Fischer and Pfab (*70*). The former group suggested a pentagonal prism or antiprism, a so-called "sandwich" structure; the latter, from X-ray measurements of unit cell dimensions, established the presence of a center of symmetry and hence of the antiprismatic "Doppelkegelstruktur" (double-cone structure). Fourier analyses completely confirm this conception (*30, 31, 33*); Fig. 1 shows a Stuart model of ferrocene.

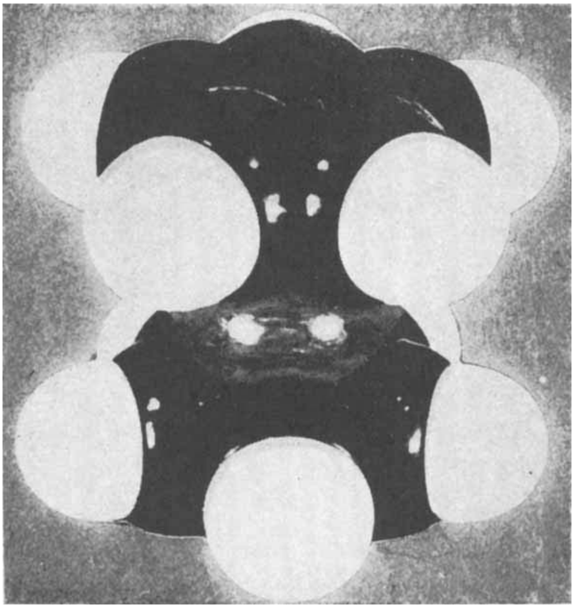


FIG. 1. Model of the ferrocene structure.

B. Preparative Methods for Metal Cyclopentadienyls

The field of metal complexes of cyclopentadiene has subsequently been extended mainly by the two groups of workers who elucidated the structure of ferrocene. New methods for the preparation of such compounds were essential to further progress.

1. Interaction of Metals and Cyclopentadiene

By this method, which had formerly been employed only for the alkali metals and iron, the magnesium derivative, $Mg(C_5H_5)_2$, has recently been prepared in the vapor phase. Cyclopentadiene vapor was passed over magnesium powder at 500-600° and under suitable conditions crystals of mp 176° were obtained (*4*). Thallium and indium reacted similarly with cyclopentadiene vapor at 350°, giving the compounds TlC_5H_5 and InC_5H_5 (*55*). Attempts to develop a more general method of preparation from cyclopentadiene and molten metals met with no success (*121*).

2. Interaction of Metal Salts and Cyclopentadienyl Magnesium Bromide

The reaction of the Grignard reagent C_5H_5MgBr with metal salts proved to be the most widely applicable method. Depending on the resulting oxidation state of the metal, either the uncharged cyclopentadienyl compound or a cationic complex is obtained (*52*, *207*, *217*), the reaction taking the course

$$2C_5H_5MgBr + MeX_n \rightarrow (C_5H_5)_2MeX_{n-2} + 2MgBrX. \qquad (2)$$

For the preparation of uncharged complexes which are sensitive to oxidation, excess of the Grignard reagent (which acts simultaneously as a reducing agent) is employed, and the experiment is carried out in an atmosphere of nitrogen. The compound $Mg(C_5H_5)_2$, which is formed as a by-product, is converted into the magnesium salt of cyclopentadiene carboxylic acid by the passage of carbon dioxide through the ethereal solution, and is thus precipitated and separated (*51*). As the source of the metal in this reaction Wilkinson used the acetylacetonates as well as the halides, and we have employed complex ammine thiocyanates with advantage. Yields are 50-70%.

3. Interaction of Alkali Metal Salts of Cyclopentadiene and Metal Halides

Another method for the preparation of the complexes was early developed by us. As is well known, Thiele, at the turn of the century, obtained the white saline compound KC_5H_5 (the first metal derivative of a five-membered ring system) by the action of metallic potassium on freshly prepared cyclopentadiene in benzene solution (*191*). It was found that a suitable method for the preparation of the alkali metal salts consisted of the action of the metals on cyclopentadiene in liquid ammonia, according to the equation

$$2C_5H_6 + 2Me \xrightarrow{\text{liq } NH_3} 2MeC_5H_5 + H_2 \text{ (Me = Cs, Rb, K, Na, and Li).} \qquad (3)$$

The hydrogen which is produced hydrogenates some of the cyclopentadiene (*108*, *232*):

$$C_5H_6 + H_2 \rightarrow C_5H_8. \qquad (4)$$

It was shown that the alkali metal compounds increase steadily in solubility along the series given above, and that they are dissociated to an extent sufficient to enable precipitation reactions involving the $C_5H_5^-$ ion to be possible. On adding anhydrous metal salts which are soluble in liquid ammonia, such as nitrates and thiocyanates, the following type of reaction takes place:

$$Co(NH_3)_4(SCN)_2 + 2LiC_5H_5 \xrightarrow{\text{liq } NH_3} [Co(NH_3)_6](C_5H_5)_2 + 2LiSCN. \qquad (5)$$

The saline ammine complexes lose ammonia when heated in vacuo, and the uncharged dicyclopentadienyl compounds of Fe, Co, Ni, Cr, and Mn are thereby obtained (*50, 58, 59*). The method generally gives yields of about 70% except for chromium and manganese. It has further been shown that other strongly polar solvents (provided they do not contain reactive hydrogen) can be used instead of liquid ammonia: Wilkinson (*211, 214*) has introduced tetrahydrofuran as probably the most elegant and versatile solvent, and we have shown that other liquids (dimethylformamide and tertiary butyl alcohol) may occasionally also be used with advantage (*48, 49*).

4. Interaction of Metal Halides and Cyclopentadiene

This possible route to the corresponding organometallic compound arises from the use of bases such as triethylamine, diethylamine, or pyridine (*10*), roughly according to the equation:

$$2C_5H_6 + FeCl_2 + 2\,\text{Base} \rightarrow Fe(C_5H_5)_2 + 2\,\text{Base}\cdot HCl. \tag{6}$$

This method, which has been described as giving only a low yield, has been developed industrially to an extraordinary extent, in the case of $Fe(C_5H_5)_2$.

5. Interaction of Metal Carbonyls and Cyclopentadiene

A method which has been used mainly for the preparation of cyclopentadienyl metal carbonyls, but which is occasionally applicable, is that represented roughly by the equation

$$Me(CO)_x + 2C_5H_6 \rightarrow Me(C_5H_5)_2 + xCO + H_2. \tag{7}$$

The yields are 10-30%; for the nickel compound substantially lower (*159, 208*).

6. Special Methods

a. For Ferrocene. For ferrocene itself another synthesis, also involving an intermediate organometallic compound, has recently been described (*109*). By the action of mercuric chloride in methanol on cyclopentadiene a mixture of the compounds C_5H_5HgCl and $Hg(C_5H_5)_2$ is obtained, which with finely divided iron gives ferrocene in yields of up to 30%.

b. For Cyclopentadienyl Thallium. An unusual method for the preparation of this compound has been described recently (*129*). This is similar to one reported earlier by Thiele (*192*) for the preparation of the copper, silver, and mercury compounds; Thiele, however, did not fully establish his claims. The thallium compound, in contrast to those of the alkali metals, is obtained almost quantitatively when an aqueous solution of the hydroxide is shaken with cyclopentadiene:

$$TlOH + C_5H_6 \rightarrow TlC_5H_5 + H_2O. \tag{8}$$

The reaction proceeds so nearly to completion that it has been suggested as the basis of a method for the separation of thallium or of the hydrocarbon.

C. Chemical Properties of the Pure Cyclopentadienyl Metal Compounds

The chemical properties of these new compounds will now be summarized, with special reference to their role in inorganic chemistry. It was seen soon after the discovery of ferrocene, that these new compounds not only present a host of new problems for the inorganic chemist (e.g., in the variation of the metal and in the preparation of complexes containing other ligands), but because of the aromatic character of the cyclopentadienyl rings they are also of fundamental significance in organic chemistry. The hydrogen atoms of the rings in ferrocene can be substituted and, as will be described later, undergo a large number of the reactions characteristic of aromatic systems. In determining the chemical properties of the cyclopentadienyl compounds, the oxidation state of the transition metal at the center of the compound is the controlling factor. If it is one which is usual in other complexes of the metal, the cyclopentadienyl compound is for the most part quite stable. If, however, it is abnormally low, sensitivity towards oxidizing agents results, and in all work with the compound air must then be excluded. The extreme sensitivity to oxidation of $Co(C_5H_5)_2$, in contrast to $Fe(C_5H_5)_2$, is typical of the behavior of these substances as complexes, and will be discussed later. The $[Co(C_5H_5]^+$ ion, on the other hand, is extraordinarily resistant to chemical attack. The uncharged dicyclopentadienyl complexes of the ferrocene type are readily volatile, crystallize very well, and dissolve easily in the common organic solvents. As a rule, oxidation and reduction may be brought about without difficulty. For those dicyclopentadienyl cations which are stable to hydrolysis, a large number of precipitation reactions are available, the most important being those with the reineckate, $[Cr(SCN)_4(NH_3)_2]^-$ *(70)*; tetraphenylborate, $[(C_6H_5)_4B]^-$ *(57)*; and picrate, $(C_6H_2N_3O_7)^-$ *(219)* ions. Perchlorate, hexafluorophosphates, fluoroborates, chloroplatinates and cobaltinitrites are also often only sparingly or moderately soluble. Polyhalides (e.g., tribromides and triiodides) are also slightly soluble, but common anions such as sulfate, carbonate, nitrate, cyanide, fluoride, chloride, bromide, iodide, and phosphate yield no precipitate.

Alkali and alkaline-earth metal cyclopentadienyls are, in contrast to the transition metal complexes, typically saltlike in character; so, too, are the tricyclopentadienyl compounds of the rare-earth metals. Their ionic structure is shown by their dissociation in nonacidic strongly polar solvents such as liquid ammonia, tetrahydrofuran, *N*,*N*-dimethylformamide, and glycol dimethyl ether. The compounds of various main group elements such as zinc, mercury, tin, lead, and bismuth occupy an intermediate position; they show varying degrees of stability towards hydrolysis, and their molecular structures are not yet fully understood.

1. Cyclopentadienyl Compounds Known at the Present Time

In Fig. 2, in the framework of the periodic table, are shown the elements (both transition elements and typical elements) for which

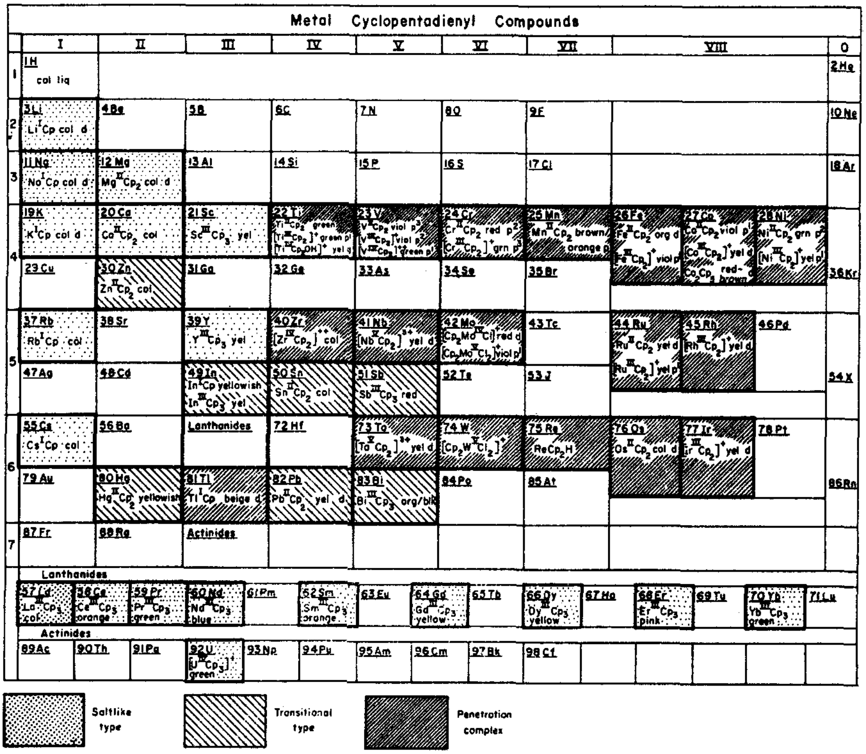


FIG. 2. Metal cyclopentadienyl compounds. Key: Cp, cyclopentadiene; dotted squares, saltlike type; shaded squares, penetration complexes; squares with diagonals, transitional type; d, diamagnetic; p^1, p^2, p^3, paramagnetic with one, two, and three unpaired electrons, respectively; col, colorless; yel, yellow; viol, violet; cryst, crystalline.

cyclopentadienyl compounds have so far been isolated. The division into saltlike compounds, true organometallic penetration complexes, and intermediate substances is also shown, though it is not considered that an unequivocal classification is at present always possible. Oxidation states of the metals (that of an aromatic cyclopentadienyl residue being taken as −1) and net charges on complexes are also shown.

2. *First Main Group*

The white saline potassium compound KC_5H_5 was obtained by Thiele as early as 1901 by the action of the metal on a solution of cyclopentadiene in benzene (*191*); compounds of all the alkali metals except francium have now been made by the interaction of the metal and the hydrocarbon in liquid ammonia (*38*). They are without exception colorless salts which decompose immediately, with consequent discoloration, on exposure to the atmosphere. They are dissociated to a large extent in polar solvents, and the Na-C bond has been estimated as 50% ionic (*205*). They are insoluble in nonpolar solvents, and in solvents which contain active hydrogen (e.g., water) they at once undergo hydrolysis according to the equation

$$MeC_5H_5 + H_2O \rightarrow MeOH + C_5H_6. \tag{9}$$

3. *First Subgroup*

In this group, too, the first observations were made by Thiele (*192*), who found that cuprous and silver ions are precipitated from aqueous ammoniacal solution by cyclopentadiene, but gave no analytical data. Thallium was later found to be precipitated similarly. Copper(I), however, also yields a white crystalline cyclopentadienyl-triethylphosphine complex, $C_5H_5CuP(C_2H_5)_3$, which is stable to water (*215*); this was, in fact, analogous to an earlier method described by van Peski and Melsen. Attempts to make a complex by the Grignard reagent method or by the action of cyclopentadienyl sodium on cuprous halides were unsuccessful.

4. *Second Main Group*

The dicyclopentadienyl derivatives of these elements which are known at the present time (those of magnesium and calcium) are in many respects similar to those of the alkali metals, being colorless, saltlike compounds. The magnesium compound was successfully prepared by the interaction of sodium cyclopentadienyl and magnesium bromide in tetrahydrofuran (*214*), by thermal decomposition of cyclopentadienyl magnesium bromide (*214*) and, recently, by the action of cyclopentadiene vapor on magnesium powder at 500-600° (*4*). It forms colorless needles, mp **176-178°**, and reacts vigorously with water, with the formation of cyclopentadiene and magnesium hydroxide. With carbon dioxide and carbon disulfide, formation of the magnesium salts of cyclopentadienecarboxylic and -thiocarboxylic acids results. It is soluble in ether and is immediately decomposed on exposure to the atmosphere.

The calcium compound is obtained by the reaction

$$CaC_2 + 2C_5H_6 \rightarrow Ca(C_5H_5)_2 + C_2H_2 \qquad (10)$$

but it has not yet been prepared in a pure state (*231*).

5. *Second Subgroup*

The colorless zinc compound, $Zn(C_5H_5)_2$, which sublimes at 160° under partial decomposition, is obtained in small yield from zinc chloride and cyclopentadienyl sodium in diethyl ether; however, the less stable cadmium compound decomposes, with separation of cadmium, under these conditions (*55*). The mercury compound, $Hg(C_5H_5)_2$, is produced in 20% yield by the action of the sodium derivative on mercuric chloride in tetrahydrofuran (*215*). The action of cyclopentadiene on the complex $K_2(HgI_4)$ in aqueous alkaline solution results in the precipitation of a mixture of C_5H_5HgI and $Hg(C_5H_5)_2$, from which the latter compound may be obtained in good yield by extraction with a mixture of tetrahydrofuran and petroleum ether (*62*). It forms pale yellow crystals which begin to decompose at about 60° and which melt at 83-85°. The compound is readily soluble in most solvents; it decomposes slowly even when kept in the dark at room temperature; it is insoluble in water and reacts with neither water nor bases. On the other hand, decomposition occurs in dilute hydrochloric acid. It converts ferric chloride to ferrocene quantitatively, and it yields an adduct with maleic anhydride (*215*).

By the action of monomeric cyclopentadiene on mercuric chloride in methanol, in the presence of sodium acetate, a bright yellow crystalline deposit, consisting of a mixture of C_5H_5HgCl and $Hg(C_5H_5)_2$, is obtained (*109, 192*). Neither treatment with solvents (e.g., tetrahydrofuran or dioxan) nor vacuum sublimation effects a separation of this mixture, since with slight increase in temperature the crude product decomposes (*109*).

Cyclopentadiene reacts with mercuric cyanide in aqueous solution, giving the insoluble cream compound C_5H_5HgCN. Like the corresponding iodide (which is also cream) this compound is fairly stable in air, but does not melt sharply (*62*). By the reaction of indenyl lithium and mercuric chloride in dry ether, indenyl mercuric bromide (the bromine being derived from the indenyl bromide used at an earlier stage in the synthesis) is obtained as a yellow substance of mp 118°. Attempts to make diindenyl- and difluorenyl-mercury have not been successful (*27*).

6. Third Main Group

Sodium cyclopentadienyl reacts with indium trichloride in ether, tetrahydrofuran, or dioxan, forming the volatile compound InC_5H_5, which may be obtained as pale yellow needles by sublimation (*56*). This substance does not melt sharply, but slowly decomposes and darkens at 110°. It is very sensitive to oxidation and is slightly soluble in benzene, in which decomposition takes place; it is, however, rather less soluble in ether and petroleum ether. Water has no action on the compound, but on addition of a little sulfuric acid it is vigorously decomposed. The crystals are slightly sensitive to light. In the preparation of InC_5H_5 an intermediate product, $In(C_5H_5)_3$, can be isolated in very small yield as golden crystals. On sublimation at above 160° it decomposes to form the monocyclopentadienyl compound.

Thallous hydroxide or thallous salts in the presence of alkali react with cyclopentadiene to yield TlC_5H_5 (*129*). This substance, which is stable in air, crystallizes at 0° in colorless needles (in pale yellow needles at 60°), and is practically insoluble in water; it is, however, moderately soluble in methanol, acetone, pyridine, etc. It does not melt when heated, but it sublimes at 100° in a high vacuum (*81*).

7. Third Subgroup

All known cyclopentadienyl compounds of this group are prepared by the action of the sodium derivative on the metal chlorides in tetrahydrofuran (*9, 167, 212*). With the exception of $(C_5H_5)_3UCl$ and $Th(C_5H_5)_4$, all are ionic compounds of general formula $Me(C_5H_5)_3$. The results of Wilkinson and his co-workers are summarized in Table I. All of these substances have similar properties. All are unstable in air, especially the cerium compound, which is noteworthy for being blue-green in the vapor state. Water effects immediate decomposition; the uranium compound is converted into the unstable green $[U(C_5H_5)_3]^+$ ion, which may be precipitated as its reineckate; the thorium derivative yields the still more unstable $[Th(C_5H_5)_2]^{++}$ or $[Th(C_5H_5)_3]^+$ ion; the others are decomposed immediately to cyclopentadiene and the metal hydroxide. All the neutral cyclopentadienyl complexes are almost insoluble in petroleum ether, cyclohexane, and benzene, but are moderately soluble in pyridine, tetrahydrofuran, and dioxan. They are rapidly decomposed by carbon disulfide, carbon tetrachloride, or chloroform. The compounds $U(C_5H_5)_3$ and $U(C_5H_5)_2Cl$ have also been made and analyzed, but because of the

TABLE I

CYCLOPENTADIENYL COMPOUNDS OF SUB-GROUP THREE ELEMENTS

Compound $Me(C_5H_5)_3$ Me =	Melting point, closed tube (°C)	Color	Sublimation temperature, 10^{-4} mm Hg (°C)	Yield (%)
Sc	240	yellow	200	75
Y	295	pale yellow	220	85
La	395†	colorless	260	25
Ce	435†	orange-yellow	230	72
Pr*	415†	blue-green	220	83
Nd	380	reddish-blue	220	78
Sm*	365	orange	220	75
Gd	350	yellow	220	84
Dy	302	yellow	220	85
Er	285	pink	200	88
Yb	273	dark green	150	82
$(C_5H_5)_3UCl$	260	dark red	245	82
$(C_5H_5)_4Th(?)$		colorless	250	1

* Ammoniates of these compounds have been observed.

† Decomposes.

smallness of the yields in which they were obtained they have not yet been investigated further (*167*).

8. *Fourth Main Group*

Silicon compounds of formula $(C_5H_5)Si(CH_3)_3$ and $(C_5H_5)_2Si(CH_3)_2$ are obtained by the action of cyclopentadienyl magnesium bromide on trimethylchlorosilane and dimethyldichlorosilane; they are colorless liquids which boil at 43-44° (19 mm pressure) and 73° (25 mm), respectively (*89*). The monocyclopentadienyl compound darkens on exposure to air, and it forms an adduct of mp 105° with maleic anhydride, thus showing the retention of the conjugated system in the compound.

Stannous chloride reacts with cyclopentadienyl lithium in dimethylformamide to give the compound $Sn(C_5H_5)_2$ (*48*). This substance is unstable in air, forms colorless crystals (mp 105°), and is moderately soluble in benzene, ether, and petroleum ether. Cold water does not effect hydrolysis, but acids bring about decomposition with liberation of cyclopentadiene. The interaction of aryl tin(IV) chlorides and cyclopentadienyl magnesium bromide leads to a series of dicyclopentadienyltin(IV) aryl compounds (*93*) which are unstable in air or in light and are rapidly hydrolyzed by water.

The lead compound $Pb(C_5H_5)_2$, which may be obtained by the action of the sodium derivative on lead nitrate in dimethylformamide, has similar properties. It occurs as well-formed, strongly refracting yellow crystals which do not melt sharply, but which after sintering at 139° or higher temperatures become deep orange in color. Since this color change is reversed on cooling, the compound is thermochroic. The compound dissolves in benzene, acetone, ether, and petroleum ether, but not in water, and does not undergo hydrolytic fission, with liberation of cyclopentadiene, in the cold (*49*).

The interaction of indenyl- and fluorenyl-lithium and phenyl-substituted plumbic chlorides produces the corresponding phenyl lead derivatives (*27*), but attempts to prepare difluorenyl lead and diindenyl lead were not successful.

9. *Fourth Subgroup*

Dark red crystals of the complex $(C_5H_5)_2TiBr_2$ (mp 314°) are obtained by the action of cyclopentadienyl magnesium bromide on titanium tetrachloride in toluene; the compound is moderately soluble in aromatic solvents, but water slowly decomposes it, producing a yellow solution which gives the usual precipitation reactions for dicyclopentadienyl metal cations. The almost colorless complex $(C_5H_5)_2ZrBr_2$ (mp 260° with decomposition) is obtained by an analogous method (*211, 217*).

By reduction with zinc at 275°, $(C_5H_5)_2TiCl_2$ is converted into the green crystalline compound $(C_5H_5)_2TiCl$ (*209*). In addition, the compound $Ti(C_5H_5)_2$ is obtained in 40% yield by the interaction of titanium dichloride and sodium cyclopentadienyl in tetrahydrofuran (*37*). Dark green crystals are formed, which sublime at 120-180°, and start decomposing at 130° without melting; oxidation is rapid in air. In benzene, ether, and petroleum ether it forms green solutions; carbon disulfide and carbon tetrachloride decompose it; oxygen-free water, in which it is insoluble, very slowly oxidizes it to the compound $(C_5H_5)_2Ti(OH)_2$. Two modifications of an etherate exist. By the action of $(C_5H_5)_2TiCl_2$ on lithium aryls, a series of crystalline orange compounds of the type $(C_5H_5)_2$ $Ti(aryl)_2$ are obtained (*188, 189, 190*). Grignard reagents react similarly (*157*), from which it is deduced that the aryl groups are σ-bonded to the metal.

10. *Fifth Main Group*

Mention must first be made of some interesting compounds in which the $C_5H_5^-$ ion is bonded to nitrogen; these are pyridine cyclopentadienylide (*125*) and diazocyclopentadiene (*28*). Triphenylphosphonium cyclopentadienylide (*161*) is a pale yellow crystalline compound (mp 230°) which is stable to boiling alkali and which (in contrast to triphenylphosphine-methylenes) does not react with ketones.

Tricyclopentadienyl bismuth, $Bi(C_5H_5)_3$, which is obtained from cyclopentadienyl sodium and bismuth trichloride in solvents which do not contain reactive hydrogen, exists as an orange modification which at 18° is converted irreversibly into a black form. It is hydrolyzed by water (*73*). The analogous carmine compound $Sb(C_5H_5)_3$, which is also hydrolyzed by water, is prepared by a similar method at low temperature (*73*).

11. Fifth Subgroup

Dicyclopentadienyl metal halides of vanadium, niobium, and tantalum may be made by the action of cyclopentadienyl magnesium bromide on the appropriate metal salt in benzene-ether solution, or by interaction of the sodium derivative and the salt in tetrahydrofuran or dimethylcellosolve (*211, 217*). Starting from vanadium tetrachloride, the compound of quadrivalent vanadium is obtained; the pentabromides of niobium and tantalum yield derivatives of the elements in the quinquevalent state. The vanadium compound, $(C_5H_5)_2VCl_2$, forms light green crystals which decompose without melting at 250°; it is soluble in alcohol and in chloroform, slightly soluble in ether, benzene, carbon disulfide, and carbon tetrachloride, and insoluble in petroleum ether. It dissolves in water to give an unstable green solution containing the $[V(C_5H_5)_2]^{++}$ ion, which in the Jones reductor can be reduced to the purple $[V(C_5H_5)_2]^+$ ion (*211*).

The uncharged compound $V(C_5H_5)_2$ was first prepared from vanadium tetrachloride and an excess of cyclopentadienyl magnesium bromide in the absence of air (*51*); it was later obtained by reduction of the dichloride by lithium aluminum hydride (*209*). It forms readily volatile violet-black crystals of mp 167-168°. It is very soluble in benzene, ether, and petroleum ether, and is stable in the absence of air.

Dicyclopentadienyl niobium tribromide, $(C_5H_5)_2NbBr_3$, forms fine, dark reddish-brown needles which decompose without melting at about 260°. The compound is readily soluble in polar solvents, but does not dissolve in petroleum ether. On exposure to the atmosphere it is slowly hydrolyzed, with the formation of the orange-red compound $(C_5H_5)_2Nb(OH)Br_2$ (*211*). The tantalum compound, $(C_5H_5)_2TaBr_3$, forms rose-colored crystals (mp 280° with decomposition) which are extremely sensitive to moisture. It is soluble in polar solvents, the solutions resembling those of the niobium compound.

12. Sixth Subgroup

Dicyclopentadienyl chromium was first made in very small quantity by thermal decomposition of the ammine $[Cr(NH_3)_6](C_5H_5)_3$ (*50*); it was later also obtained by vapor phase interaction of chromium carbonyl and cyclopentadiene (*208*) or by the action of the sodium compound on chromous or chromic chloride in tetrahydrofuran (*22*). The compound sublimes at 60-80° in a high vacuum, forming ruby-red needles (mp 173°). In the absence of oxygen it is stable up to 300°; it is not decomposed by light, and it is not attacked by oxygen-free water. Treatment with acids yields transient blue solutions which may contain cationic binuclear monocyclopentadienyl-hydroxychromium compounds. Dicyclopentadienyl chromium reacts with iodine to form the green iodide $(C_5H_5)_2CrI$, which is soluble in, e.g., tetrahydrofuran or dioxan to form green solutions (*63*). By means of the third method given for the preparation of $Cr(C_5H_5)_2$, cationic dicyclopentadienyl derivatives of molybdenum and tungsten may be prepared (*22*).

When the Grignard reagent reacts with molybdenum pentachloride, a red solution containing the $[(C_5H_5)_2MoCl]^+$ ion, which may be precipitated as its reineckate or silicotungstate, is produced; this is converted by oxidation into the violet-red dichroic $[(C_5H_5)_2MoCl_2]^+$ ion, which yields an insoluble chloroplatinate. From molybdenum pentachloride and sodium cyclopentadienyl in tetrahydrofuran the compound $(C_5H_5)_2MoCl_2$ is obtained in the form of green needles (*22*). Tungsten hexachloride reacts similarly, and the compound $[(C_5H_5)_2WCl_2]_2(PtCl_6)$ may be isolated.

13. Seventh Subgroup

Dicyclopentadienyl manganese was first obtained by thermal decomposition of the ammine $[Mn(NH_3)_6](C_5H_5)_2$ (*50, 111*). Shortly afterward, it was made in good yield by the reaction between manganese bromide and cyclopentadienyl sodium in tetrahydrofuran (*214*), and it may also be prepared by the interaction of manganese chloride and an ethereal solution of the Grignard reagent, followed by sublimation (*60*). At ordinary temperatures it forms brown crystals.

The compound is exceedingly reactive, and is vigorously decomposed by deaerated water with the separation of cyclopentadiene. It is only sparingly soluble in benzene or ether, forming brownish-yellow solutions. When it is heated in a sealed tube, it becomes almost colorless at 158-159°, and then melts sharply, without decomposition, at 172-173° (*214*). On slow cooling the color change is reversed at 159°, but by chilling the white form the transformation may be retarded. By an analogous reaction of rhenium pentachloride and cyclopentadienyl sodium in tetrahydrofuran, a yellow crystalline substance which sublimes at 120-170°, melts at 162°, and has the formula $Re(C_5H_5)_2H$, is obtained (*213*). The compound is unaffected by water, but reacts moderately rapidly with air. It is readily soluble in benzene, ether, and petroleum ether. The hydrogen atom is not acidic, and the compound does not react even with $6N$ sodium hydroxide. Surprisingly, the compound acts as a base, and will dissolve in, for example, hydrochloric acid, to form the complex ion $[(C_5H_5)_2ReH_2]^+$; addition of alkali reverses this process.

14. Eighth Group

The most important compound in this group is, of course, ferrocene; since, however, it has been described in detail in Section IIA as the parent substance of the whole group of five-membered ring complexes, only a further brief reference to its properties will be made here. Although the early attempts to hydrogenate it under ordinary conditions were unsuccessful, this operation was accomplished under extreme conditions (*144*); under 280 atm of hydrogen at 300-340°, using Raney nickel in cyclohexane, pentane and cyclopentane are produced, but even after four hours over half of the ferrocene remains unchanged. A more elegant method, and one of greater significance in the preparative organic chemistry of five-membered ring compounds, is that of reductive cleavage by lithium in ethylamine (*194*). This operation may also be effected by alkali metals in liquid ammonia.

Because of the extreme stability of the "cobalticinium" ion, $[Co(C_5H_5)_2]^+$, other cyclopentadienyl compounds of cobalt were not at first obtainable. The bromide, $[Co(C_5H_5)_2]Br$, was first made by the action of cyclopentadienyl magnesium bromide on cobalt(III) acetylacetonate in benzene (*207*); it may also be obtained by oxidative hydrolysis of the product obtained from the Grignard reagent and cobalt bromide in ether (*57*). Both the bromide and the corresponding fluoride are very hygroscopic. The $[Co(C_5H_5)_2]^+$ ion is very stable to both acids and alkalis; it is unattacked even by aqua regia, alkaline hydrogen peroxide, or ozone in acetic acid, and only fusion with potassium pyrosulfate or treatment with fuming perchloric acid effects decomposition of the complex.

The neutral complex $Co(C_5H_5)_2$ has been obtained by the action of alkali metal cyclopentadienyls on the complex $[Co(NH_3)_4](SCN)_2$ in liquid ammonia (*59*) and, more recently, by lithium aluminum hydride reduction of the $[Co(C_5H_5)_2]^+$ ion (*209*). It forms deep violet-black needles, melts at 173-174°, and is exceptionally sensitive to atmospheric oxidation. In organic solvents such as benzene, petroleum ether, ether, or alcohol it forms dark reddish-brown solutions which are stable if air is completely excluded. Cold water which has been saturated with nitrogen neither attacks nor dissolves the compound. After the discovery of the tricyclopentadienyl compounds of the rare-earth metals, attempts to prepare the compound $Co(C_5H_5)_3$ were made. By the interaction of $[Co(C_5H_5)_2]Br$ and lithium cyclopentadienyl in liquid ammonia or tetrahydrofuran a new type of binuclear derivative, the reddish-brown compound $Co_2(C_5H_5)_5$, was obtained (*39*); this substance is freely soluble in solvents such as benzene and ether.

The nickel complex, $Ni(C_5H_5)_2$, has been made by the action of the Grignard reagent on nickel(II) acetylacetonate (*217*) or from potassium cyclopentadienyl and the ammine $[Ni(NH_3)_6](SCN)_2$ in liquid ammonia (*58*). It forms dark emerald-green crystals which sublime at 80-90° and which, when heated in nitrogen, melt, with decomposition and the formation of a nickel mirror, at 173-174°. It is only slowly oxidized in air, and cold water neither attacks nor dissolves it; it is, however, readily soluble in organic liquids. Oxidation of the compound yields an orange-yellow solution containing the ion $[Ni(C_5H_5)_2]^+$, which is stable for a short period in weakly acidic media, and which may be precipitated as the reineckate or tetraphenylborate.

Ruthenium, the homologue of iron in this group, was also shown to form complexes quite early. Ruthenocene, $Ru(C_5H_5)_2$, is obtained by treatment of the acetylacetonate of tervalent ruthenium with five times the theoretical quantity of the Grignard reagent (*206*), or, better, by the action of cyclopentadienyl sodium on ruthenium trichloride in tetrahydrofuran (*47*). It forms pale yellow scales which sublime at 120° and melt at 200°. Its properties are closely similar to those of ferrocene; it is soluble in organic solvents, and in the absence of air is not attacked by bases or by sulfuric or hydrochloric acid. Oxidation converts it into the pale yellow $[Ru(C_5H_5)_2]^+$ ion.

The compound $Rh(C_5H_5)_2$ has not yet been obtained, but the action of cyclopentadienyl magnesium bromide on rhodium(III) acetylacetonate yields a derivative of the cation $[Rh(C_5H_5)_2]^+$, which forms a yellow solution in water (*25*). It gives precipitates with the usual reagents and is generally similar in properties to the $[Co(C_5H_5)_2]^+$ ion.

Osmocene, $Os(C_5H_5)_2$, has recently been made, in 20% yield, by the interaction of cyclopentadienyl sodium and osmium tetrachloride (*47*). It forms colorless crystals which melt at 230°; again, it dissolves in organic solvents; water, however, has no action on it, nor does it dissolve. The hydrogen atoms in the cyclopentadienyl rings, like those in ferrocene and ruthenocene, can undergo substitution; this property has not been described for other metal cyclopentadienyl compounds, except in one reference to the $[Co(C_5H_5)_2]^+$ ion. Careful oxidation of osmocene by ferric chloride results in the formation of the brown $[Os(C_5H_5)_2OH]^+$ cation; at low concentrations the color becomes yellow.

The $[Ir(C_5H_5)_2]^+$ ion, analogous to the $[Co(C_5H_5)_2]^+$ and $[Rh(C_5H_5)_2]^+$ ions, also has been obtained and investigated; as was expected, it showed similar properties. The uncharged complex $Ir(C_5H_5)_2$, like $Rh(C_5H_5)_2$, has not yet been prepared. For palladium and platinum only simple olefin complexes are, as yet, known. Among these there is also a complex of platinous chloride with cyclopentadiene, but physical evidence excludes the possibility of a "sandwich" structure in this compound (*29*).

15. Indenyl Compounds of Eighth-Group Elements

For metals in this group several compounds have been made in which, instead of cyclopentadiene, indene is the source of the five-membered ring. Diindenyl iron, $Fe(C_9H_7)_2$, may be prepared as violet-black crystals by the action of indenyl magnesium bromide (*76*) or indenyl lithium (*151*) on ferric chloride. This compound sublimes at 90° in vacuo, sinters at about 160°, and melts at 179-180° (in an evacuated tube at 184-185°). The solid substance is relatively stable in air, but its solutions in organic solvents such as benzene, ether, or alcohol (which are dichroic), decompose rapidly. Water neither dissolves nor attacks the compound, and it is not possible to oxidize it to a stable cation. It may, however, be hydrogenated in alcoholic solution, using a platinum catalyst, and ditetrahydroindenyl iron, $Fe(C_9H_{11})_2$, an orange-colored oily liquid (fp 18.5-19°, distilling without decomposition at 125° at 10^{-3} mm pressure) is thus obtained (*77*). This substance is stable to air for a short time; it is insoluble in water, but dissolves readily in organic solvents. Suitable oxidizing agents convert it into the rather unstable blue $[Fe(C_9H_{11})_2]^+$ cation.

Diindenyl cobalt, $Co(C_9H_7)_2$, may be produced by the interaction of indenyl potassium and the ammine $[Co(NH_3)_4](SCN)_2$ in liquid ammonia (*87*). It forms black lustrous crystals which can be sublimed without decomposition; they slowly sinter at 160° and melt rather gradually at about 180°. The compound is very soluble in benzene, ether, and alcohol but less soluble in petroleum ether, forming brown solutions. It is considerably less sensitive to oxidation than the dicyclopentadienyl, $Co(C_5H_5)_2$, but powerful oxidizing agents convert it into the yellow $[Co(C_9H_7)_2]^+$ ion (*87*), which may also be obtained by a Grignard reaction (*151*).

A dark red-brown nickel compound, $Ni(C_9H_7)_2$, may also be prepared; this gives cherry-red solutions in organic solvents (*87*). It is

TABLE II

Magnetic Moments of Cyclopentadienyl Metal Compounds

Central ion	Compound ($Cp = [C_5H_5]^-$)	No. of unpaired elec- trons	Moment (Bohr magnetons) calc	Moment (Bohr magnetons) exp	Reference
Mg^{+2}	$MgCp_2$	0	0	0	*66*
In^+	$InCp$	0	0	0	*56*
Tl^+	$TlCp$	0	0	0	*71*
Sc^{+3}	$ScCp_3$	0	0	0	*9*
Y^{+3}	YCp_3	0	0	0	*9*
La^{+3}	$LaCp_3$	0	0	0	*9*
Ce^{+3}	$CeCp_3$			2.46	*9*
Pr^{+3}	$PrCp_3$			3.61	*9*
Nd^{+3}	$NdCp_3$			3.63	*9*
Sm^{+3}	$SmCp_3$			1.54	*9*
Gd^{+3}	$GdCp_3$			7.98	*9*
Dy^{+3}	$DyCp_3$			10.00	*9*
Er^{+3}	$ErCp_3$			9.45	*9*
Yb^{+3}	$YbCp_3$			4.00	*9*
U^{+4}	Cp_3UCl solid	2	2.83	3.16	*164*
	in solution	2	2.83	2.72	*164*
Sn^{+2}	$SnCp_2$	0	0	0	*71*
Pb^{+2}	$PbCp_2$	0	0	0	*71*
Ti^{+2}	$TiCp_2$	0	0	0	*37*
Ti^{+3}	$(TiCp_2)^+$	1	1.73	2.3	*211*
Ti^{+4}	Cp_2TiBr_2	0	0	0	*217, 211*
Bi^{+3}	$BiCp_3$	0	0	0	*73*
V^{+2}	VCp_2	3	3.87	3.78 ± 0.19	*66, 51, 116*
V^{+3}	$(VCp_2)^+$	2	2.83	2.86 ± 0.6	*211,*
V^{+4}	Cp_2VCl_2	1	1.73	1.95	*217, 211*
Nb^{+5}	Cp_2NbBr_3	0	0	0	*211*
Cr^{+2}	$CrCp_2$	2	2.83	3.02 ± 0.15	*66*
Cr^{+3}	$(CrCp_2)I$	3	3.87	3.81	*74*
				3.73	*71*
Mo^{+4}	$(Cp_2MoCl)^+$	0	0	0	*22*
Mo^{+5}	$(Cp_2MoCl_2)^+$	1	1.73	1.5 ± 0.1	*22*
Mn^{+2}	$MnCp_2$	1	1.73		*216, 116*
Fe^{+2}	$FeCp_2$	0	0	0	*219, 70, 34*
Fe^{+3}	$(FeCp_2)^+$	1	1.73	2.26	*219*
				2.34 ± 0.12	*34*
Co^{+2}	$CoCp_2$	1	1.73	1.76 ± 0.07	*59, 34*
	Co_2Cp_6 solid			0	*39*
	in solution			1.7	*39*
Co^{+3}	$(CoCp_2)^+$	0	0	0	*34, 207*
Ni^{+2}	$NiCp_2$	2	2.83	2.86 ± 0.1	*58, 66, 116, 218, 34*
Ni^{+3}	$(NiCp_2)^+$	1	1.73		*58, 34, 218*
Fe^{+2}	$Fe(C_9H_7)_2$	0	0	0	*151, 76, 66*
Fe^{+2}	$Fe(C_9H_{11})_2$	0	0	0	*66*
Co^{+2}	$Co(C_9H_7)_2$	1	1.73	1.76 ± 0.09	*87, 66*
Co^{+3}	$[Co(C_9H_7)_2]^+$	0	0	0	*87*
Ni^{+2}	$Ni(C_9H_7)_2$	2−	2.83	2.12 ± 0.1	*66*
Ru^{+2}	$Ru(C_9H_7)_2$	0	0	0	*66*
Ru^{+2}	$Ru(C_9H_{11})_2$	0	0	0	*71*

considerably more labile than the compound $Ni(C_5H_5)_2$—an order of stability which is common to all indenyl complexes. The orange ruthenium compound, $Ru(C_9H_7)_2$, has also been isolated (*185*); like the iron complex, on hydrogenation it absorbs only four atoms of hydrogen per six-membered ring.

D. Physicochemical and Crystallographic Properties of Pure Metal Cyclopentadienyls

1. *Magnetic Investigations*

In Table II are assembled the compounds for which measurements have been made (so far by the Gouy method) and the results obtained. The behavior of the manganese compound, $Mn(C_5H_5)_2$, is especially interesting. This compound has been investigated over the temperature range 4-530°K. (*116*, *216*), and is found to be antiferromagnetic with a Neél temperature of 134 ± 2°K. Earlier results are thereby superseded.

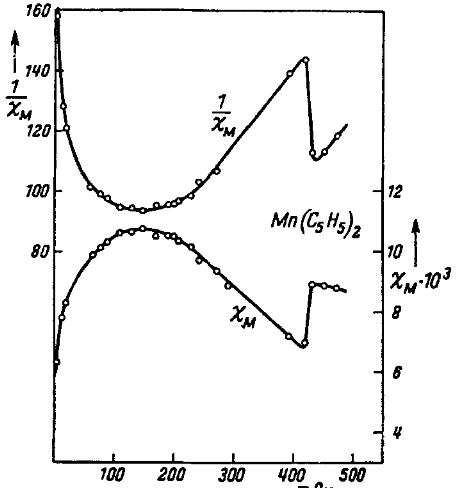


FIG. 3. Temperature dependence of the susceptibility of $Mn(C_5H_5)_2$ in the range 1.5-470°K.

The brown low-temperature form of $Mn(C_5H_5)_2$ shows a sharp transition point at 158-159°K and undergoes an enantiotropic transition into a pale pink modification. There thus takes place a sudden transition to five unpaired electrons, see Fig. 3 (corresponding to a moment of 5.9 Bohr magnetons for $\theta = 0$) and these are also observed to be present from the melting point at 170-172° to 530°K. We interpret this as being a gradual transition of a penetration complex in which relaxation occurs into a purely ionic compound with increasing temperature. However, conditions in the lattice of the brown $Mn(C_5H_5)_2$, which have not yet been conclusively elucidated, may also play a decisive part. In solid solution in $Mg(C_5H_5)_2$, as in benzene or ether solution, the compound behaves as a purely ionic complex at all temperatures (*66*, *216*). Dicyclopentadienyl vanadium is also found to be antiferromagnetic at temperatures below 13°K. (*116*).

An investigation of the parahydrogen conversion by the manganese compound in tetrahydrofuran threw little light on the problem, for the compound dissociates completely into ions, and so only the characteristic results for the Mn^{++} ion were obtained (*182*). Some others of the compounds listed in Table II have also been investigated by means of the parahydrogen conversion (*180*, *181*, *182*). Except for the uncharged complexes $Co(C_5H_5)_2$ and $Ni(C_5H_5)_2$, they gave results in harmony with those obtained by magnetic measurements. For the two compounds mentioned, there appear to be abnormally great orbital moments for the unpaired electrons (*175*).

2. Polarographic Investigations

The redox potential has been determined for a number of the new compounds; it is usually found to be similar to those of known compounds of the metal. An increased stability of the higher oxidation state of the metal with higher atomic weight is observed. Table III sets out the data. The second column gives the values measured against the

TABLE III

POLAROGRAPHIC HALF-WAVE POTENTIALS OF SOME FIVE-MEMBERED RING COMPLEXES

	Half-wave potential (v)		
Redox reaction	in water	in alcohol	Reference
$[Ti(C_5H_5)_2]^{++} \rightleftarrows [Ti(C_5H_5)_2]^+$	−0.44		*211*
$[V(C_5H_5)_2]^{++} \rightleftarrows [V(C_5H_5)_2]^+$	−0.32		*211*
$[Nb(C_5H_5)_2]^{+++} \rightarrow$?	−0.44		*211*
	−0.71		*211*
$Fe(C_5H_5)_2 \rightarrow [Fe(C_5H_5)_2]^+$		+0.31	*149*
$[Fe(C_5H_5)_2]^+ \rightarrow Fe(C_5H_5)_2$	+0.16	+0.30	*149*
$[Co(C_5H_5)_2]^+ \rightarrow$?	−1.16		*149*
$Ni(C_5H_5)_2 \rightarrow [Ni(C_5H_5)_2]^+$		−0.08	*218*
$[Ni(C_5H_5)_2]^+ \rightarrow Ni(C_5H_5)_2$	−0.21		*218*
$Ru(C_5H_5)_2 \rightarrow [Ru(C_5H_5)_2]^+$		+0.26	*149*
$[Ru(C_5H_5)_2]^+ \rightarrow Ru(C_5H_5)_2$	+0.11	+0.22	*149*
$Co(C_9H_7)_2 \rightarrow$?	−0.60		*151*

standard calomel electrode in aqueous solution; the third column the values in alcoholic solution. For the dicyclopentadienyl cations of Rh(III) and Ir(III) (also present as their perchlorates) a half-wave potential of −1.53 v in water for the former showed that the neutral $Rh(C_5H_5)_2$ was probably formed, whereas for the latter no indication of $Ir(C_5H_5)_2$ was found (*25*).

3. X-ray Investigations

This method was applied even at an early date to elucidate the molecular structure of the metal cyclopentadienyls. After the first investigations of ferrocene itself (*30, 33, 70, 152*), others, such as those of $Co(C_5H_5)_2$ (*152*), $Ni(C_5H_5)_2$ (*32, 152*), $V(C_5H_5)_2$ (*199*), $Mg(C_5H_5)_2$ (*199*), $Cr(C_5H_5)_2$ (*200*), and of the brown form of $Mn(C_5H_5)_2$ (*198*) followed. Space groups and unit cell dimensions were determined: with the exception of $Mn(C_5H_5)_2$, which crystallizes in the rhombic system, with the probable space group D_{2h}^{21} with 16 molecules in the unit cell, all the compounds have monoclinic symmetry with space group C_{2h}^{5}, with two molecules in the unit cell.

Contrary to the view first put forward (*22*), $Mg(C_5H_5)_2$ in the solid state also possesses the pentagonal antiprismatic structure first established for ferrocene (*40*). For $Mn(C_5H_5)_2$, indirect evidence, such as the volume occupied by a molecule and the formation of mixed crystals with $Mg(C_5H_5)_2$ in space group C_{2h}^{5}, makes it very likely that this compound, too, has a before sandwich-configuration. Table IV presents the results in comparative form. The form of the unit cell shown diagrammatically in Fig. 4 is valid for all of the compounds investigated except the manganese complex, and rests on Fourier analyses of ferrocene (*30, 31*). These showed that in ferrocene the C—C distance in the rings (1.403 ± 0.02 Å) is uniform and slightly greater than that in benzene, the Fe-C distance

TABLE IV

LATTICE CONSTANTS OF SOME CYCLOPENTADIENYL METAL COMPOUNDS

Substance	*a* (Å)	*b* (Å)	*c* (Å)	*β* (degrees)	Volume of unit cell (Å³)
$Fe(C_5H_5)_2$	5.91	7.59	10.51	121.1	201.8
$Co(C_5H_5)_2$	5.90	7.71	10.60	121.1	206.4
$Ni(C_5H_5)_2$	5.88	7.86	10.68	121.2	211.1
$(Mn(C_5H_5)_2)$	(9.95)	(11.70)	(28.07)		(204.1)
$Cr(C_5H_5)_2$	5.92	7.88	10.72	121.2	213.8
$V(C_5H_5)_2$	5.88	8.02	10.82	121.3	218.0
$Mg(C_5H_5)_2$	5.98	8.04	10.98	121.9	224.1

is 2.045 ± 0.01 Å, and the distance between the rings 3.32 Å. In $Ni(C_5H_5)_2$ the C—C distance is somewhat shorter, the Ni-C distance 2.20 Å, and the rings are 3.4 Å apart (*32*). On the basis of the three-dimensional Fourier analysis, rotation of both molecules in the unit cell or of both rings in individual molecules must be ruled out (*31*). The pentagonal antiprism configuration of the molecule is thus proved. Electron-diffraction studies at 400° give Fe-C as 2.03 ± 0.02 Å and C—C as 1.43 ± 0.03 Å. At this temperature free rotation of the rings appears to occur (*183*). It seems significant in this context to note that for free cyclopentadiene, values for the C=C distance of 1.34 Å and for the C—C distance of 1.54 or 1.44 Å had previously been found (*179*). From Table IV it is clearly seen that, in general, with increase in metallic radius from iron to nickel and iron to vanadium only *b* and *c* increase, while *a*, corresponding to the orientation of the molecules, remains approximately constant. The abnormal size of the unit cell of the magnesium compound is striking and a radius of the magnesium atom of about 1.6 Å can be extrapolated, although the compound is in every way essentially ionic, so that a magnesium ion with radius 0.78 Å would be expected.

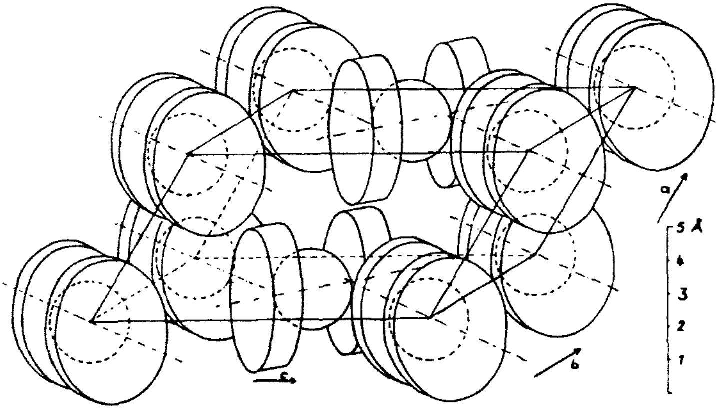


FIG. 4. The packing in the unit cell of metal dicyclopentadienyls.

These circumstances suggest that the π-electrons of the five-membered ring are not incorporated in the magnesium ion, which already has an inert gas configuration, and that they therefore act as a buffer and make the interatomic distance greater.

Numerous compounds have also been investigated by means of the X-ray absorption edge method (*11, 12, 13, 113*). This allows one to identify the lowest free *p*-orbitals which can be occupied by excited 1*s* electrons. The results obtained for ferrocene in the solid state, in solution in solvents of different polar character, and in the vapor phase, are shown in Fig. 5. For comparison, $K_4[Fe(CN)_6]$ and $Fe(CO)_5$, as complexes in which the krypton configuration has been attained, are also included. The weak first absorption band probably corresponds to a 4*p* "antibonding" absorption (Ruch) and shows therefore that the 4*p*-levels are involved in the ring to metal bonding.

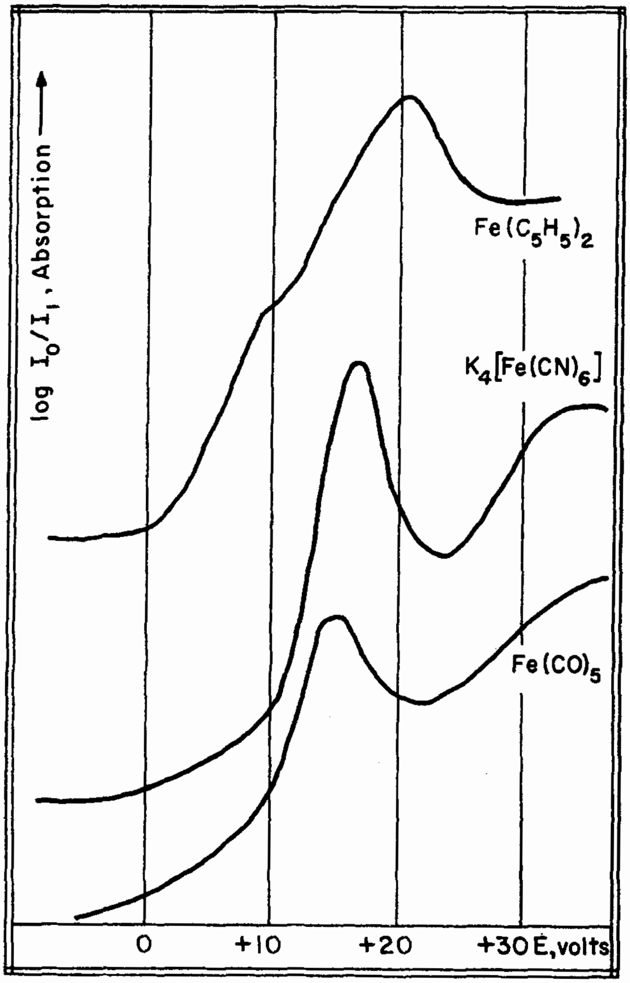


FIG. 5. X-ray absorption edges.

4. *Mass Spectrographic Investigations*

These were made on the uncharged dicyclopentadienyls of vanadium, chromium, iron, cobalt, nickel, ruthenium, manganese, and magnesium, and on the compound $(C_5H_5)_2ReH$ (*88*), and it was thus possible to show the close relationship of $Mg(C_5H_5)_2$ and $Mn(C_5H_5)_2$. The stability of the nonionic dicyclopentadienyl compounds, as compared with the ionic ones, stands out clearly in this work.

5. *Spectroscopic Investigations*

The first infrared investigations were made on ferrocene and ruthenocene (*123*). Together with the Raman measurements also made on both compounds, they constitute a relatively simple spectrum for compounds containing so many atoms, and there must thus be a high degree of symmetry in the structure. Apart from a C—H frequency at 3075 cm^{-1} (observed using a potassium bromide disk), i.e., in the aromatic C—H stretching region, only four strong bands are found in the whole range of the rock-salt prism. On the basis of the spectrum the symmetry group D_{5d} was proposed (*123*) and later confirmed (*124*). More extensive investigations, among them those on $Fe(C_5D_5)_2$, led to reliable frequency assignments for $Fe(C_5H_5)_2$, $Ni(C_5H_5)_2$, and $Ru(C_5H_5)_2$.

On the basis of these results and our own studies on numerous other metal dicyclopentadienyls, it was possible to define various bands in the infrared spectrum as characteristic of ferrocenelike $Me(C_5H_5)_2$ structures: (1) a C—H stretching frequency at 3100 cm^{-1} (ν_{CH}); (2) a C-C stretching frequency at 1410-1430 cm^{-1} (ν_{CC}); (3) an antisymmetrical ring-stretching frequency at 1100-1110 cm^{-1} (ν_{CC}); (4) a C—H bending frequency at 1000 cm^{-1} (δ_{CH}); (5) a frequency at 770-830 cm^{-1}, which can be interpreted either as a C—H bending (*124*), or as a metal-carbon stretching frequency (*32*). Frequency (4), for example, is so characteristic for unsubstituted five-membered rings, that with its aid it can be decided whether mono- or di-substitution has taken place in products of substitution reactions. Most measurements of ultraviolet absorption spectra were made in parallel with infrared and Raman measurements. Table V shows for which compounds spectroscopic investigations have been published. In the infrared region the spectra of the neutral and cationic complexes of the same metal are essentially similar, but in the ultraviolet region they are distinctly different.

6. *Thermodynamic and Other Data*

The possibility of calculating thermodynamic functions from infrared and Raman frequencies has been exploited for $Fe(C_5H_5)_2$, $Ni(C_5H_5)_2$, and $Ru(C_5H_5)_2$ (*124*). The vapor-pressure curve of ferrocene was also reported soon after its discovery (*112*). Vapor-pressure measurements for dicyclopentadienyl manganese are also available (*216*). The heats of formation of $Fe(C_5H_5)_2$ and $Ni(C_5H_5)_2$ from the C_5H_5 radical and the

TABLE V

SPECTROSCOPIC STUDIES OF CYCLOPENTADIENYL AND DIINDENYL METAL COMPOUNDS

Substance	Maxima found in ultra violet (mμ)	References	
		Ultraviolet	Infrared
$Mg(C_5H_5)_2$			*216*
$Hg(C_5H_5)_2$	238, 290	*215*	*215*
$(C_5H_5)Cu[P(C_6H_5)_3]$	247	*215*	*215*
$(Lanth)(C_5H_5)_3$	*	*9, 212*	
$(C_5H_5)_3UCl$	17 maxima in range 400-800	*164*	*164*
$(C_5H_5)Si(CH_3)_3$	240	*215*	*215*
$(C_5H_5)_2TiBr_2$			*211*
$(C_5H_5)_2ZrBr_2$			*211*
$(C_5H_5)_2VCl_2$			*211*
$(C_5H_5)_2NbBr_3$			*211*
$(C_5H_5)_2TaBr_3$			*211*
$[(C_5H_5)_2MoCl]^+$			*22*
$[(C_5H_5)_2MoCl_2]^+$			*22*
$[(C_5H_5)_2WCl_2]^+$			*22*
$Mn(C_5H_5)_2$			*216*
$Fe(C_5H_5)_2$	325, 440	*219, 112*	*219, 112, 123, 124*
$[Fe(C_5H_5)_2]^+$	253, 619	*219*	
$[Co(C_5H_5)_2]^+$	260, 310, 410	*25, 207*	
$Ni(C_5H_5)_2$	308, 700	*58, 218*	*124, 218*
$Ru(C_5H_5)_2$	275, 320	*206*	*123, 124*
$[Ru(C_5H_5)_2]^+$	320	*206*	
$[Rh(C_5H_5)_2]^+$	230	*25*	
$[Ir(C_5H_5)_2]^+$	below 200, 300	*25*	
$Fe(C_9H_7)_2$	270, 430, 565	*76*	*151*
$Fe(C_9H_{11})_2$	215, 320, 435	*77*	
$Co(C_9H_7)_2$	274, 322, 410	*87*	
$[Co(C_9H_7)_2]^+$	322	*87*	*151*

* Absorption like that by the free ions of the lanthanides.

gaseous metal were found to be −147 and −123 kcal/mole, respectively, and those from elements in their standard states to be 33.8 and 62.8 kcal/mole (*218*). Spectroscopic measurements led to values of 40.7 and 62.8 kcal/mole, respectively (*124*). Conductivity measurements have been made on a series of compounds (*164, 216*). Measurements of dipole moments of cyclopentadienyl metal complexes have so far been made for only a limited number; the results are collected in Table VI. From measurement of the dipole moments of mono- and diacetylferrocenes in benzene solution (3.03 and 4.23 Debye units, respectively) it was

TABLE VI

Dipole Moments of Some Complexes in Benzene

Substance	Dipole moment (Debye units)	Reference
$Sn(C_5H_5)_2$	1.02	*197*
$Pb(C_5H_5)_2$	1.63	*197*
$V(C_5H_5)_2$	0	*74*
$(C_5H_5)_2ReH$	1.28	*74*
$Fe(C_5H_5)_2$	0	*197*, *219*
$Co(C_5H_5)_2$	0	*74*
$Co_2(C_5H_5)_5$	0	*197*
$Ni(C_5H_5)_2$	0	*74*
$Os(C_5H_5)_2$	0	*74*
$Ru(C_9H_7)_2$	0	*42*, *197*

concluded that both rings are rotating freely (*165*). The dipole moment of di-(*p*-chlorophenyl-cyclopentadienyl) iron in benzene is 3.12 ± 0.03 Debye units. This eliminates free rotation in this compound, since the moment is in closest agreement with those calculated for the 1,1′ prismatic and 1,1′ antiprismatic structures (*184*).

The method of proton or nuclear magnetic resonance has been applied to the compounds $(C_5H_5)_2ReH$ and $Fe(C_5H_5)_2$ (*213*, *132*). Furthermore, attempts were made by spectrophotometric methods to establish the formation of a thermodynamically stable molecular complex of ferrocene (*14*). According to these measurements, ferrocene and iodine together in solution show no charge transfer complex, but are merely in thermal equilibrium with ferricinium triiodide.

E. Ferrocene as an Organic Compound

The inorganic problems in the chemistry of the cyclopentadienyl metal compounds (i.e., the varying of the central metal atom) were dealt with in section II.C. Those on the organic side (i.e., the behavior of the five-membered ring bound in the complex) will now be briefly reviewed. The outstanding results here are those showing the surprisingly easy substitution of the hydrogen atoms in ferrocene. So much work has been published on this aspect of ferrocene chemistry that within the pattern of this survey, which is orientated more toward inorganic chemistry, only a condensed summary can be given.

Any idea of describing each compound that has been prepared must be abandoned. In the following, only the most important types of ferrocene derivatives and reactions are dealt with; as for the rest, however, an attempt will be made to give as complete a review as possible of the literature which has appeared so far.

1. *Substitution Reactions*

Woodward was the first to show that ferrocene, in its reactivity, is to be considered as an aromatic system (*224*), and it was by him that, on analogy with benzene, the name ferrocene was given. He was the first to carry out a Friedel-Crafts reaction, in which on treatment with acetyl chloride and aluminum chloride ferrocene gave diacetyl ferrocene, which was converted by hypoiodite into the dicarboxylic acid, esters of which could easily be obtained. At first, it was thought that this reaction is not generally applicable to ferrocene, and that, for example, oxalyl chloride, ethyl bromide, isopropyl chloride, or benzyl chloride in the presence of aluminum chloride did not react (*166*). Later, however, it was shown that from the last three of these compounds and ferrocene, alkyl ferrocenes may be prepared under suitable conditions (*135*). It was also found that ethylene dichloride and ferrocene can be converted into a highly polymeric resin (*135*). Alkyl ferrocenes can also be made directly from alkyl halides and ferrocene (*135*), by reduction of acyl ferrocenes (*3, 137, 195*), or by reduction of carboxylic acids (*139*). The reactions of the acyl compounds obtained by the Friedel-Crafts synthesis have been investigated (*94, 95, 100, 148, 163, 204*). They give many of the characteristics of carbonyl groups. Many comparative studies of the influence of conventional and of ferrocenyl substituents on organic systems have been made (*140, 145*); orientation on substitution has also been investigated (*138, 165, 171*).

The preparation and structure of homoannular diacetyl ferrocenes (*164*), and intramolecular cyclizations, both homoannular (*168*) and heteroannular (*148, 168*), have been exhaustively investigated. As part of this work, ferrocene ω-carboxylic acids have been prepared (*170*). A rearrangement with ortho-substitution of a quaternary ammonium ion derived from ferrocene is also noteworthy (*99*). Work has been done on the isolation of optical isomers of substituted ferrocene derivatives (*6, 166*) and on cis-trans isomerism (*169*).

The usefulness of catalysts other than aluminum chloride, e.g., anhydrous hydrogen fluoride (*202, 223*), boron trifluoride (*100*), and phosphoric acid (*94*), has been examined. The mercuration reaction which is characteristic of aromatic systems takes place also for ferrocene, as has been described by Nesmeyanov and his co-workers (*143, 147*). Through the mercury compounds these workers have also obtained the halogenoferrocenes.

Interaction of ferrocene and diazonium compounds, which is followed by loss of nitrogen, leads to a large number of derivatives (*17, 141, 142, 143, 203*); most of them, naturally, are aryl-substituted compounds. Ferrocene cannot only be mercuriated, but can also be metalled by lithium butyl or similar compounds such as sodium phenyl. A great variety of possibilities for substitution is afforded by the interaction of ferrocenyl lithium and halogen-containing compounds (*5, 128, 143, 162*). Carboxylic acids, in particular, may easily be obtained by formation of the lithium derivative of ferrocene and treatment with carbon dioxide.

It was soon discovered that ferrocene condenses with aldehydes: under suitable conditions either condensation with elimination of water or carbinol formation may occur (*136, 166, 202*). Further, base-catalyzed aldol and Claisen condensations involving the α-hydrogen atom of acetylferrocene can be carried out (*100*).

In addition to all these possible reactions, substituted ferrocenes can also be prepared directly from the corresponding cyclopentadiene derivatives (*150*). Most of these, it is true, are difficult to obtain or even, at present, unknown. It seems, therefore, that the reverse way of making substituted cyclopentadiene derivatives through the ferrocenyl compounds, followed by abstraction of the metal, is of greater practical significance. The splitting off of the ring may be brought about by hydrogenolysis or by the action of halogens; the application of a pressure of 280 atm of hydrogen at a temperature of 300° makes the former process difficult to handle, however, and a much more elegant way is by reductive cleavage with lithium in ethylamine (*194*).

The simplest substitution, the replacement of hydrogen by deuterium, has not yet been achieved, though under the conditions used all six hydrogen atoms of cyclopentadiene are replaced (*115*).

2. Basic Types of Ferrocene Derivatives

The number of derivatives now known is so great that, in addition to those mentioned in the preceding section, some other basic types can be distinguished among the multitude of acyl, alkyl, and aryl derivatives of ferrocene. Except for a nitro-compound all the general aromatic derivatives are known. This has been the case for the longest time for the carboxylic acids and the di- and monosulfonic acids obtained by the action of sulfuric acid (in acetic acid or acetic anhydride) on ferrocene. The disulfonic acid forms large hygroscopic crystals. Salts and methyl esters of both acids are known (*146, 202*).

Ferrocenylamine, $Fe(C_{10}H_9NH_2)$, is obtained by the Kosheshkov reaction from ferrocenyl lithium and the benzyl ether of hydroxylamine

(*140, 142*) or, alternatively, from ferrocene monocarboxylic acid by the Curtius degradation (*3*). It is an orange crystalline substance which has a transition point at 110° and which melts at 153-155°. It can be sublimed in vacuo, is easily soluble in organic solvents, and forms acetyl and benzoyl derivatives (mp 170.5-172° and 177-178° respectively). The amine hydrochloride is readily soluble in water but only slightly soluble in hydrochloric acid. At 20° in 80% alcohol it has the following dissociation constant and pK values (*140*), which may be compared with those of aniline.

	K_{diss}	pK
Ferrocenylamine	1.55×10^{-9}	8.81
Aniline	7.2×10^{-11}	10.14

Ferrocenylamine is therefore a considerably stronger base than aniline.

The preparation of ferrocene aldehyde, $Fe(C_{10}H_9CHO)$, may be achieved by direct formylation of ferrocene with N-methylformanilide (*16, 94, 95, 172*); by this method only one —CHO group is introduced. The aldehyde is also formed by the action of hexamethylenetetramine on ferrocenylmethyltrimethylammonium iodide (*18*). Further methods are by the conversion (*120*) of N,N-dimethylaminomethylferrocene (obtained by aminomethylation of ferrocene) into the aldehyde and via the transformation of the methiodide of this compound (*102*). The aldehyde is a red crystalline substance which is seen under the polarizing microscope to have a transition point at 45°; it melts at 124.5°. It forms a bisulfite compound, an oxime, a semicarbazide, a 2:4-dinitrophenylhydrazone, and an acetal. It is soluble in aqueous acids and organic solvents, and it undergoes the Cannizzaro reaction, but, surprisingly, it does not give the corresponding acid on oxidation (*94*). The typical aldehyde reactions of formylferrocene have been extensively investigated (*101*), e.g., the aldehyde can be converted through its oxime into ferrocenyl-cyanide, $Fe(C_{10}H_9CN)$ (*18*).

The first phenolic derivative of ferrocene to be reported, di(1-hydroxy-3-methyl-cyclopentadienyl) iron, was prepared by the reaction between 3-methyl-2-cyclopentanone, sodamide, and ferrous chloride in liquid ammonia. This compound is remarkably unstable, being extremely sensitive to air. It is a yellow substance which sublimes at 130-140° at 0.1 mm pressure, and is readily soluble in methylene dichloride but insoluble in carbon tetrachloride and in n-heptane. In water saturated with nitrogen a yellow solution is produced which rapidly becomes blue-green on exposure to air. The compound forms a benzoate (mp 121-123.5°) which is stable in air. An analogous derivative of the dicyclopentadienyl cobalt(III) cation has also been obtained (*6*).

Many derivatives have been prepared from ferrocene monocarboxylic acid (*3*). Acetylferrocene was reduced by lithium aluminum hydride to the carbinol, and this was then converted into vinylferrocene. From this, polymers and copolymers with other polymerizable substances have been obtained. The polymers are easily obtainable in the cationic form and in the reduced, uncharged form, which are interconvertible (*3*). Urethanes (*3*), amino acids and urea, hydantoin and pyrazoline derivatives with ferrocenyl substituents have also been prepared (*100, 178*).

Halogenoferrocenes were isolated, as already mentioned, via the mercury compounds (*147*). The iodo compound, $Fe(C_{10}H_9I)$ was described as not forming a Grignard reagent.

For the preparation of unsymmetrical ferrocenes, two ways by which only mono-substituted derivatives are produced have been suggested. One route starts from iron tetracarbonyl and a substituted cyclopentadiene; the other from monocyclopentadienyl iron dicarbonyl bromide, which on treatment with a substituted cyclopentadienyl lithium is finally converted into the corresponding mono-substituted ferrocene. Experience shows the first method to be more suitable for the preparation of aryl, and the latter method for the preparation of alkyl, derivatives (*97*). Corresponding work already carried out on substitution in $Ru(C_5H_5)_2$ and $Os(C_5H_5)_2$ has also been fruitful. It is found that in the Friedel-Crafts reaction with acetyl or benzoyl chloride there is a distinct predominance of mono- over disubstitution as the atomic weight of the central atom increases (*47, 72*).

F. MIXED CYCLOPENTADIENYL METAL COMPLEXES

In addition to the complexes of cyclopentadiene and indene, described already, in which the metal usually lies between two rings, a great number of complexes in which the central metal atom is surrounded on one side by a ring and on the other by conventional ligands are also known.

1. Cyclopentadienyl Metal Carbonyls

The group of monocyclopentadienyl metal carbonyls is the most extensive. In this, in contrast to the pure cyclopentadienyl compounds, it is found that complexes are formed only by transition elements of groups 5 to 8, i.e., metals which can enter into true ferrocene-type bonding. There is a regular relationship for this series: transition elements of odd atomic number yield readily volatile compounds of formula $C_5H_5Me(CO)_x$, while the even-numbered members form dimers of composition $[C_5H_5Me(CO)_x]_2$. The actual value of x, the number of ligand carbon monoxide molecules, corresponds to the number of pairs of electrons required for the attainment of the next inert gas configuration if it is assumed (a) that the five-membered aromatic ring is again bonded to the central metal atom with all six of its π-electrons, and (b) that a metal-metal bond contributes in the case of the dimeric compounds (*86*). In accordance with these principles the following series of diamagnetic complexes may be adduced for the first period of transition metals: $C_5H_5V(CO)_4$, $[C_5H_5Cr(CO)_3]_2$, $C_5H_5Mn(CO)_3$, $[C_5H_5Fe(CO)_2]_2$, $C_5H_5Co(CO)_2$, and $[C_5H_5Ni(CO)]_2$. The cyclopentadienyl carbonyl complexes known at the present time are described more fully in the following sections.

a. Fifth Subgroup. In this, only the complexes of vanadium have to be considered. The longest-known monomeric compound of the mixed type is $C_5H_5V(CO)_4$, which is obtained by the action of carbon monoxide under pressure on dicyclopentadienyl vanadium at elevated temperatures (*51*). It is an orange-colored substance of mp 138° which is readily sublimed at 60-70° and is stable for a short time in air. Solutions in organic media decompose more rapidly. From this compound it proved possible to prepare the first derivative of a monomeric cyclopentadienyl metal carbonyl. By decomposition of $C_5H_5V(CO)_4$ with sodium in liquid ammonia the yellow sodium salt, $Na_2[C_5H_5V(CO)_3]$, which is soluble in ammonia, is obtained. From this, also in liq. NH_3, the corresponding potassium, rubidium, and caesium salts, which are sparingly soluble and diamagnetic, may be precipitated on addition of their iodides. In all these compounds vanadium has the oxidation number −1 (*80*).

b. Sixth Subgroup. The green diamagnetic compound $(C_5H_5)_2Cr_2(CO)_5$ was the first chromium compound of this type to be mentioned. It was described as being produced by interaction of chromium hexacarbonyl and cyclopentadiene in the liquid phase (*22*). According to our own detailed study of the action of carbon monoxide under pressure on the cyclopentadienyl $Cr(C_5H_5)_2$ at various temperatures, there results first, at 100-110°, mainly brown-black crystalline $(C_5H_5)_3Cr_2(CO)_3$, which sublimes at 130° and melts with decomposition at 190-193°. It is practically insoluble in nonpolar solvents but dissolves freely in some polar compounds such as dimethylformamide. It is assumed to have the saltlike structure $[Cr(C_5H_5)_2]^+[C_5H_5Cr(CO)_3]^-$. On increasing the temperature to 150-170°, the chief product becomes the blue-green crystalline compound $[C_5H_5Cr(CO)_3]_2$, which sublimes at 90-100° and melts at 163-168° with decomposition. It forms solutions which are deep green in nonpolar solvents such as benzene and yellow-green in alcohol, and which rapidly decompose in air (*52*). If hydrogen is added in the pressure reaction, the readily volatile yellow monomeric hydride, $C_5H_5Cr(CO)_3H$, is obtained at about 75°, and this readily decomposes, with loss of hydrogen, to form the dimeric cyclopentadienyl carbonyl compound. When pure, the carbonyl hydride, which is golden yellow, melts at 58-58°; it gives yellow solutions in organic solvents which are stable if oxygen is excluded. Its acidic character is shown by the ready transformation with aqueous alkalis to give salts containing the air-stable anion $[C_5H_5Cr(CO)_3]^-$; these yield precipitates with suitable cations. When such solutions are acidified, the sparingly soluble weak acid is reprecipitated (*52*). Alkyl esters are obtained by treatment of the sodium salt with alkyl halides (*157*) or dimethyl sulfate (*62*).

The first mixed cyclopentadienyl metal acetylacetonate to be made is the dark green compound $C_5H_5Cr(CH_3COCHCOCH_3)Br$, which may be sublimed, and which results from the reaction of cyclopentadienyl magnesium bromide with chromium(III) acetylacetonate in benzene (*193*).

The homologues of chromium have also been very fully studied. Thus, the dark purple compound $(C_5H_5)_2Mo_2(CO)_5$ (mp 215-217°) was first described as formed from molybdenum carbonyl and cyclopentadiene at about 300° (*208*). It is readily soluble in chloroform, less so in carbon tetrachloride, benzene, carbon disulfide, and alcohol, and scarcely soluble in ligroin. Probably, however, the substance was in fact the dimer $[C_5H_5Mo(CO)_3]_2$ (*154*). The hydride $C_5H_5Mo(CO)_3H$ was obtained as a yellow, readily volatile compound, decomposing at 50-52°, by the interaction of molybdenum carbonyl and cyclopentadienyl lithium in dioxane and acidification of the resulting solution (*52*). As in the case of the chromium compound, dimerization with loss of hydrogen occurs, and alkyl esters may be prepared by the action of the alkali metal salts on alkyl halides (*154, 155, 157*). The corresponding chloride, $C_5H_5Mo(CO)_3Cl$, was obtained in the form of orange crystals, which decomposed at about 145°, from the hydride and carbon tetrachloride. The crystalline iodide, $C_5H_5Mo(CO)_3I$ (mp 134°) can be made as red crystals from the mercury salt $[C_5H_5Mo(CO)_3]Hg$ and iodine (*154*). Oxidation of the carbonyl hydride gives the cyclopentadienyl carbonyl $[C_5H_5Mo(CO_3)]_2$ (*154*).

In the case of tungsten, reaction of the carbonyl with cyclopentadiene gives the purple-red crystalline compound $[C_5H_5W(CO)_3]_2$ (mp 240-242° with decomposition), which is readily soluble in chloroform, much less soluble in other organic solvents, and insoluble in ligroin. It is not attacked by acids or bases. If tungsten carbonyl reacts with cyclopentadienyl lithium in dimethylformamide, a yellow solution of the lithium salt is formed, from which the hydride, $C_5H_5W(CO)_3H$, may be isolated on acidification as a readily volatile yellow substance melting at 66-67°. In this case no loss of hydrogen occurs up to 180°. Reaction of the hydride with diazomethane gives the methyl ester (*86*), while other alkyl derivatives are formed by the action of the sodium salt on alkyl halides (*154, 155*).

c. Seventh Subgroup. Yellow $C_5H_5Mn(CO)_3$ may be obtained in good yield by the interaction of the cyclopentadienyl compound, $Mn(C_5H_5)_2$, and carbon monoxide at elevated temperatures. It sublimes above 60°, melts at 77°, smells like camphor, is completely stable in air, and dissolves readily in organic solvents without decomposition (*60*). The compound $CH_3C_5H_4Mn(CO)_3$ has recently become of technical interest as a fuel additive (*2*).

On treating the compound $(C_5H_5)_2ReH$, which has been mentioned earlier, with carbon monoxide at 90° and 250 atm it is possible to obtain the carbonyl $(C_5H_5)_2ReH(CO)_2$, which has neither acidic nor basic properties (*82*). It sublimes at 90-100°, melts at 111-112°, and is freely soluble in all the usual solvents such as benzene, ether, petroleum ether, and acetone. Unlike cyclopentadienyl rhenium hydride, it is stable in air.

d. Eighth Group. The compound $[C_5H_5Fe(CO)_2]_2$ (*22, 43, 98, 159*), which was originally formulated (*22*) as $(C_5H_5)_2Fe_2(CO)_5$, is obtained by interaction of iron pentacarbonyl and cyclopentadiene dimer in the liquid phase. It forms dark red-brown crystals (mp 194°) which are readily soluble in pyridine, chloroform, and alcohol, less soluble in carbon tetrachloride and carbon disulfide, and almost insoluble in petroleum ether. It is neither attacked nor dissolved by water, but it can be transformed by oxidation in an aqueous medium into what is presumably the hydrated $[C_5H_5Fe(CO)_2H_2O]^+$ cation. In organic solvents an anhydrous chloride (*159*), cyanide (*159*), bromide (*98*), and iodide (*156*) may be obtained. From the bromide $C_5H_5Fe(CO)_2Br$ and cyclopentadienyl sodium, the fairly labile dicyclopentadienyl metal carbonyl, $(C_5H_5)_2Fe(CO)_2$, may be isolated in the form of deep red crystals of mp 46°. The existence of the $[(C_5H_5)_2Fe(CO)_2]^+$ cation is judged to be probable (*96*). The dimeric compound $[C_5H_5Fe(CO)_2]_2$, which has already been mentioned, may be reduced in methanol solution by sodium amalgam to a yellow anion, $[C_5H_5Fe(CO)_2]^-$. With mercuric cyanide this yields the golden yellow mercuric compound, $Hg[C_5H_5Fe(CO)_2]_2$, which is stable in air and is soluble in all the usual organic solvents. When it is sublimed at 80-90° partial decomposition occurs, with loss of mercury and formation of the dimer once more (*43*). A variety of alkyl and aryl compounds of the type $C_5H_5Fe(CO)_2R$ can be obtained from the halides (*155*).

The compound $C_5H_5Fe(CO)_2Si(CH_3)_3$ was prepared as orange needles, subliming at about 60° and melting at about 70°, by the interaction of the sodium salt $[C_5H_5Fe(CO)_2]Na$ and trimethylchlorosilane

(*160*). This compound is thermally stable up to about 200° and is soluble in the usual organic solvents.

Interaction of dicyclopentadienyl cobalt and carbon monoxide at 90-150° and 200 atm yields the red-brown compound $C_5H_5Co(CO)_2$ as a readily volatile liquid (mp −22°, bp 139-140°/710 mm with partial decomposition) which is decomposed in air but forms stable solutions in organic solvents if air is excluded. With water neither solution nor rapid hydrolysis is observed (*60, 61, 159*).

The first cyclopentadienyl metal carbonyls to be discovered have the formulas $(C_5H_5)_2Co_2(CO)_4$ and $(C_5H_5)_2CoFeH(CO)_4$, but are saltlike compounds having the structures $[Co(C_5H_5)_2]^+[Co(CO)_4]^-$ and $[Co(C_5H_5)_2]^+[FeH(CO)_4]^-$ (*57*). For nickel also, the dimer $[C_5H_5Ni(CO)]_2$ has recently been discovered; it is a red substance which is obtained by the reaction between nickel carbonyl and dicyclopentadienyl nickel in benzene (*69*). By raising the reaction temperature, in experiments on cleavage with sodium amalgam in methanol, or at a higher sublimation temperature, a very stable complex having the surprising composition $(C_5H_5)_3Ni_3(CO)_2$ results.

2. Cyclopentadienyl Metal Nitrosyls

a. Sixth Subgroup. An almost quantitative yield of the nitrosyl $C_5H_5Cr(CO)_2NO$ may be obtained from the cyclopentadienyl carbonyl, $[C_5H_5Cr(CO)_3]_2$, and nitric oxide in benzene (*85*). This orange-red-colored compound (mp 67-68°) is soluble in all organic solvents, and is stable in air at room temperature. When chromic chloride is allowed to react with cyclopentadienyl sodium in tetrahydrofuran and the resulting green solution is treated with nitric oxide, the compound $C_5H_5Cr(NO)_2Cl$ is obtained (*156*). It forms yellow-green crystals which decompose at about 140° without melting; with sodium thiocyanate, the corresponding thiocyanate complex is obtained. With methyl magnesium iodide it gives a green crystalline compound (mp 83°) of composition $C_5H_5Cr(NO)_2CH_3$. With diazomethane the chloride gives $C_5H_5Cr(NO)_2CH_2Cl$, while with ethyl- and phenyl-magnesium bromides the products are $C_5H_5Cr(NO)_2C_2H_5$ and $C_5H_5Cr(NO)_2C_6H_5$, respectively (*153*). The cation $[C_5H_5Cr(NO)_2]^+$, which can be obtained in aqueous solution, will react in suitable solvents with cyclopentadienyl sodium to form the compound $(C_5H_5)_2Cr(NO)_2$ as amber-colored crystals of mp 65° (*153*).

Nitrosyl derivatives of the homologues of chromium may be made directly as insoluble precipitates by decomposing the complex anions $[C_5H_5Mo(CO)_3]^-$ and $[C_5H_5W(CO)_3]^-$ with nitric oxide in aqueous media (*85*). After high-vacuum sublimation at 55-60° the orange-red crystals of the molybdenum compound, $C_5H_5Mo(CO)_2NO$, which is somewhat lighter in color than its chromium analogue, melt at 85°; the tungsten compound melts at 105-107°. The former compound may also be obtained from the carbonyl hydride, e.g., by decomposition with nitrogen dioxide (*154*).

b. Seventh Subgroup. The cation $[C_5H_5Mn(CO)_2NO]^+$ is obtained in the reaction of the carbonyl $C_5H_5Mn(CO)_3$ with $6M$-nitric acid in ethanol, and is isolated as its chloroplatinate, which is fairly soluble in water and which decomposes without melting at 165-175° (*159*). Reaction of nitric oxide with dicyclopentadienyl manganese in tetrahydrofuran gives a compound $(C_5H_5)_3Mn_2(NO)_3$ in the form of purple-black crystals which decompose at 100° and are moderately soluble in organic media. They are insoluble in water and do not react with it (*156*). When the compound is treated with sulfur in carbon disulfide solution, brown-black crystals of the sulfide $C_5H_5MnNOS_2$, which have a metallic glance and decompose on warming without melting, are obtained. This substance probably exists as a tetramer or hexamer (*158*).

c. Eighth Group. The interaction of dicyclopentadienyl nickel and nitric oxide in petroleum ether yields the compound C_5H_5NiNO as a stable red-brown liquid, boiling at 144-145° at 715 mm, and miscible with the usual organic solvents (*60, 85, 159*).

3. Physicochemical Investigations

Apart from the compounds $(C_5H_5)_3Cr_2(CO)_3$ (*52*), which has three unpaired electrons, and $(C_5H_5)_3Ni_3(CO)_2$ (*69*), which has one, all the complex compounds described here are diamagnetic. For most of them the infrared spectrum has also been described in outline. Essentially two kinds of C-O bands are found. First, there is the normal carbonyl frequency at 1900-2000 cm^{-1}, which also occurs in the pure metal carbonyls, but sometimes in the cyclopentadienyl metal carbonyls with a small displacement towards longer wavelengths. Secondly, frequencies still more displaced towards longer wavelengths are observed at 1700-1800 cm^{-1}, and these are associated with bridging carbonyl groups. A further frequency, situated between these two regions, has been attributed by some authors to carbonyl groups forming a sort of closed ring between the metal atoms of binuclear cyclopentadienyl metal carbonyls; but an X-ray study of the structure of $[C_5H_5Mo(CO)_3]_2$ (*221*) has very recently shown that this interpretation cannot be correct. Crystallographic data are available for the compounds $[C_5H_5W(CO)_3]_2$ (*220*), $[C_5H_5Mo(CO)_3]_2$ (*220, 222*), $[C_5H_5Fe(CO_2]_2$ (*98, 220*), $C_5H_5Mn(CO)_3$ (*7*), and C_5H_5NiNO (*8*).

G. MOLECULAR STRUCTURE AND BONDING

1. *Molecular Structure*

The configuration of the solid ferrocene-like dicyclopentadienyl derivatives is well established by X-ray methods as a pentagonal antiprism. In ferrocene the rings are rigidly fixed in the staggered positions, but they become freely rotating at about 360° (*183*). It has, accordingly, proved possible to isolate stereoisomeric ring-substituted derivatives of these substances (*6*, *167*). Alone among the dicyclopentadienyls so far examined, the tin and lead compounds $Sn(C_5H_5)_2$ and $Pb(C_5H_5)_2$ show pronounced dipole moments in benzene. In view of the great similarity between the infrared spectra of these two compounds and those of ferrocene and ruthenocene, the sandwich arrangement of the rings must be present in the tin and lead derivatives; the rings may, however, be slightly inclined towards one another. A certain degree of polarization, i.e., departure from the completely symmetrical sandwich structure, is also considered by E. Ruch to be possible from theoretical considerations.

An interesting suggestion has been made (*118*) for the structure of dicyclopentadienyl rhenium hydride, $(C_5H_5)_2ReH$, which might also be considered for the cyclopentadienyl hydrides of chromium, molybdenum, and tungsten. According to this, the proton resides within one of the cones formed by the metal atom and the ring. The second proton which is readily taken up by the complex, with formation of the $[(C_5H_5)_2ReH_2]^+$ ion, is then assumed to go into the other cone.

For the saline mono-, di- and tricyclopentadienyls [e.g., KC_5H_5, $Mg(C_5H_5)_2$, and $Bi(C_5H_5)_3$] it is probable that the metal atom occupies a central position with respect to the rings and that these are symmetrically arranged; this has already been found to be so for the magnesium compound.

A complicated structural problem arises in the case of the compound $Co_2(C_5H_5)_5$ (*39*). It may be assumed that there is one ring between the cobalt atoms; of the two outer rings, one may be σ-bonded to the metal and the other attached centrally with π-electrons. In accordance with the zero dipole moment, the two like rings should occupy *trans* positions relative to one another. An earlier structure, in which all three rings were placed centrally with respect to the two metal atoms, seems less likely. For mixed compounds of the type $C_5H_5Mn(CO)_3$ or $(C_5H_5)NiNO$ the structure should certainly be one having a symmetrical geometrical arrangement. The location of the hydrogen atoms in the cyclopentadienyl carbonyl hydrides of chromium, molybdenum, and tungsten presents a problem, however; a central position between the carbonyl groups seems probable (*86, 118*).

For dimeric compounds of the type $C_5H_5Me(CO)_nMeC_5H_5$ a cylindrical (triple-decker-sandwich) structure was originally proposed. According to Wilson and Shoemaker (*221*), however, the compound $[C_5H_5Mo(CO)_3]_2$ possesses a completely different structure: each molybdenum atom lies at the center of a cube, one side of which is occupied by the five-membered ring; the three carbonyl groups are directed towards three of the corners of the opposite side of the cube; and the metal-metal bond, which forms the only link between the two halves of the molecule, lies in the direction of the remaining corner. In the compound $(C_5H_5)_3Cr_2(CO)_3$ there is a major transition to the ionic structure $[Cr(C_5H_5)_2]^+[Cr(C_5H_5)(CO)_3]^-$ (*52*). In this way the anion acquires the krypton configuration, while the cation, by likewise including all of the π-electrons of the ring, should have three unpaired electrons, a conclusion in keeping with the results of magnetic measurements.

In the rhenium compound $(C_5H_5)_2ReH(CO)_2$, one of the cyclopentadienyl rings is assumed to be σ-bonded, and the other π-bonded to the rhenium atom. The hydrogen atom should then, as in the case of dicyclopentadienyl rhenium hydride, $(C_5H_5)_2ReH$ (*118*), lie in the cone formed by the metal and the centrally bonded ring (*82*). For dicyclopentadienyl iron dicarbonyl, $(C_5H_5)_2Fe(CO)_2$, a very similar structure is proposed in which the ring that is σ-bonded and that which is π-bonded to the metal are inclined to one another, and both lie on the side of the metal atom opposite the two carbonyl groups (*97*). For the alkyl and aryl derivatives of cyclopentadienyl metal carbonyls of chromium, molybdenum, tungsten, and iron (large numbers of which are known), as well as for some similar derivatives of the compound $C_5H_5Cr(NO)_2Cl$, a metal-carbon σ-bond specially stabilized by the five-membered ring has been assumed (*97, 153*).

2. Bonding

The nature of the bonding in the metal cyclopentadienyls and their derivatives is still the subject of much discussion, although the compounds have been known for some years. It is now quite certain that in the saltlike alkali, alkaline earth, and rare-earth metal cyclopentadienyls the bonding between the ring and the metal is essentially ionic. Compounds such as dicyclopentadienyl vanadium and chromium also show hydrolytic cleavage. On the other hand, however, cyclopentadienyl thallium, for which the recent investigations of Cotton and Reynolds (*20*) suggest an ionic bond, may be sublimed and is precipitated from an aqueous medium as an insoluble product. In our judgment this clearly indicates an essentially covalent bond. In the fifth main group of the periodic table we find in antimony and bismuth elements which tend towards an intermediate type between purely ionic and covalent ferrocenelike bonding; zinc and mercury are probably similar. For the compounds $Sn(C_5H_5)_2$ and $Pb(C_5H_5)_2$ π-complex bonding must probably be assumed, at least in part, while for mixed cyclopentadienyl compounds of silicon normal σ-covalent bonding has been proposed (*89, 215*).

There are, in essence, two concepts of the type of bonding in the transition metal dicyclopentadienyls. Both are based on a sterically central position of the metal with respect to the rings. It is well known that true organometallic derivatives of the transition metals, in which the metal and carbon each provide one electron towards the formation of a single bond, are (except in the case of elements of the second subgroup) extraordinarily labile, if indeed they can be made at all. In the first place, such a bond may be stabilized by hybridization of the *d*-orbitals (which by themselves are not suitable for bonding) with the *s*- and *p*-orbitals. The coordinative covalencies formed by electron pairs then bring about stabilization of metal-carbon bonds, e.g., in carbonyls, cyanides, isocyanides, acetylides, and fulminates. The decisive factors in this process are the filling, or approximate filling, of the orbitals of the metal to the next inert gas configuration, and the double-bonding component of the metal-carbon bond.

After the elucidation of the real molecular structure of ferrocene, it was at first generally assumed that the metal attained the inert gas structure (*70, 219*). Wilkinson, Woodward, and their co-workers (*219*) associated five π-electrons with each five-membered ring, and these, together with the eight electrons of the central Fe(O) atom, built up the electron shell of the latter to eighteen. According to our concept (*70*) ferrocene is a completely new type of penetration complex. The two parallel staggered aromatic cyclopentadienyl anions each possess three pairs of π-electrons, and the central Fe^{++} ion interacts with each pair, forming six coordinate covalencies, distributed around it in a trigonal antiprism, i.e., almost octahedrally arranged. Figure 6 shows this concept clearly; according to it, the central Fe^{++} ion retains its characteristic coordination number of six.

Theoretical studies by E. Ruch (*173-177*) proved the correctness of this concept of the bonding, with which the retention of the aromatic character of the ring is in harmony. The nature of the bonding in the dicyclopentadienyl metal compounds was discussed by him in terms of molecular and equivalent orbitals, and on the basis of calculated overlap integrals for ferrocene an energy-level diagram was suggested which

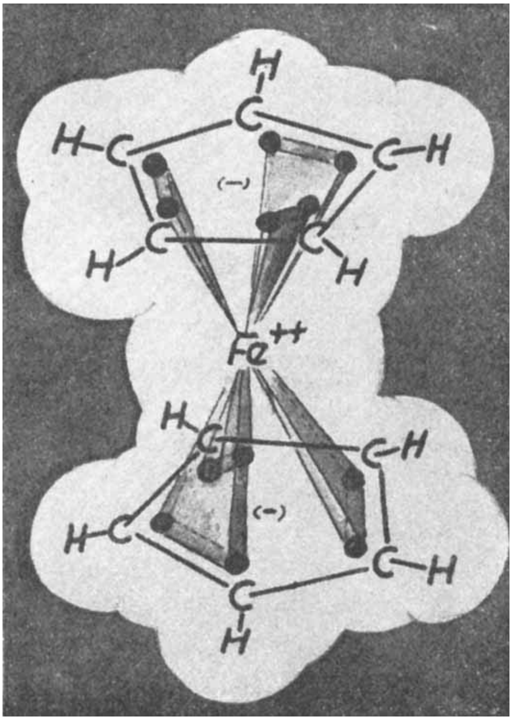


FIG. 6. The electronic configuration of ferrocene.

indicates the orbitals occupied (denoted σ, π, or δ according to their symmetry) in, for example, compounds of titanium, vanadium, niobium, chromium, molybdenum, iron, cobalt, rhodium, and nickel, shown in Fig. 7. There are two other proposals for the bonding in ferrocene which, although differently developed, also lead to the krypton configuration (*110, 186*).

Against this view are comprehensive theoretical studies which put only a single covalent d_π-p_π bond between the metal and the ring in all the transition metal compounds (*23, 26, 32, 119, 131*). On this basis, ferrocene, for example, should show only a closed $3d$ shell. Four π-electrons would then remain in the rings, which could be considered as radicals, without taking part in the bonding.

Experimental results, such as those obtained by X-ray absorption edge measurements, lead us to prefer the penetration complex concept, which involves the characteristic tendency of transition metals to complete their electron shells and assume their typical coordination numbers (*41*).

In the course of our own work, which had as its object the further

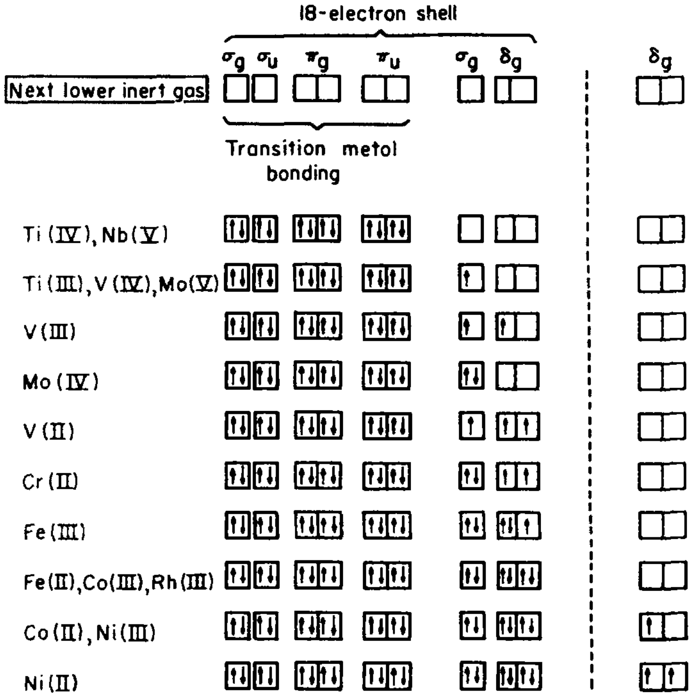


Fig. 7. Electronic configurations

confirmation of our idea of the bonding, we were able to show, among other things, that diindenyl compounds may be hydrogenated in the six-membered ring, but that only four hydrogen atoms per ring were absorbed (*185*). The π electrons of the third double bond of the benzene ring are thus drawn into the five-membered ring to form the complex. Our concept of the type of bonding also receives important support from the surprising reaction for the preparation of cyclopentadienyl thallium from aqueous solution, as well as from the isolation of cyclopentadienyl indium. In these cases the assumption that the three pairs of π-electrons belonging to the cyclopentadienyl anion are attracted into the free 5*p* or 6*p* orbitals of In(I) or Tl(I) also leads to the attainment of the xenon or radon configuration. The stability of the cation $[Co(C_5H_5)_2]^+$ towards ozone in acetic acid again, in our opinion, proves that all the π-electrons are drawn upon to form the metal complex (*41*). The gradation in complex stability is consistent with our theory and is, indeed, to be expected. Maximum stability must occur in the uncharged type of compound having an inert gas configuration. This is in fact the case for ferrocene, ruthenocene, and osmocene, and for cations such as $[Co(C_5H_5)_2]^+$ which are isoelectronic with them. Decrease in the extent to which the metal electron shells are filled is paralleled by an increase in sensitivity to hydrolysis, as, for example, in the case of the dicyclopentadienyl compounds of chromium and vanadium.

For the almost invariably diamagnetic mixed complexes of transition metals with cyclopentadienyl and other ligands, such as carbon monoxide and nitric oxide, completion of the inert gas configuration is the controlling factor to an even greater extent (*41*). It is characteristic that in this case maximum stability is encountered in the monomeric cyclopentadienyl metal carbonyls [for example, $C_5H_5Mn(CO)_3$], corresponding to the preferred coordination number of six for the metal. In keeping with this idea, particularly for the last compound, the presence of a shell of 18 electrons has been concluded on theoretical grounds (*122, 126*). Linnett (*122*) showed that the two theories are not incompatible, for he also established, from consideration of molecular and equivalent orbitals, that the attainment of the inert gas configuration is essential.

H. TECHNICAL APPLICATIONS OF CYCLOPENTADIENYL METAL COMPLEXES

Metal cyclopentadienyls have already proved to be of considerable technical interest. According to investigations carried out mainly in the United States, ferrocene is able to bring about smokeless combustion of fuel oil when added in amounts of 0.05% (*1*). Its use as an oil additive for jet motors and as an antiknock has also been proposed. Liquid ferrocene is said to have advantages as a thermally stable heat-transfer medium. Dicyclopentadienyl nickel also has possible applications, and dicyclopentadienyl titanium-dichloride has been studied in association with aluminum alkyls for the polymerization of ethylene (*15, 133, 134*). Finally, the carbonyl $CH_3C_5H_4Mn(CO)_3$ has been considered as a fuel additive in conjunction with tetraethyl lead (*2*). Other information is given in the patent literature (*42*).

III. Complex Formation by Six-Membered Ring Systems

A. INTRODUCTION

Shortly after the discovery of ferrocene and the elucidation of its molecular configuration, one of us (*70*) put forward a suggestion for the nature of the bonding in this compound, according to which ferrocene was a penetration complex, the essential feature being the filling of the electron shells of the central atom to the krypton configuration by the three pairs of π-electrons of the aromatic ring. On this hypothesis it should be immaterial, at least as far as the bonding is concerned, whether the rings are charged or uncharged, provided that the condition of the availability of the π-electron sextet is fulfilled. Since the same view was put forward by E. Ruch from the theoretical standpoint, experiments aimed at the preparation of a dibenzene chromium (O) seemed to be not without some prospect of success. The investigation was made with chromium since in this case it was hoped that the addition of two rings would give the inert gas configuration, and with it maximum stability. The problem then became experimental in character.

In 1954 a new synthesis for chromium carbonyl was developed in collaboration with W. Hafner. The system $CrCl_3/AlCl_3/Al/C_6H_6/CO$ used in this case was found, when the reaction was more closely studied, to open the way to the compound $Cr(C_6H_6)_2$ *(53)*. It was shown that in an autoclave at 180°, without the carbon monoxide, a mixture resulted which contained the $[Cr(C_6H_6)_2]^+$ cation, produced as follows:

$$3CrCl_3 + 2Al + AlCl_3 + 6C_6H_6 \rightarrow 3[Cr(C_6H_6)_2](AlCl_4). \qquad (11)$$

The cation could be isolated by precipitation as the picrate or the reineckate. By reduction with sodium dithionite it could be converted directly into brown-black dibenzene chromium, $Cr(C_6H_6)_2$, which can be sublimed *(53, 54)*:

$$2[Cr(C_6H_6)_2]^+ + S_2O_4^{=} + 4OH^- \rightarrow 2Cr(C_6H_6)_2 + 2H_2O + 2SO_3^{=}. \qquad (12)$$

This process is analogous to the preparation of ferrocene from ferricinium ions. It was soon possible to extend the work to the preparation of a large number of aromatic metal complexes containing two six-membered rings, with a wide variety of both metals and aromatic ligands. Figure 8 shows the metals which behave in this way.

		IV	V	VI	VII	VIII			
4		22 Ti *	23 V $V^{0}Ar_2$ $[V^{I}Ar_2]^{+}$	24 Cr $Cr^{0}Ar_2$ $[Cr^{I}Ar_2]^{+}$	25 Mn	26 Fe $[Fe^{II}Ar_2]^{+2}$	27 Co $[Co^{III}Ar_2]^{+3}$	28 Ni	
5		40 Zr	41 Nb	42 Mo $Mo^{0}Ar_2$ $[Mo^{I}Ar_2]^{+}$	43 Tc	44 Ru $[Ru^{II}Ar_2]^{+2}$	45 Rh $[Rh^{III}Ar_2]^{+3}$	46 Pd	
6		72 Hf	73 Ta	74 W $W^{0}Ar_2$ $[W^{I}Ar_2]^{+}$	75 Re $[Re^{I}Ar_2]^{+}$	76 Os $[Os^{II}Ar_2]^{+2}$	77 Ir $[Ir^{III}Ar_2]^{+3}$	78 Pt	

FIG. 8. Complexes of uncharged aromatic compounds with transition metals.

B. PREPARATIVE METHODS

The synthesis from metal chloride, aluminum chloride, the aromatic compound, and aluminum powder (in those cases where reduction was necessary), which was developed in the case of chromium, proved to be extraordinarily successful and widely applicable (*53*). In the course of a detailed study of the preparation of dibenzene chromium it was soon found possible to introduce important simplifications. Although initially an autoclave was essential in order to reach the necessary reaction temperature of 140°, it was found that addition of catalytic amounts of mesitylene enabled the synthesis to be carried out simply under reflux. At an earlier time, by adding an eightfold excess of aluminum chloride [calculated on the basis of Eq. (11)] it was possible to attain an almost quantitative yield (*75*). Alkyl and aryl homologues of benzene, on the other hand, reacted under reflux from the start to form the corresponding chromium complexes.

A further synthesis of metal complexes containing two six-membered aromatic rings, which was limited to chromium, was based on the interaction of phenyl magnesium bromide and chromic chloride, and subsequent hydrolysis of the reaction mixture to the $[Cr(C_6H_6)_2]^+$ cation (*107, 227, 228*).

C. COMPLEXES CONTAINING TWO SIX-MEMBERED RINGS

1. *Fifth Subgroup*

In this group it was possible after a long series of trials to obtain the yellow cation $[V(C_6H_6)_2]^+$ from the system $VCl_4/AlCl_3/Al/C_6H_6$, this time, surprisingly, only under reflux; unlike its chromium analogue, the $[V(C_6H_6)_2]^+$ ion is unstable to hydrolysis. However, just as in the case of the molybdenum and tungsten compounds, red-brown dibenzene vanadium, $V(C_6H_6)_2$, can be obtained by a rapid hydrolytic disproportionation. In the form of large crystals it is black; it sublimes at 120-150°, tends to sinter at about 120°, melts sharply at 277-278°, and decomposes above 330°. It is instantly oxidized in air, but gives red-brown solutions in organic solvents if air is excluded. It is only slightly soluble in methanol. With water which is saturated with nitrogen there is neither dissolution nor hydrolysis, but on allowing access of air the complex is oxidized without formation of a stable cation (*64*). Red-brown dimesitylene vanadium, $V[sym\text{-}(CH_3)_3C_6H_3]_2$, which is extremely sensitive to air, may likewise be obtained. Attempts to reduce $V(C_6H_6)_2$ to the $[V(C_6H_6)_2]^-$ anion by means of alkali metals in liquid ammonia were unsuccessful.

2. *Sixth Subgroup*

Dibenzene chromium is prepared by the methods which have already been mentioned (*53, 107, 227, 228*). The compound may be sublimed in a high vacuum at 150°, and deposits as brown-black crystals of mp 284-285°. It is only moderately soluble in organic solvents such as benzene (16 mg/ml), forming yellow or, at higher concentrations, brown, solutions. Its solubility in ether is lower; it is relatively rapidly oxidized in air. Water neither dissolves nor attacks the compound. Thermal decomposition sets in at about 300°, with formation of a metallic mirror.

The uncharged compound is the best starting point for the preparation of salts, since it may easily be oxidized by atmospheric oxygen in a two-phase system comprising water and an organic solvent. The iodide, tetraphenylborate, reineckate, picrate, and perchlorate are typical insoluble salts. Various compounds of the cation are sensitive to light. Neutral or weakly alkaline solutions may be kept for weeks in air without appreciable decomposition, but acidic solutions soon decompose. The perchlorate and similar compounds with oxidizing anions are explosive in the dry state. Instead of benzene, many of its alkyl and aryl homologues, such as toluene, *o*-, *m*-, and *p*-xylenes, mesitylene, pseudocumene, hexamethylbenzene, diphenyl, and tetralin, may be used as ligands in the complex. In all these cases the aluminum chloride method may be employed.

Dibenzoic acid chromium is reported as produced when the mixture formed in the preparation of dibenzene chromium by the Grignard reaction is treated with carbon dioxide (*227*). Substitution reactions for the hydrogen atoms in the rings of the complex, such as are known to occur readily for ferrocene, do not occur in this case (*90*).

Complex formation for molybdenum, the first homologue of chromium, was brought about by means of the aluminum chloride method (*79*). Red-brown $[Mo(C_6H_6)_2]^+$ is formed, and is then reduced to the green uncharged compound, $Mo(C_6H_6)_2$, by sodium dithionite. A more elegant method is the recently discovered disproportionation in an alkaline medium (*64*), which occurs according to the equation

$$6[Mo(C_6H_6)_2]^+ + 8OH^- \rightarrow 5Mo(C_6H_6)_2 + MoO_4^{=} + 4H_2O + 2C_6H_6. \qquad (13)$$

Dibenzene molybdenum forms glistening green crystals which sublime at 90-100°, decompose without melting at about 115°, with separation of a metallic mirror, and are readily soluble in organic liquids. In keeping with its much greater sensitivity to oxidation than the chromium compound, dibenzene molybdenum ignites in air. Uncharged dimesitylene molybdenum and additional salts of the cation have also been characterized (*79, 187*).

The preparation of uncharged yellow-green dibenzene tungsten, $W(C_6H_6)$, was recently carried out by using a similar disproportionation with the mixture resulting from the interaction of tungsten hexachloride, aluminum chloride, aluminum, and benzene (*187*). This compound, which is much more sensitive to oxidation than dibenzene molybdenum, sublimes in a high vacuum at 50° and decomposes at 110°. In this case the orange-yellow iodide of the cation may also be prepared.

3. Seventh Subgroup

Although attempts made so far to prepare complexes of the type $Mn(aromatic)_2$ or $[Mn(aromatic)_2]^+$ have been unsuccessful, it has been possible to isolate a bright yellow tetraphenylborate of the $[Re(C_6H_6)_2]^+$ ion (as fine needles) and a red-brown reineckate of the $[Re(sym\text{-}(CH_3)_3C_6H_3)_2]^+$ ion by the aluminum chloride method. The free bases are stable, but attempts at reduction to the uncharged complex of the element were unsuccessful (*83*).

4. Eighth Group

In this case complex formation was first observed for iron. It was necessary, however, to use mesitylene in place of benzene as a ligand more resistant to hydrolytic fission. The orange-red $[Fe(sym\text{-}(CH_3)_3C_6H_3)_2]^+$ ion, which is relatively stable in weakly acidic media, was obtained and characterized as the fire-red iodide, the orange tetraphenylborate and the light red reineckate. Tetralin and alkyl benzenes may likewise enter into complex formation (*44*). In the case of the homologues ruthenium and osmium, the light yellow cations $[Ru(sym\text{-}(CH_3)_3C_6H_6)_2]^{++}$ and $[Os(sym\text{-}(CH_3)_3C_6H_3)_2]^{++}$ were found in the same way. They are considerably more stable than the iron complex, and the same increase in stability is found in the series cobalt, rhodium, and iridium. The red-brown $[Co(sym\text{-}(CH_3)_3C_6H_3)_2]^{3+}$ ion is considerably more labile than its lighter-colored rhodium analogue, and the light brownish-yellow iridium cation is the most stable. All three of these complex ions may be isolated as reineckates, and that of rhodium also as the iodide (*84*). In the case of platinum(IV) experiments carried out up to the present lead to the hope that the corresponding complex will be isolated.

D. MIXED COMPLEXES CONTAINING SIX-MEMBERED RINGS

1. Carbonyls

The preparation of a compound of this type, $C_6H_6Cr(CO)_3$, was first achieved by the interaction of chromium carbonyl and dibenzene chromium in benzene in an autoclave (*67*). This substance was also obtained more simply by the reaction (*68*)

$$Cr(CO)_6 + C_6H_6 \rightarrow C_6H_6Cr(CO)_3 + 3CO. \qquad (14)$$

The compound forms yellow crystals (mp 162-163°) which may be sublimed and which dissolve in the usual organic solvents. It is diamagnetic and, in contrast to dibenzene chromium, is stable in air. This reaction, which opened up fundamentally new possibilities for the addition of six-membered aromatic rings to transition metals, soon proved to be extraordinarily widely applicable. Thus, by means of it, yellow molybdenum and tungsten compounds $C_6H_6Mo(CO)_3$ and $C_6H_6W(CO)_3$ (decomposition temperatures 120-125° and 140-145°, respectively) were prepared directly. In place of benzene itself, a great number of its alkyl derivatives can take part in complex formation. Mention may be made of the compounds *sym*-$(CH_3)_3C_6H_3Mo(CO)_3$ (decomposition temperature 130-140°), *sym*-$(CH_3)_3C_6H_3W(CO)_3$ (mp 160°), and the exceptionally stable $(CH_3)_6C_6Cr(CO)_3$ (mp 232°). The compound $CH_3C_6H_5Cr(CO)_3$ (mp 80°), which is to be regarded as isoelectronic with the cyclopentadienyl derivative $CH_3C_5H_4Mn(CO)_3$, is, in surprising contrast to the latter, no longer liquid. The isomers *o*-$(CH_3)_2C_6H_4Cr(CO)_3$ (mp 88-90°), *m*-$(CH_3)_2C_6H_4Cr(CO)_3$ (mp 104-105°), and *p*-$(CH_3)_2C_6H_4Cr(CO)_3$ (mp 97-98°) differ only slightly in stability.

Surprisingly, it was found possible by this method to prepare complexes of benzene derivatives which had not previously given diaromatic complexes by the aluminum chloride method. Thus, by decomposing chromium carbonyl with chlorobenzene a quite stable yellow compound of formula $ClC_6H_5Cr(CO)_3$ (mp 96-98°) was obtained; with aniline the product was the basic yellow substance ($H_2NC_6H_5Cr(CO)_3$ (mp 161°); with phenol, acidic water-soluble yellow $HOC_6H_5Cr(CO)_3$ (mp 114°); with methyl benzoate, orange $CH_3OCOC_6H_5Cr(CO)_3$ (mp 93-95°); and with anisole, the compound $CH_3OC_6H_5Cr(CO)_3$ (mp 80-82°). Naphthalene, the simplest condensed six-membered ring compound, reacts with chromium carbonyl to give the complex $C_{10}H_8Cr(CO)_3$ (which decomposes at 150-160°). All of the complexes mentioned are readily soluble in organic media and, in the solid state, are relatively stable in air. For the neighboring elements of the seventh subgroup only the cation [*sym*-$(CH_3)_3C_6H_3Mn(CO)_3]^+$ has been described (*19*); it is isolated as the cream-colored iodide after reaction of the carbonyl bromide $Mn(CO)_5Br$ with boiling mesitylene in the presence of aluminum chloride.

2. Mixed Five- and Six-Membered Aromatic Ring-Metal Complexes

After the green complex $[Cr(C_6H_6)_2]^+$ $[C_5H_5Cr(CO)_3]^-$ (which can be sublimed) had been obtained by precipitation (*63*), showing aromatic five- and six-membered ring systems as ligands on two different metal atoms, the combination of two such ligands with the same metal atom was achieved only quite recently. The compound $CH_3C_5H_4MnC_6H_6$ was obtained, as ruby-red crystals (mp 116-118°) which could be sublimed and which were relatively stable in air, by interaction of phenyl magnesium bromide and methylcyclopentadienyl manganese chloride or dicyclopentadienyl manganese in tetrahydrofuran (*19*). Another uncharged complex, $C_5H_5CrC_6H_6$ (mp 227-229° with decomposition), was obtained as a volatile orange solid by the reaction between chromic chloride and equivalent quantities of phenyl magnesium bromide and cyclopentadienyl magnesium bromide (*65*). In Group VIII, the cation $[C_5H_5FeC_6H_3(CH_3)_3]^+$ was obtained by treatment of cyclopentadienyl iron dicarbonyl chloride, $C_5H_5Fe(CO)_2Cl$, with boiling mesitylene and aluminum chloride, and was isolated as the ivory-colored iodide (*19*).

E. Physicochemical Investigations

X-ray work was particularly important in settling the problem of the structure of dibenzene chromium, and showed that this compound, unlike the dicyclopentadienyl metal compounds studied earlier, possessed a cubic lattice with the same space group as carbon dioxide, *Pa*3-T_h^6. The unit cell contained four molecules, and had a side of 9.67 ± 0.03 Å: the volume occupied by one molecule was found to be 226 $Å^3$. The hexagonal prismatic structure of dibenzene chromium is shown clearly in Fig. 9.

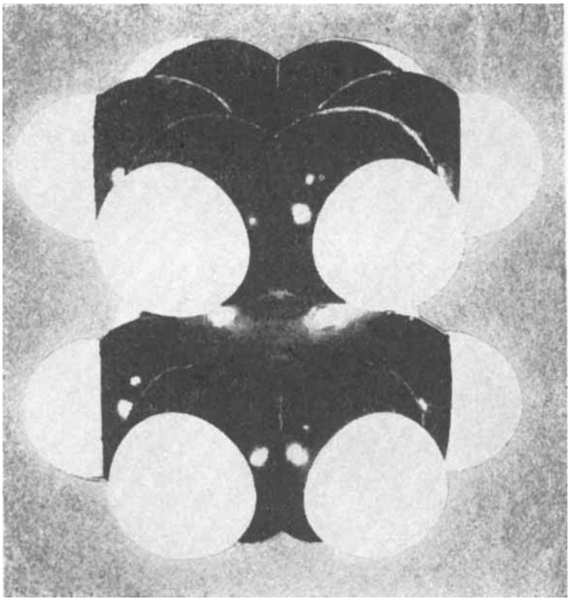


FIG. 9. Model of the structure of dibenzene chromium.

Distances in the centrosymmetric molecule have been determined provisionally as C-C = 1.38 ± 0.05 Å and Cr-C = 2.19 ± 0.1 Å (*201*) Dibenzene vanadium and dibenzene molybdenum do not have a cubic lattice. $V(C_6H_6)_2$ crystallizes like the dicyclopentadienyl metal complexes in the monoclinic system with the space group C_{2h}^5 and $a = 6.27$ Å, $b = 7.74$ Å, $c = 11.06$ Å, $\beta = 119.3°$ (*197*).

A polarographic study of the $Cr(C_6H_6)_2$– $[Cr(C_6H_6)_2]^+$ transition has been made (*91*). The dipole moments of the compounds $Cr(C_6H_6)_2$ (*196*), $Cr(sym\text{-}(CH_3)_3C_6H_3)_2$ (*196*), and, surprisingly, $C_5H_5CrC_6H_6$ (*74*) are all zero.

Magnetic measurements have been made on a large number of the new six-membered ring complexes with a view to elucidating the nature of the bonding. The values found for the metals forming uncharged complexes or cations are shown, together with their oxidation states, in Table VII. It is striking to note how the formation of complexes is always controlled so as to lead to diamagnetism and the closest possible approach to the inert gas configuration, showing that all the π-electrons are being drawn into the electronic shell of the metal. The hypothesis of the bonding of the aromatic system by threefold coordination again seems to be the best explanation. Isoelectronic series may be constructed on the basis of these relationships; they also give a survey of the whole system and of the possibilities of its extension, e.g., $W(C_6H_6)_2$, $[Re(sym\text{-}(CH_3)_3C_6H_3)_2]^+$, $[Os(sym\text{-}(CH_3)_3C_6H_3)_2]^{++}$, and $[Ir(sym\text{-}(CH_3)_3C_6H_3)_2]^{3+}$.

TABLE VII

MAGNETIC MOMENTS OF COMPLEXES CONTAINING TWO SIX-MEMBERED RINGS

Central metal	Compound investigated	No. of unpaired electrons	Moment (Bohr magnetons) Calc	Moment (Bohr magnetons) Exp	Reference
V^0	$V(C_6H_6)_2$	1	1.73	1.68	*64*
Cr^0	$Cr(C_6H_6)_2$	0	0	0	*53*
Cr^{+1}	$[Cr(C_6H_6)_2]^+$	1	1.73	1.73	*53*
Mo^0	$Mo(C_6H_6)_2$	0	0	0	*79*
W^0	$W(C_6H_6)_2$	0	0	0	*79*
Re^{+1}	$[Re(C_6H_6)_2]^+$	0	0	0	*83*
Fe^{+2}	$[Fe(sym\text{-}(CH_3)_3C_6H_3)_2]^{+2}$	0	0	0	*44*
Ru^{+2}	$[Ru(sym\text{-}(CH_3)_3C_6H_3)_2]^{+2}$	0	0	0	
Os^{+2}	$[Os(sym\text{-}(CH_3)_3C_6H_3)_2]^{+2}$	0	0	0	
Rh^{+3}	$[Rh(sym\text{-}(CH_3)_3C_6H_3)_2]^{+3}$	0	0	0	

It is also characteristic that the diversity of the oxidation states exhibited, in contrast to those in the corresponding five-membered ring complexes, is very limited. This must be attributed to generally weaker bonding of the uncharged aromatic ligand relative to the charged one, for which there is additional electrostatic attraction between the ring and the metal ion.

Just as in the case of cyclopentadienyl metal complexes, six-membered ring aromatic complexes have infrared absorption bands in characteristic regions. On the basis of compounds examined up to the present time, unsubstituted six-membered rings bound in complexes are characterized by intense bands in five frequency ranges in the rock salt prism region (*45*). These, given below, are also valid for mixed complexes such as the compounds $C_5H_5CrC_6H_6$ and $C_6H_6Cr(CO)_3$: (1) a C—H stretching frequency at 3010-3060 cm^{-1} (ν_{CH}); (2) a C-C stretching frequency at 1410-1430 cm^{-1} (ν_{CC}); (3) a C-C stretching frequency at 1120-1140 cm^{-1} (ν_{CC}); (4) two or three C—H deformation frequencies at 955-1000 cm^{-1} (δ_{CH}); (5) one or two C—H deformation frequencies at 740-790 cm^{-1} (δ_{CH}). From recent investigations, including those on $Cr(C_6D_6)_2$, the number of intense infrared absorption bands for dibenzene chromium leads to the conclusion that the compound has no sixfold symmetry, but very probably the symmetry group D_{3d} (*127*). These results provide convincing evidence for our view of the structure, with approximately octahedrally distributed metal-carbon bonds and perhaps weakly puckered rings which certainly exhibit threefold symmetry. On geometrical grounds, an analogous variation of symmetry in cyclopentadienyl rings in a complex is impossible. Measurements of electron spin resonance in the cation $[Cr(C_6H_6)_2]^+$ have been made (*35, 36*): they show that the one unpaired electron in the ion is distributed over the whole complex.

The enhanced tendency to form only complexes in which an inert gas configuration is approached more closely comes to light in an impressive way for the mixed six-membered ring-metal complexes. Without exception, the aromatic hydrocarbon-metal carbonyls of the sixth subgroup elements are diamagnetic; so, too, are the complexes of formulae $[(CH_3)_3C_6H_3Mn(CO)_3]^+$, $CH_3C_5H_4MnC_6H_6$, and $[C_5H_5FeC_6H_3(CH_3)_3]^+$. The absorption of all the π-electrons is therefore established for these cases, too. The fact that a shell of thirty-five electrons provides sufficient stability for the formation of a π-complex (as in diaromatic complexes such as those of Cr(I), Mo(I), or V(O), which have already been mentioned) is shown by the existence of the compound $C_6H_6CrC_5H_5$, the only instance of its kind known at present. This complex has a moment of 1.70 Bohr magnetons, corresponding to a single unpaired electron.

F. STRUCTURES AND BONDING

On the basis of chemical properties and physicochemical investigations dibenzene chromium is considered to have the same spatial distribution of bonds as ferrocene. X-ray studies have shown that the molecule is centrosymmetric, and that all the C-C and Cr-C distances are practically equal. One may therefore decide with certainty on the double cone structure (see Fig. 9). As already mentioned, it may be concluded that the metal-carbon bonds have an approximately octahedral arrangement and that the benzene rings have threefold symmetry.

It is not yet possible to say whether the rings exhibit free rotation. From the zero dipole moment of ditoluene chromium (*201*), it can be concluded that under certain circumstances there is unhindered rotation. Electron-diffraction studies at various temperatures might throw light on this point. In keeping with the theory of bonding in ferrocene, we assume a central chromium atom of zero oxidation state; it attains the krypton configuration by accepting coordinate links from the three pairs of π-electrons of each aromatic ring. This accords with the diamagnetism of the compound, since otherwise the chromium in zero oxidation state would have six unpaired electrons. The existence of the complex cation, which is exactly analogous to the dichroic red-blue ferricinium ion (which also contains one unpaired electron), shows that an electron can be removed from the three doubly-occupied $3d$-orbitals that are not involved in ring-metal bonding; this is just like the ferrocyanide to ferricyanide ion transformation (*53*). This view of the bonding is also applicable without difficulty to the diaromatic complexes of other transition metals, as well as to the mixed types of compound. A molecular orbital theory of the covalent bonding between chromium and the two benzene rings, based on that for ferrocene, has also been developed (*119*).

G. THE ELUCIDATION OF THE CONSTITUTION OF THE CHROMIUM PHENYL COMPOUNDS

All of the developments so far described are specially significant in relation to the chromium phenyl compounds obtained by interaction of chromic chloride and phenyl magnesium bromide, which were investigated by F. Hein after 1919. These were originally considered to be true organometallic compounds, possessing chromium-carbon σ-bonds, of general composition $Cr(C_6H_5)_n$ ($n = 3$ or 4), and $Cr(C_6H_5)_nX$ ($n = 3$, 4, or 5), where X represents anions such as iodide and anthranilate. J. Zernike in 1939 first considered them to be some sort of "hypercomplexes," and for the saltlike compounds the chromium was assumed to be in the unipositive state (*230*). In 1953 a ferrocene-like structure was discussed, though an incorrect oxidation state was attributed to the chromium (*92*). At about this time H. H. Zeiss had begun a critical repetition of Hein's work and had confirmed his analytical results completely (*228*). On the basis of these, L. Onsager and Zeiss proposed a basic structure for the compounds which was in accord with all the experimental results (*226, 229*).

In the chromium(I) salts, the metal ion should lie between two rings in a double cone structure and have a shell of 35 electrons, including all the π-electrons of both rings. According to this view, "$Cr(C_6H_5)_3$" may be written as $C_6H_6Cr(C_6H_5 \cdot C_6H_5)$, "$Cr(C_6H_5)_4$" as $Cr(C_6H_5 \cdot C_6H_5)_2$, and "$Cr(C_6H_5)_5OH$" as a phenate of the $[Cr(C_6H_5 \cdot C_6H_5)_2]^+$ cation. This idea received strong support from hydrogenation experiments with lithium aluminum deuteride, and from the recovery of deuterated benzene and diphenyl on reduction of the complex which results in the Grignard reaction with lithium aluminum deuteride, though not on treatment with lithium aluminum hydride and working up with deuterium oxide (*228*). In 1955 the entirely independent synthesis of dibenzene chromium and the X-ray proof of its structure afforded the opportunity for an investigation in collaboration with Hein. The compound $Cr(C_6H_5)_4I$ was prepared by the Grignard reagent method, and the complex $[Cr(C_6H_5 \cdot C_6H_5)_2]I$ was obtained from the system $CrCl_3/AlCl_3/Al/C_6H_5 \cdot C_6H_5$ and precipitation with iodide ion. The identity of these products, shown by comparison of their infrared and ultraviolet absorption spectra, X-ray absorption edges, and magnetic properties, provided unambiguous proof of the aromatic-complex nature of the chromium phenyl compounds (*78, 103*). In a similar way, the compound $Cr(C_6H_5)_3$ was later shown to have the constitution $C_6H_6CrC_6H_5 \cdot C_6H_5$ (*104*). An old problem in the chemistry of organometallic compounds was thus solved. The presence of the $[Cr(C_6H_6)_2]^+$ ion was also shown by separating the products of the Grignard reaction on a chromatographic column (*105, 107*). The mechanism of formation of the complex by the Grignard method (*227, 228*), and the thermal degradation of "triphenyl chromium" (*106*) have also been studied. This work provides further support for the π-complex theory.

IV. The Existence of Complexes of Seven-Membered Aromatic Systems

Now that complex formation with suitable metals has been established for anionic aromatic $(C_5H_5)^-$ rings and for uncharged aromatic compounds like benzene, the question arises as to whether the aromatic $(C_7H_7)^+$ cation, which has become known in recent years, can function similarly. We have made investigations with tropylium bromide, $(C_7H_7)^+Br^-$, obtained from benzene by expansion of the ring with diazomethane, bromination of the resulting tropylidene and abstraction of hydrogen bromide, according to the method of E. Doehring (*45*).

Carbonyls such as those of chromium, molybdenum, or iron were first allowed to react with tropylium bromide, but, unlike those with benzene or cyclopentadiene, these experiments were unsuccessful, even when an autoclave was used. Attempts were then made to obtain a seven-membered ring complex by the thermal decomposition of tropylium salts of carbonyl hydrides, but it was found that the great sensitivity of tropylium bromide to reduction, coupled with the strong reducing power of the carbonyl hydrides, militated against success. Thus, the interaction of the sodium salt $Na[C_5H_5Cr(CO)_3]$ and tropylium bromide, followed by sublimation of the resulting green product, led, by the redox reaction

$$2Na[C_5H_5Cr(CO)_3] + 2C_7H_7Br \rightarrow [C_5H_5Cr(CO)_3]_2 + C_{14}H_{14} + 2NaBr$$

to dimeric cyclopentadienyl chromium tricarbonyl and ditropyl instead of proceeding according to the equation

$$[C_5H_5Cr(CO)_3](C_7H_7) \rightarrow C_5H_5CrC_7H_7 + 3CO.$$

In compounds of the type $Cr(CO)_3(NH_3)_3$, too, it is impossible to replace the labile ammonia ligands by the tropylium ring. The method of Grignard reagent formation and simultaneous reaction with metal halides (e.g., starting from cyclopentadiene or bromobenzene) was applied to bromocycloheptatriene (obtained by ring expansion of bromobenzene) and chromic chloride, but proved unsuccessful. The same was true of attempts to expand the ring in dibenzene chromium by reaction with diazomethane and ultraviolet irradiation.

The next step was to prepare suitable salts of the tropylium ion and to try to obtain the complex from these. In order to demonstrate the existence of the tropylium ion in solution, a precipitating agent was sought, and was found in the tetraphenylborate ion, which in dilute acetic acid solution gives a bright yellow precipitate of composition $(C_7H_7)[B(C_6H_5)_4]$. Red-brown plates of composition $(C_7H_7)H_3[Fe(CN)_6]$ are precipitated by potassium ferrocyanide from solutions containing hydrobromic acid, and an analogous reaction occurs with potassium ruthenocyanide. Using energetic thermal conditions, an attempt was made to introduce the ring into a complex, but only decomposition products resulted, and the cyanide ligands were not displaced. By interaction of tropylium bromide and cuprous bromide the diamagnetic tropylium salt of the acid $H(CuBr_2)$ was obtained. Tropylium bromide and $H_2(PtBr_6)$ in glacial acetic acid likewise gave only a saltlike orange-red compound $(C_7H_7)_2(PtBr_6)$. The reaction of C_7H_8 on platinic bromide or $H_2(PtBr_6)$ surprisingly led to a diamagnetic compound of the composition $C_7H_8PtBr_2$ or $C_7H_7PtBr_2$, which forms orange needles of mp 154.5-155°, is almost insoluble in water as well as in usual organic solvents and cannot be sublimed under usual conditions. Although some of the chemical properties are similar to those of olefin complexes of the type $(\text{olefin} \cdot PtBr_2)_2$, the infrared spectrum of the compound clearly shows the existence of an equilateral hydrocarbon ring, so that we assume the structure $(C_7H_7PtBr_2)_2$. Because of the fact, that more than four infrared (IR) active normal frequencies, as predicted for $(C_7H_7)^+$ in symmetry group D_{7h}, can be found, we regard the original group D_{7h} as changed to symmetry group C_{7v}. The selection rules of C_{7v} predict seven IR-active fundamental frequencies for $(C_7H_7)^+$. The absorption bands typical for $(C_7H_7)^+$ in $(C_7H_7)Br$ appear at nearly the same position in the spectrum of $(C_7H_7PtBr_2)_2$. Just as in a likewise orange-colored compound of the approximate composition $C_7H_7PtBr_3$, the assumption of d^2sp^3-configurated metal atoms would lead to genuine π-complexes of the aromatic seven-membered ring, the possible existence of which was discussed earlier (*174*). Our work is still in progress, but some results will be published soon (*46*).

Very interesting in connection with the above-mentioned work is the recently reported (*210*) preparation of a compound $C_7H_8Mo(CO)_3$. Formation of a seven-membered ring complex with metals in a negative oxidation state, e.g. Re^- in the compound KRe, is opposed by the relatively strong oxidizing action of the tropylium ion. In tropylium compounds of main group elements, such as $S(C_7H_7)_2$, the rings do not (according to Doering) form a "sandwich" complex but are bonded normally, as in a thioether.

An important contribution to the problem of π-electron bonding with seven-membered rings is probably made by measurements of the chemical shifts of ring protons as studied by the nuclear magnetic resonance method. It has recently been shown (*117*) that the displacement of the electron density of the ring protons increases along the series $(C_5H_5)^-$, C_6H_6, $(C_7H_7)^+$. Perhaps this expresses the decreasing tendency to enter stable π-bonds.

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