PROGRESS IN
INORGANIC CHEMISTRY

EDITED BY
F. ALBERT COTTON
DEPARTMENT OF CHEMISTRY,
MASSACHUSETTS INSTITUTE OF
TECHNOLOGY, CAMBRIDGE,
MASSACHUSETTS

VOLUME I

1959

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Introduction to the Series

The remarkably broad and rapid development of inorganic chemistry since the end of World War II is well recognized. If we chose to define inorganic chemistry as the study of all of the chemical and many related physical properties of inorganic substances, the extent of the field is very great indeed. It includes among its ramifications the organo derivatives of all of the elements, the study of mixed oxide systems, the quantum mechanical treatment of the spectral and magnetic properties of transition metal ions, the study of a wide variety of catalytically active solids, the preparation of a host of the less familiar elements and their compounds, as well as radically new types of compounds, along with the many classically recognized aspects of inorganic chemistry. The wide interest and the rapid growth and expansion of the field are attested by the great and persistent demand for inorganic chemists for both industrial and academic positions. The new Division of Inorganic Chemistry of the American Chemical Society, which received permanent status recently, symbolizes the general recognition of inorganic chemistry as a distinct and plenary branch of the science.

Because of the breadth and diversity of the discipline, the problem of maintaining effective, fruitful communication among the different branches of inorganic chemistry has become highly important. It is my belief that a new forum for the exchange of views and for critical and authoritative review and evaluation of advances in the various branches of the discipline would be of great value. The annual series of volumes of which this is the first has been initiated with the hope that it will contribute to meeting the need for communication.

It is intended that all articles be written by one of the leading researchers in the field. The treatment is intended to be such that the article should be comprehensible, but not necessarily *readily* comprehensible, to a competent Ph.D. level research worker in some branch of inorganic chemistry, but not necessarily the one under discussion. However, it is my belief that the author's responsibility and privilege of giving a scholarly and accurate account of his subject should not be curtailed by any feeling of a need for oversimplification. If, for ex-

ample, a subject is intrinsically complicated or mathematical, no useful purpose can be served by dealing with it as if it were not.   Thus I have hoped to include articles which avoid both of the extremes, first, of dry and terse summarizing of the literature and, second, of superficiality suitable perhaps for light reading but not very helpful to the reader desiring accurate, thorough information.   I have encouraged a degree of informality so that where responsible differences of opinion exist the expression of the author's own viewpoint, consistent with fairness and decorum, may be presented.   Length and style will also be found to vary from one article to another, since I have assumed that the author is best qualified to determine the style, length, and general nature of the treatment appropriate to his subject.

It is also my hope that these volumes will be regarded as, and become progressively more of, an international venture, which is in the true spirit of science.   With this in mind, articles will be published in any of the three languages, English, German and French, which research chemists are assumed to read.

I should greatly welcome comments and suggestions with regard to any aspect of these volumes.

In conclusion, it is my duty to emphasize that it is the authors of the articles who are responsible for their excellence and it is my pleasure to express my gratitude for their efforts.

F. A. COTTON

Cambridge, Mass.
June 25, 1959

Contributors to Volume I

MARGOT BECKE-GOEHRING
> *Chemisches Institut der Universität, Heidelberg, Germany*

F. ALBERT COTTON
> *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts*

PHILIP GEORGE
> *John Harrison Laboratory of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania*

GERHART R. HENNIG
> *Argonne National Laboratory, Lemont, Illinois*

WILLIAM L. JOLLY
> *Department of Chemistry and Lawrence Radiation Laboratory, University of California, Berkeley, California*

DONALD S. McCLURE
> *RCA Laboratories, Radio Corporation of America, Princeton, New Jersey*

LAMBERTO MALATESTA
> *Instituto di Chimica Generale, Universita di Milano, Italy*

ROLAND WARD
> *Department of Chemistry, University of Connecticut, Storrs, Connecticut*

GEOFFREY WILKINSON
> *Department of Chemistry, Imperial College of Science and Technology, London, England*

Contents

Cyclopentadienyl and Arene Metal Compounds

By G. WILKINSON
Imperial College of Science and Technology, London, England
and F. A. COTTON
Massachusetts Institute of Technology, Cambridge, Mass.

CONTENTS

I. Introduction

A. SCOPE

This review covers the chemistry of compounds formed between transitional metals and the cyclopentadienyl group, benzene and related aromatic systems, and certain other unsaturated hydrocarbons. It deals also with the ionic derivatives of the cyclopentadienide ion and with the cyclopentadienyl derivatives of certain nontransition metals.

While the first metal derivatives of cyclopentadiene were prepared by Thiele over fifty years ago, the interest in metal derivatives of cyclopentadiene, and subsequently of aromatic hydrocarbons, stems from the independent and accidental discoveries of the molecule of formula $C_{10}H_{10}Fe$, now called ferrocene, by Miller, Tebboth, and Tremaine (B.9) and by Kealy and Pauson (B.1).* These authors did

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* Ferrocene was first obtained in 1948 during studies of possible reactions of olefins with nitrogen over metallic catalysts in the laboratories of the British Oxygen Company (S. A. Miller, private communication to G. W.).

not fully appreciate the unique nature of the compound either struc-
turally or in its chemical behavior, and shortly thereafter the now
well-known "sandwich"* structure was advanced by Wilkinson,
Rosenblum, Whiting, and Woodward (B.2) and later, independently,
by Fischer and Pfab (B.10). It was also shown by Rosenblum, Whit-
ing, and Woodward (O.0) that the molecule behaves as an aromatic
system undergoing, for example, Friedel-Crafts acylations; they also
coined the name "ferrocene" for $(\pi\text{-}C_5H_5)_2Fe$.

The early studies in the field were comprehensively reviewed in
1955 (E.20) and other reviews of parts of the field have been made
(E.2,F.33,F.34,G.25,H.16,H.34,H.35). The present review is con-
cerned primarily with the general inorganic and physical chemistry of
the compounds and with theoretical treatments of bonding. The now
exceedingly extensive organic chemistry of ferrocene is not discussed,
although a literature guide is provided. The references are believed
to be complete up to July 1, 1958.

Excluding various salts, e.g., picrates, Reineckates, etc., of cations
such as $(\pi\text{-}C_5H_5)_2Co^+$ and $(C_6H_6)_2Cr^+$ and organic derivatives of
ferrocene, the tables presented subsequently indicate that since the
discovery of ferrocene in all over 200 new metal-hydrocarbon com-
pounds have been prepared. It is pertinent to note, however, that
while many of the cyclopentadienyl and arene compounds discussed
herein have been described by different workers, often quite simul-
taneously, in the scientific literature, it is known that many of these
derivatives were made and studied at least simultaneously and in
quite a few cases earlier in industrial laboratories. It is not pos-
sible to give these often unknown industrial investigators due credit
except in occasional patent references, where detailed studies are
seldom given. Thus it appears that $(\pi\text{-}C_5H_5)_2Ni$ was first made by
Thomas (P.3) and several carbonyl derivatives, e.g., $\pi\text{-}C_5H_5M\text{-}$
$(CO)_3H$ (M = Cr, Mo, W), appear to have been made first in indus-
try (P.21,P.21a). Attention may be drawn at this point to the
remarkable patent (P.21,P.21a), which would appear from its date of
filing to anticipate much published work not only on carbonyl com-
pounds but on preparative methods for di-π-cyclopentadienyl com-
pounds and cyclopentadienides. The patent is remarkable in other

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* The first users of this term were Dunitz and Orgel (C.6).

ways, too, indeed having semblance in parts to science fiction; thus even those "skilled in the art" would have some difficulty in isolating compounds mentioned in the claim, such as $(C_5H_5)_5La(PBr_3)_2$ or $(C_5H_5)Li(H_2O)$, and in proving that "$(C_5H_5)Ti(NO)_3$ is more stable than $(C_5H_5)V(NO)_2H_2$."

It may be noted, finally, that since the discovery of ferrocene, we have listed over 300 notes and papers on the sandwich compounds reviewed herein.

B. NOMENCLATURE

The nomenclature adopted is as follows:

1. Cyclopentadienyl Compounds

(a) Two rings present with "sandwich" bonding: di-π-cyclopentadienyl-, e.g., di-π-cyclopentadienylchromium(II), $(\pi\text{-}C_5H_5)_2Cr$. The name *ferrocene* is used for $(\pi\text{-}C_5H_5)_2Fe$; the cation $[(\pi\text{-}C_5H_5)_2Fe]^+$ is termed the ferricenium ion. Similar trivial names are ruthenocene, osmocene, cobaltocene, nickelocene, etc.

(b) One ring present with "sandwich" bonding: π-cyclopentadienyl-, e.g., π-cyclopentadienylchromium(II) dinitrosyl chloride, $\pi\text{-}C_5H_5Cr(NO)_2Cl$.

(c) One or two rings present with localized metal–carbon bonds: σ-cyclopentadienyl-, e.g., π-cyclopentadienyl(σ-cyclopentadienyl)-chromium(II) dinitrosyl, $\pi\text{-}C_5H_5Cr(NO)_2\sigma\text{-}C_5H_5$.

(d) Ionic derivatives: cyclopentadienide ion, $C_5H_5^-$; cyclopentadienides. e.g., manganese cyclopentadienide, $Mn(C_5H_5)_2$.

2. Arene Compounds

(a) Two rings present: diarene-, e.g., dibenzenechromium(0), $(C_6H_6)_2Cr$.

(b) One ring present: arene-, e.g., toluenechromium(0) tricarbonyl, $C_7H_8Cr(CO)_3$. A similar nomenclature is used for other aromatic or pseudoaromatic systems, e.g., cycloheptatrienechromium(0) tricarbonyl, $C_7H_8Cr(CO)_3$.

3. Abbreviations

π-Cp	= π-C$_5$H$_5$		d.	= decomposes without melting
σ-Cp	= σ-C$_5$H$_5$		MeCp	= methylcyclopentadiene
Cp$^-$	= C$_5$H$_5^-$		Me	= methyl
π-ind	= π-indenyl		Et	= ethyl
σ-ind	= σ-indenyl		bz	= benzene
σ-fluor	= σ-fluorenyl		tol	= toluene
m.p.d.	= melting point with decompo-		mes	= mesitylene
	sition		ϕ	= phenyl

II. Cyclopentadienides

A. GENERAL REMARKS

It is pertinent to include in this review some brief notes on the ionic derivatives of cyclopentadiene—the cyclopentadienides—since not only are the alkali metal and magnesium salts used in preparations of other metal derivatives, but the manganese compound of formula $C_{10}H_{10}Mn$ has been shown to be a cyclopentadienide unlike the other $(\pi$-C$_5$H$_5)_2$M compounds of the elements of the first transitional series.

The acidity of cyclopentadiene was first recognized by Thiele, who obtained the potassium salt (A.3,A.4) as an air-sensitive product by treating dispersed potassium in benzene with C_5H_6 at room temperature; he obtained no reaction with sodium (A.4). Thiele's discovery led to similar work with substituted cyclopentadienes, and the potassium salt from fluorene was first made (A.5) by melting fluorene with KOH at 250–280°C. Sodium indenylide was obtained somewhat later (A.6) by the reaction of sodium with indene in the presence of ammonia or organic bases; sodium and lithium derivatives were subsequently made of indene, fluorene, and their derivatives.

The Grignard reagent, MgBrC$_5$H$_5$, and the corresponding indene derivative have long been known and used preparatively (A.1,A.2, A.7). These are obtained by treating an alkyl Grignard reagent in ether, or preferably in a higher boiling solvent such as benzene, with the hydrocarbon. The fluorene derivative was similarly obtained.

Concerning the cyclopentadienides, little further work was done for many years, until Greenlea (A.8) showed that in liquid ammonia solution cyclopentadiene reacted rapidly with sodium, without evolution of hydrogen, according to reaction 1. He isolated cyclo-

$$2\,\mathrm{Na} + 3\,\mathrm{C_5H_6} = \mathrm{C_5H_8} + 2\,\mathrm{NaC_5H_5} \tag{1}$$
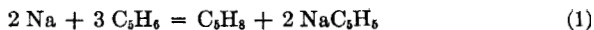
pentenes in yields consistent with this stoichiometry. This work anticipated by fourteen years similar studies using liquid ammonia (F.4,F.5) in which the same conclusions were drawn concerning the stoichiometry of the sodium reaction and the formation of cyclopentenes; both the later groups noted that the stoichiometry of the reaction given by Fischer *et al.* (C.7–C.10) requiring the evolution of hydrogen is false. The properties of sodium cyclopentadienide and the preparation of the calcium salt, either by reaction of cyclopentadiene with calcium carbide at elevated temperatures or by reaction in liquid ammonia, were also given by Ziegler *et al.* (D.1,F.5).

The formation of solutions of sodium cyclopentadienide in ether solvents (D.3,F.23) is now widely used for preparative work and is perhaps the most generally useful method for preparing all types of nonionic cyclopentadienyl metal compounds and indeed even sublimable cyclopentadienides such as those of manganese and the lanthanides. The use of the sodium salt is more expeditious than methods requiring the use of lithium cyclopentadienide or the Grignard reagent. Suitable ethers for carrying out the reaction of granular or dispersed sodium with cyclopentadiene (or substituted cyclo-pentadienes) are tetrahydrofuran, ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, etc., of which the first two are most commonly employed. Sodium may be dispersed in mineral oil, to which the ether is then added (P.21) or may be granulated in toluene which is then removed and the ether run in (F.23). Details for a laboratory preparation have been given (F.32).

It has been shown (D.8) that potassium tertiary butoxide converts cyclopentadiene quantitatively to its potassium salt; this fact, together with the fact that indene and fluorene do not react with the sodium tertiary butoxide (F.5), confirms estimates (D.8 and references therein) that the pK_a value for cyclopentadiene is greater than 19 and less than the 21 of indene. The formation of sodium, potassium, and lithium cyclopentadienides in alcohols and in other solvents of high dielectric constant is possible, e.g., lithium cyclopentadienide has been made in dimethylformamide (F.39,F.44), and calcium cyclopentadienide has been made in ethylenediamine (F.5). The sodium salt has also been made in inert solvents containing a small amount of alcohol (F.5).

Equations 2 and 3 illustrate the general behavior of cyclopentadienides. Thus, in tetrahydrofuran, rather weakly conducting solu-

$$M^+C_5H_5^- = M^+ + C_5H_5^- \tag{2}$$

$$C_5H_5^- + H^+ = C_5H_6 \tag{3}$$
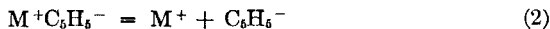
tions of NaC_5H_5, $Mn(C_5H_5)_2$, and $Mg(C_5H_5)_2$ were obtained (F.23), indicating that while dissociation does occur, it is not, however, substantial. With acids which are stronger than cyclopentadiene, e.g., water, cyclopentadienides react instantaneously to form cyclopentadiene and the metal hydroxide or other salt. The cyclopentadienides generally react vigorously with air, inflaming or smoldering in the solid state. They also react with carbon dioxide to give carboxylic acid salts (A.4) and with dienophiles such as maleic anhydride; with chloroform and with alkyl halides they give alkylated cyclopentadienes.

The dissociation is also shown by the fact that all cyclopentadienides react instantaneously in an ionic reaction, and quantitatively* with ferrous chloride (or other metal halides) to give ferrocene (eq. 4). The criteria for ionic bonding in metal cyclopentadienyl

$$2 C_5H_5^- + Fe^{2+} = (\pi\text{-}C_5H_5)_2Fe \tag{4}$$
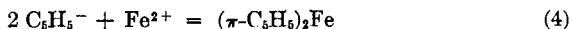
compounds based on both physical measurements and chemical reactions such as those above have been discussed at some length in studies of manganese cyclopentadienide (F.23).

The high resolution nuclear magnetic resonance chemical shift of the equivalent protons of the $C_5H_5^-$ ion has been measured and compared to the shifts for protons in benzene and the tropylium ion $C_7H_7^+$ (G.39). The Pople free electron theory of shifts in aromatic rings predicts that the resonance in the $C_5H_5^-$ ion should be upfield, and that in $C_7H_7^+$ downfield, from that in benzene. Qualitatively, these predictions are confirmed, but quantitatively the agreement is rather poor, the observed shifts being much larger than those calculated. The differences may perhaps be accounted for by the reasonable assumption that part of the negative charge in the $C_5H_5^-$ ion spreads to the hydrogen atoms, thus putting them further upfield, while the opposite occurs in the $C_7H_7^+$ ion.

* While the reaction of pure cyclopentadienides, e.g. $Mn(C_5H_5)_2$ and $Pr(C_5H_5)_3$, was shown to be quantitative with Fe^{2+}, the reaction of NaC_5H_5, prepared in ether from C_5H_6 and Na, does not give quantitative yields of ferrocene, presumably since some reduction to cyclopentenes occurs. Although not quantitatively studied, this reduction appears to be much less in the ethers than in liquid ammonia; hydrogen is certainly evolved from the reaction in ether.

B. SOME INDIVIDUAL COMPOUNDS

In addition to the alkali metal and calcium cyclopentadienides noted above, the following compounds deserve brief comment.

1. Magnesium Cyclopentadienide

The original preparation of this compound (D.3,F.23) was by the thermal decomposition of the cyclopentadienyl Grignard reagent. However, it may now be obtained, potentially in very substantial quantities, by the direct reaction of magnesium with cyclopentadiene at 500–600°C. (G.35). The compound forms readily sublimable colorless crystals and can be stored under nitrogen. It is miscible in all proportions with manganese cyclopentadienide (F.23).

2. Scandium, Yttrium, and Lanthanide Cyclopentadienides

Numerous lanthanide compounds, $M(C_5H_5)_3$, have been made (F.15). They are all rather air-sensitive but are thermally very stable indeed. The chemical reactivities are similar to those of other cyclopentadienides. The magnetic susceptibilities of the paramagnetic compounds are those to be expected for the lanthanide M^{3+} ions. No X-ray studies have been made, and the relative dispositions of the anions are not known, but it was suggested that in the free molecules the rings lie perpendicular to axes directed from the metal atom to their centers, at angles of 120 degrees.

3. Manganese Cyclopentadienide

Unlike the other elements of the first transition series which give di-π-cyclopentadienyl compounds, the manganese analog, $Mn(C_5H_5)_2$, first reported by Wilkinson and Cotton (D.3) is ionic. In a subsequent comprehensive study of the compound and a comparison with the other $C_{10}H_{10}M$ compounds by Wilkinson, Birmingham, and Cotton (F.23) considerable physical and chemical evidence (see Table III) was obtained for the ionic formulation. Mass spectral studies on $MgCp_2$ and $MnCp_2$ (E.11) showed that they behaved very similarly with respect to the nature and yields of the ionic species produced in electron bombardment but that they differed strikingly from the neutral di-π-cyclopentadienyl metal compounds. The manganese compound was also shown (F.23) to possess unique magnetic proper-

ties (Section VII-B-2), being antiferromagnetic at low temperatures and with considerable spin-spin interaction up to 433°K., where a sharp magnetic transition occurred which was associated also with a change in color, from amber-brown* to the pink of the Mn^{2+} ion. Below 433°K. the crystal was rhombic, and above this temperature, to the melting point of 445–446°K., monoclinic. In the latter form, the compound has five unpaired electrons. Paramagnetic resonance studies (G.51; Section VII-B-2) have subsequently completely confirmed the ionic nature of the compound and its antiferromagnetism. In view of the similarity in vapor pressure (see Table V) and melting points of $MnCp_2$ and π-Cp_2Fe the former was considered, on electrostatic grounds, also to have (together with $MgCp_2$) the same "sandwich" configuration of ferrocene. Preliminary X-ray studies on $MnCp_2$ (E.23) and $MgCp_2$ (E.22) have indeed shown that this is the case.

4. Thallium Cyclopentadienide

This compound was first reported in the literature by Fischer (G.5). It was made by the unusual aqueous reaction (eq. 5), whereupon the compound precipitates from

$$C_5H_6 + TlOH = C_5H_5Tl + H_2O \tag{5}$$
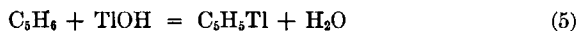
solution. This reaction has been suggested as an analytical method for the thallous ion (G.6).

The formulation of the compound as a cyclopentadienide by Cotton and Reynolds (H.6) is based on infrared spectral measurements, a consideration of ionization potentials, and a calculation of overlap integrals. It was concluded that while the compound has a π-cyclopentadienyl geometry (cf. $MnCp_2$), which could result from overlap of the ring e_1 orbitals with the metal e_1 (p_x, p_y) orbitals, the bonding in C_5H_5Tl is largely ionic.** The unusual thermal and chemical stability, e.g., toward air, of this compound must be due largely to an extremely stable crystal lattice, since it may be noted that the methylcyclopentadienide (I.8) is vigorously oxidized by air. Any objection to the ionic formation for TlC_5H_5 on the ground that the

* Amber in thin sections by transmitted light, brown by reflected light. Solutions in ethers are yellow.

** Microwave spectra of C_5H_5Tl at 100°C. by J. K. Tyler, A. P. Cox, J. Sheridan, *Nature*, *183*, 1182 (1959), have confirmed this view.

TABLE I. Cyclopentadienides

Compound	m.p. (b.p.)	Color	Prep.	IR	UV	Remarks
LiCp(sol)		colorless	E.10			
Liind(sol)		colorless	A.13,D.2			
Lifluor		colorless	A.10,A.13			
NaCp	d. ≪ 300	white powder	F.5,F.23		I.13	
Naind		white powder	A.5,A.9			
Nafluor		white powder	F.6			
KCp		white powder	A.4,D.8		I.13	
CaCp2		grey powder	D.1,F.5			
MgCp2	176	colorless cryst.	F.23 G.35	F.23,H.6	I.13	sub. ~50 in vac.
MgCpX		colorless cryst.	A.2,A.7			
Mg ind Br		colorless cryst.	A.2, A.7			
ScCp3	240	straw cryst.	F.15			sub. ~150 in vac.
YCp3	295	greenish yellow cryst.	F.15			sub. ~150 in vac.
LaCp3	395d.	colorless cryst.	F.15			
CeCp3	435d.	orange yellow cryst.	F.15			
PrCp3	415	green cryst.	F.15		F.15	exceed. sens. to air
NdCp3	380	reddish blue cryst.	F.15			sub. ~150 in vac.
Nd(MeCp)3	165	reddish blue cryst.	F.15,I.8			sub. ~150 in vac.
SmCp3	365	orange cryst.	F.15			sub. ~90 in vac.
GdCp3	350	yellow cryst.	F.15			sub. ~150 in vac.
DyCp3	302	yellow cryst.	F.15			sub. ~150 in vac.
ErCp3	285	pink cryst.	F.15		F.15	sub. ~150 in vac.
YbCp3	273	green cryst.	F.15			sub. ~150 in vac.
MnCp2	172–3[a]	amber cryst.	F.23,P.21	F.23	I.13	sub. 50; sol. ethers; sp. sol. hydrocarbons
Mn(MeCp)2	61–63 (85–90/1 mm.)	reddish brown cryst.	I.8,P.21			
TlCp	d. ~230	pale yellow powder	G.5	H.6		insol. H2O
Tl(MeCp)	88–89d.	pale yellow powder	I.8			insol. H2O
ZnCp2	?	colorless	G.8[b]			

[a] Of pink form (160–73°).   [b] No analysis; a white ppt. is obtained on adding ZnCl4 to NaCp in THF (G. W. 1953; P.5) which does not sublime in vacuum at 250° C.

compound does not react with water, as do the other cyclopenta-
dienides, may be met by noting that if it is indeed a high lattice
energy which accounts for its stability, this would also account for its
resistance to hydrolysis. The well-known case of oxides can be quoted
for comparison; while the O^{2-} ion is immediately hydrolyzed by
water, there are innumerable metallic oxides of predominantly ionic
nature which are insoluble in and unattacked by water due to their
high lattice energies.

The established cyclopentadienides (and a few substituted cyclo-
pentadienides) are listed in Table I.

III. Di-π-cyclopentadienyl Compounds

A. GENERAL REMARKS

Essentially all* of the elements of the three series of transition
metals have been shown to form di-π-cyclopentadienyl compounds of
the general formula $[(\pi\text{-}C_5H_5)_2M^n]X_{n-2}$, where n is the oxidation
number of metal M and X is a univalent anion. The known com-
pounds, together with references, are listed in Table II.

The elements of the *first transitional series* (excepting Mn, *q.v.*) have
been obtained as the neutral compounds, $(\pi\text{-}C_5H_5)_2M$, as well as in
cationic species. For the *second* and *third transitional series*, the
neutral compounds, which obviously involve the $+2$ oxidation state
of the metal, have been obtained only for Ru and Os; it is well known
that the relative stability of the lower oxidation states in these series
tends to be less than that of the higher ones, but for the larger metal
ions there may also be poorer overlap of the d orbitals of the metal
with the π-orbitals of the rings leading to weaker bonding. In some
cases where the preparative methods, e.g., sodium borohydride reduc-
tion of the cations or of the NaCp reaction mixture, might have been
expected to lead to the neutral compound, unusual behavior has been
observed and for Re, Mo, and W, di-π-cyclopentadienyl metal hy-

* Hafnium has not been reported; it will undoubtedly behave like zirconium.
Technetium may be expected to give a hydride comparable to the rhenium com-
pound (see Section III-E-1); it appears unlikely to form an ionic derivative as
manganese does. Platinum has not been obtained as a di-π-cyclopentadienyl
compound, but $(\pi\text{-}C_5H_5)_2Pd$ has been obtained (G. W., unpublished work, 1953)
as cherry red, thermally unstable crystals. Neutron activation of π-Cp$_2$Ru has
been reported (I.21) to give traces of a volatile rhodium compound which is
probably π-CpRHC$_5$H$_6$ (see Section IV-D-2).

drides (see Section III-E-1) have been obtained instead; with Co and Rh, reduction of the cations $(\pi\text{-}C_5H_5)_2M^+$ with sodium borohydride has led to the cyclopentadiene compounds, e.g., $\pi\text{-}C_5H_5RhC_5H_6$. With LiAlH$_4$, however, reduction of $\pi\text{-}Cp_2Co^+$ and $\pi\text{-}Cp_2V^+$ to the neutral species has been reported (E.18).

In the +3 oxidation state, cationic species, e.g., $(\pi\text{-}C_5H_5)_2Co^+$, are obtained. Salts of small anions can be occasionally obtained, e.g., $(\pi\text{-}C_5H_5)_2CoBr$, but these salts are usually very deliquescent. The ions can be precipitated from aqueous solution by large anions, e.g., silicotungstate, Reineckate, tetraphenylborate, picrate, tribromide or polyiodide, tetracarbonylcobaltate. etc. The precipitation reactions of $\pi\text{-}Cp_2M^+$ ions are very similar to those of the heavy alkalies, Rb and Cs, and the tetraphenylborate is essentially quantitatively precipitated in weakly acid solution. The first cationic di-π-cyclopentadienyl compounds characterized (B.2)—of the ferricenium ion—were the tetrachloroaluminate and tetrachlorogallate, which were obtained as long blue needle crystals by allowing solutions of ferrocene and the anhydrous metal halide in ether to stand in dry air. In the +4 and +5 oxidation states where compounds are formed (Ti and V groups), di-π-cyclopentadienyl metal halides are obtained. These have appreciable covalent character and are readily soluble in polar, and to some extent nonpolar, organic solvents. In water, hydrolysis occurs, hydrolyzed species being obtained; no systematic study of such hydrolyses has yet been made, and there is no information as to whether polymeric species are formed. The hydroxy ions which we can write, not necessarily implying this formulation, as $\pi\text{-}Cp_2TiOH^+$, $\pi\text{-}Cp_2NbOH^{2+}(?)$, etc., again give precipitates with large anions; on increasing the halogen acid concentration the undissociated halides can be extracted with, say, chloroform; halogen interchanges can be effected by halogen acids.

The only di-π-cyclopentadienyl metal ions which are stable in alkaline solution are those of Co^{III}, Rh^{III}, and Ir^{III}, whose hydroxides are strong bases, absorbing carbon dioxide from air. All other cationic species are destroyed in alkaline solution.

B. PREPARATIONS

References to the preparation of individual compounds are given in Table II.

TABLE II

Di-π-cyclopentadienyl Metal Compounds

Compound	m.p.	Color	Prep.	IR	UV
Group IV					
π-Cp₂Ti	d. > 130	dark green microcryst.	F.24		
π-Cp₂TiC₄H₈O	81 ± 0.5	brown and green cryst. forms	F.24		
π-Cp₂Ti$^{III}_{aq}$+		green	D.11		
π-Cp₂Ti^{III}Cl₂AlEt₂	126-30	blue cryst.	G.20		
π-Cp₂TiF₂		yellow cryst.	D.11		
π-Cp₂TiCl₂	289 ± 2	red cryst.	D.11	D.11	
π-Cp₂TiBr₂	314 ± 2	dark red cryst.	D.11	D.11	
π-Cp₂TiI₂	319 ± 3d.	purple cryst.	D.11	D.11	
π-Cp₂TiOHBr		orange powder	D.11		
[π-Cp₂TiOH]⁺(ClO₄)aq		yellow	D.11		
π-Cp₂TiMe₂	d. ~100	orange yellow cryst.	F.27	F.27	
π-Cp₂Tiφ₂	146-48	orange yellow cryst.	E.10		
π-Cp₂Ti(p-tol)₂	?	orange yellow cryst.	E.10		
π-Cp₂Ti(m-tol)₂	135-40	orange yellow cryst.	E.10		
π-Cp₂Ti(p-methylamino-phenyl)₂	?	maroon	E.10		
π-MeCp₂TiCl₂	217-18d.	red cryst.	I.8	I.8	
π-Cp₂ZrCl₂	232	white cryst.	D.11		
π-Cp₂ZrBr₂	260d.	white cryst.	D.11	D.11	
π-MeCp₂ZrCl₂	180-81d.	white cryst.	I.8	I.8	

Group V					
π-Cp₂V	167–68	purple cryst.	D.20(F.23)ᵃ		I.13
π-Cp₂Vᴵᴵᴵ aq⁺		purple	D.11		
π-Cp₂VCl₂	d. ~250	pale green microcryst.	D.11	D.11	
π-Cp₂VBr₂	d. ~25	dark green cryst.	D.11	D.11	
π-Cp₂NbBr₃	d. ~260	red-brown cryst.	D.11	D.11	
π-Cp₂NbOHBr₂		orange powder	D.11		
π-Cp₂TaBr₃	280d.	rust cryst.	D.11	D.11	
Group VI					
π-Cp₂Cr	172–73	scarlet cryst.	D.4(F.23)ᵃ		I.13
π-Cp₂CrI?	?	green	F.3		
[π-Cp₂Cr] [π-CpCr(CO)₃]	190–93	brown-black	E.24		
π-Cp₂MoH₂		yellow cryst.	I.3	I.3	
π-Cp₂MoCl₂	?	dark green cryst.	D.18	D.18	
[π-Cp₂MoᴵⱽCl]⁺ aq		red	D.18		
[π-Cp₂MoⱽCl₂]⁺ aq		violet	D.18		
π-Cp₂WH₂		yellow	I.3	I.3	
[π-Cp₂WⱽCl₂]⁺ aq		red	D.18	D.18	
Group VII					
π-Cp₂ReH	161–62	lemon cryst.	E.9,I.1	I.1	
π-Cp₂ReD	168–69	lemon cryst.	I.1	I.1	
[π-Cp₂ReH₂]Cl	d. ~140	white powder	I.1	I.1	
[π-Cp₂ReD₂]Cl	d. ~140	white powder	I.1	I.1	

(continued)

TABLE II (continued)

Compound	m.p.	Color	Prep.	IR	UV
Group VIII					
π-Cp₂Fe	173 ± 0.5	orange-brown cryst.	B.1,B.9	D.5,H.19	B.2,B.4,G.43, I.13
(π-C₅D₅)₂Fe	?	orange-brown cryst.	H.19	H.19	
π-Cp₂Fe⁺aq and salts		blue	B.2	D.11	B.2,G.43,G.42
π-Cp₂FeI₂₀	170–72	black powder	O.6		
π-Cp₂FeI₆	125–30d.	black needles or plates	O.6		
π-MeCp₂Fe	37–39 (b.p. 115/10 mm.)	orange-brown cryst.	I.8	I.8	
π-ind₂Fe	184–85 (H.1)	purple cryst.	D.6,C.12	D.6	D.6,C.12
(π-tetrahydroindenyl)₂Fe	19.5–20.5 (b.p. 126/1 mm.)	orange-red liq. and cryst.	C.12,O.16		C.12,O.16
π-Cp₂Ru	195–96 (B.6) 199–200 (H.4)	white cryst.	B.6	B.6,H.19	B.6
π-Cp₂Ru⁺ and salts		v. pale yellow	B.6		B.6
π-ind₂Ru	?	white	E.25ᵇ		
(π-tetrahydroindenyl)₂Ru	?	white	F.25ᵇ		
π-Cp₂Os	218–19° 230 (H.4)	white	H.4	H.4	

π-Cp₂Co	173 ± 1	purple cryst.	D.5,C.9		I.13
π-Cp₂Co⁺$_{aq}$ and salts		yellow	B.7,C.7	I.3	B.7
π-Cp₂Co[π-CpCr(CO)₃]	190–93d.	brown-black	E.24		
π-Cp₂Co[Co(CO)₄]		carmine	C.7		
π-Cp₂Co[FeH(CO)₄]		rust brown	C.7		
π-MeCp₂Co⁺$_{aq}$ and salts		wine-red	I.3	I.3	
π-ind₂Co	178–81	black cryst.	C.11		C.12
π-ind₂Co⁺$_{aq}$ and salts		orange	D.6,C.11	D.6	C.12
π-Cp₂Rh⁺$_{aq}$ and salts		yellow	C.1		C.1
π-CpIr⁺$_{aq}$ and salts		yellow	C.1		C.1
π-Cp₂Ni	173d.	green cryst.	P.3,D.5,C.8	D.5,H.19	D.5,I.13
π-Cp₂Ni⁺$_{aq}$ and salts		yellow	D.5,C.8		D.5
π-MeCp₂Ni	36–38 (b.p. 85–90/1 mm.)	green cryst.	I.8	I.8	
π-ind₂Ni(?)	d.?	red	C.11		
π-Cp₂Pd	d ~40	cherry red cryst.	d		
Tri-π-C₅H₅ compound					
π-Cp₃UCl	260–65	dark red cryst.	F.25	F.25	F.25

ᵃ Recommended preparation.
ᵇ Magnetic properties mentioned only.
ᶜ E. R. Lippincott, quoted in E.20.
ᵈ G. W., unpublished work, 1953; no analysis.

Numerous preparative methods are now extant, some of use only in specific cases.

1. From Cyclopentadienides

Many of the methods are based on the use of cyclopentadienides of the alkalies, in liquid ammonia, ethers, dimethylformamide, ethanol, tertiary butanol, etc., and the transition metals are added as anhy-drous halides, thiocyanates, acetylacetonates, etc. The Grignard reagent which was initially used rather widely is now seldom employed.

The most generally convenient and universally applicable method and indeed the *only method that need be employed* is the reaction of anhydrous metal chlorides (or other halides) with a solution of sodium cyclopentadienide in tetrahydrofuran or a polyether such as ethylene glycol dimethyl ether (F.23). A detailed laboratory procedure for the preparation of the reagent and of ferrocene as an example has been given (F.32); this method has the advantage that it can be used for the preparation of all types of cyclopentadienyl compounds and can be used also for nontransition metal compounds, e.g., $(C_5H_5)_2Sn$ from $SnCl_2$; for complex compounds, e.g., π-C_5H_5Rh-cy-clooctc-1,5-diene from $(C_8H_6RhCl)_2$; and for cyclopentadienides, e.g., $Mn(C_5H_5)_2$ from $MnCl_2$. There is no danger of solvolysis of the metal halide or other salt interfering with the preparation, as can occur using liquid ammonia or alcohols.

The reaction product, after removal of solvent ether, may be isolated by solvent extraction or in the case of air-sensitive compounds by direct sublimation from the dry residue in vacuum. The sodium in ether method is also applicable to the preparation of derivatives from methyl and other substituted cyclopentadienes, and indene.

It may be noted that unlike the reaction in liquid ammonia (Section II), hydrogen is evolved in the reaction of sodium with cyclopentadiene in ether, but some reduction ($\sim$10%) to cyclopentene occurs and yields over 90% have not been obtained, although it is known that the reaction of pure cyclopentadienides with, say, ferrous chloride, is quantitative (F.15,F.23).

Should magnesium cyclopentadienide (Section II) become commercially available, this would provide a simple method for preparing many derivatives.

2. From Cyclopentadiene

A method which has been applied in a few cases and is particularly convenient for the preparation of $(\pi\text{-}C_5H_5)_2Fe$, -Co, and -Ni is the reaction of the anhydrous halide with cyclopentadiene in an amine, such as diethylamine, pyridine, or piperidine, which acts both as solvent and as halogen acceptor (F.23), e.g., reaction 6. Again, a

$$FeCl_2 + 2C_5H_6 + 2\text{ amine} = (\pi\text{-}C_5H_5)_2Fe + 2\text{ amine·HCl} \qquad (6)$$
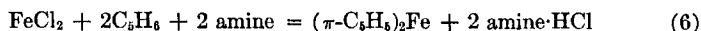
detailed laboratory procedure has been given (F.32); the above-noted compounds can be made in $\sim 80\%$ yield, while $(\pi\text{-}C_5H_5)_2\text{-}Ti(Zr)Cl_2$ can be got in $\sim 50\%$ yields.

Other less generally useful methods for preparing the $(\pi\text{-}C_5H_5)_2M$ compounds are the reaction of $Cr(CO)_6$ and $Co_2(CO)_8$ with cyclopentadiene at elevated temperatures, the thermal decomposition of the binuclear carbonyl (Section IV), $[\pi\text{-}C_5H_5Fe(CO)_2]_2$, and the direct reaction of cyclopentadiene with Fe or iron oxides.

C. PHYSICAL PROPERTIES OF DI-π-CYCLOPENTADIENYL METAL COMPOUNDS

A great variety of physical measurements on the $[(\pi\text{-}C_5H_5)_2M^n]\text{-}X_{n-2}$ compounds have been made and these are now presented in summary form. The significance of some of the measurements is discussed in more detail in Section VIII. There has been a discussion of covalence in neutral $\pi\text{-}Cp_2M$ compounds in terms of valence states and electronegativities (G.34).

1. Crystal Structures

Of all the di-π-cyclopentadienyl compounds prepared to date, only ferrocene (F.1), ruthenocene (G.44), dibenzoylferrocene (G.37), and di(π-indenyl)iron (H.1) have been comprehensively studied by X-ray methods. Even in the case of ferrocene, further refinement by low temperature studies is desirable in view of the acknowledged motion in the lattice at room temperature. The published data on all cyclopentadienyl compounds are collected in Table III.

It is interesting to note that in contrast to ferrocene, which has the staggered configuration in the crystal (Fig. 1A), ruthenocene is eclipsed (Fig. 1B). This difference is due to differences in the lattice forces and/or to smaller van der Waals' forces when the rings are

TABLE III. Structural Data: A. Crystal Data

Compound	Ref.	Form	Space group	a, Å.	b, Å.	c, Å.	β	Mol. vol., Å.
π-Cp₂Fe	F.1s,i	monoclinic	$P2_1/a$	10.561	7.597	5.952	121.02	
π-Cp₂Ru	G.44[a]	orthorhombic	62 $Pnma$	7.13	8.99	12.81		
(π-ind)₂Fe	H.1[a]	monoclinic	C_s^2-P_s, C_{2h}^4-P_2/a or C_{2h}^5-$P_{2_1/a}$	11.32	7.85	8.09	115.3	650
π-Cp₂V	E.22	monoclinic		10.82	8.02	5.88	121.3	218
π-Cp₂Cr	F.36	monoclinic		10.74	7.89	5.93	121.2	215
π-Cp₂Fe	B.3,C.6,B.10	monoclinic	$P_{2_1/a}$	10.74	7.89	5.93	121.2	202
π-Cp₂Co	C1.4	monoclinic		10.60	7.71	5.90	121.1	206
π-Cp₂Ni	C1.4	monoclinic		10.68	7.86	5.88	121.2	211
Dibenzoylferrocene	G.37[a]	monoclinic	$P_{2_1/u}$					
Diacetylferrocene	G.37	monoclinic	$P_{2_1/a}$					
Dipropionylferrocene	G.37	monoclinic	P_{bca}					
Dibutyrylferrocene	G.37	monoclinic	Aba					
π-Cp₂TiCl₂	b	triclinic						
π-Cp₂TiCl₂AlEt₂	H.3,H.7		$Pnma$ or $Pn2_1a$	15.77	14.24	7.54	90 ($\alpha = \beta = \gamma$)	
π-Cp₂ZrCl₂	H.2[c]	monoclinic	~C_{2h}-$2/m$(point) C_4-T (site)	6.20	6.58	13.33	89	
[π-CpMo(CO)₃]₂	F.30,G.29[a]	monoclinic		10.3₆	7.9₆	12.0₆	125.11	
[π-CpW(CO)₃]₂	F.30	monoclinic	P_{2_1}/c	10.3₈	8.0₄	12.0₆	125.08	
[π-CpFe(CO)₂]₂	F.30,I.4[a]	monoclinic	P_{2_1}/c	7.0₈ / 7.0₇	12.4₉ / 12.46	8.0₁ / 7.99	108.1 (F.30) / 108.07 (I.4)	
NaCp	F.5		powder photograph					
MgCp₂	E.22	monoclinic		10.98	8.04₁	5.98	121.9	224
MnCp₂	E.23	rhombic[d]	$C_{2h}^{21}cmma$	[28.1]	[11.7]	[9.9₅]		
bz₂Cr	F.37	cubic	$Pa3$-T_h^6	$a_0 = 9.67$				226

B. Distances in Sandwich Compounds

Compound	Ref.	M–C, Å	C–C, Å	Other distances, Å
π-Cp₂Fe	F.1	2.045 ± 0.01	1.403 ± 0.02	Inter-ring 3.32
(π-ind)₂Fe	H.1	2.10	1.43	
Dibenzoylferrocene[e]	G.37	2.05 ± 0.02	1.41 ± 0.03	C–C (bz) 1.39 ± 0.03 C–O 1.21 ± 0.01
π-Cp₃Y	E.22	2.3[f]		
π-Cp₂Cr	F.36	2.2[f]		
π-Cp₂Co	C.14	2.1[f]		
π-Cp₂Ni	C.14	2.2[f]		
π-Cp₂TiCl₂AlEt₂	H.7	2.3		Ti–Cl = Al–Cl = ~2.5
[π-CpFe(CO)₂]₂	I.4	2.11 ± 0.03	1.41 ± 0.04	{Fe–Fe = 2.49 Fe–C(non-br) = 1.75 Fe–C(br) = 1.85 {C–O (non-br) = 1.12 C–O(br) = 1.21
π-CpNiNO[g]	H.15	2.107 ± 0.001		N–O 1.10 ± 0.03
π-Cp₂Fe[g]	E.14	2.03 ± 0.02	1.43 ± 0.03	C–H 1.09 (assumed) Inter-ring 3.25
bz₂Cr	F.37	2.19 ± 0.1[h]	1.38 ± 0.05[h]	
π-Cp₂Ru	G.44	2.208 ± 0.02	1.434 ± 0.03	Inter-ring 3.68

[a] Full structure determinations.
[b] D. P. Shoemaker, Massachusetts Institute of Technology, private communication.
[c] Refractive indices also given.
[d] Amber-brown form.
[e] Benzoyl groups lie out of plane of C_6H_5 ring and are displaced by rotation about C–C single bonds, which reduces steric hindrance. In crystal, molecular asymmetry corresponds to 1,2'-position.
[f] By interpolation using ferrocene as reference.
[g] Electron diffraction.
[h] Estimated by trial and error.
[i] In F.1 the z coordinates of C_1, C_2, and C_3 should be negative.

farther apart. It may be noted that in di(π-indenyl)iron, the benzene rings are in the *gauche* position, this form again being stabilized in the crystal by crystal forces or by weak van der Waals' forces between the atoms of the six-membered rings (3.43 A. apart). As with the other π-cyclopentadienyl compounds, in solution or in the vapor, the rings are probably freely rotating in the indenyl compound, or nearly so.
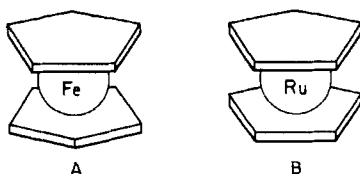
Fe

Ru

A   B

Fig. 1. Staggered and eclipsed configurations found for (A) ferrocene and (B) ruthenocene, respectively, in their crystals.

For the other neutral compounds, (π-C_5H_5)$_2$V, -Cr, -Co, and -Ni, X-ray measurements have shown that they are isomorphous with ferrocene, being monoclinic. Using ferrocene as a reference, M–C distances have been estimated for the other molecules (Table III). It is to be noted that the M–C distance for π-Cp$_2$Ni (2.18–2.20 A.) is considerably longer than that for π-Cp$_2$Fe (2.045 A.), which is consistent with the much diminished chemical and thermal stability. The only X-ray structural studies on a di-π-cyclopentadienyl metal compound other than neutral species have been recently made on the binuclear halogen-bridged compound (π-C_5H_5)$_2$TiCl$_2$Al(C_2H_5)$_2$ (H.7: Section III-E). In view of the fact that in this case the π-C_5H_5 rings were found to be *not* parallel, as in the neutral compounds, but that the metal–ring axes were at a small angle, the question may be raised as to whether in other di-π-cyclopentadienyl compounds, e.g., (π-C_5H_5)$_2$TiX$_2$ and (π-C_5H_5)$_2$ReH, where additional atoms or groups are bound to the metal, a similar situation holds. It is certainly quite possible, and further X-ray studies on this type of compound are much needed.

2. Electron Diffraction

The only published work is on ferrocene (E.14). The derived bond length data (Table III) agree well with the X-ray data and in addi-

tion suggest that rotation of the rings about the main molecular axis occurs under the high temperature conditions of the measurement.

3. Dipole Moments

The dipole moments of ferrocene and nickelocene are zero. Dipole moments of mono- and diacetylferrocenes have been reported, and the values are close to those to be expected assuming free rotation of the π-cyclopentadienyl rings about the metal–ring axis. The data and references are collected in Table IV. It has been estimated from studies on mononuclear π-cyclopentadienyl compounds (F.40) that the π-C_5H_5 metal moment is about 2–2.5 D.

TABLE IV
Dipole Moments

Compound	μ, Debyes	Ref.
π-CpVOCl$_2$	4.93 ± 0.09	H.24
π-CpV(CO)$_4$	3.17 ± 0.05 (10%)[a]	F.40
π-CpCr(CO)$_2$NO	3.19 ± 0.05 (10%)[a]	F.40
bz$_2$Cr	0	F.41
tol$_2$Cr	0	F.41
π-CpMn(CO)$_3$	3.30 ± 0.05 (10%)[a]	F.40
π-Cp$_2$Fe	0	B.2,F.41
Monoacetylferrocene	3.20	E.8
Diacetylferrocene	4.23	E.8
Di(p-chlorophenyl)ferrocene	3.12	G.19
Di(π-ind)Ru	0	F.41
π-CpCo(CO)$_2$	2.87 ± 0.1 (10%)[a]	F.40
π-Cp$_2$Ni	0	D.5
Cp$_2$Sn	1.02 ± 0.06	F.41
Cp$_2$Pb	1.63 ± 0.06	F.41
C$_{25}$H$_{25}$Co$_2$	0	F.41

[a] Indicates that atom polarization was taken as 10% of electronic polarization.

4. Mass Spectra

Measurements on neutral compounds of the elements of the first transitional series and of (π-C_5H_5)$_2$Ru, (π-C_5H_5)$_2$ReH, and Mg(C_5H_5)$_2$ have been made (E.11). The ionization potentials and appearance potentials for the various species formed in electron bombardment, e.g., $C_5H_5M^+$, were obtained. Significant differences in the behavior of the (π-C_5H_5)$_2$M compounds were observed; e.g., the yields show

that the ions $C_5H_5Ni^+$ and $C_5H_5V^+$ are more stable than $C_5H_5Cr^+$, -Fe$^+$, or -Co$^+$. No theoretical treatment of these differences has yet been attempted.

The mass spectra also allowed a clear distinction to be made between the π-cyclopentadienyl compounds and the cyclopentadienides $MnCp_2$ and $MgCp_2$; quite a different spectrum was obtained for the latter compounds, the yields of the ions M^+ and $C_5H_5M^+$ being very significantly higher. The higher yield of $C_5H_5V^+$ noted above is consistent with a view (G.34) that π-Cp$_2$V is more ionic than other sandwiches, and it may be noted also in this respect that π-Cp$_2$V readily forms ammoniates (F.23).

The neutral π-cyclopentadienyl compounds provide useful vehicles for the introduction of metal atoms into electron-impact-type ion sources. The natural abundances of Ru isotopes were studied in this way (C.2) and the isotopic ratios in V and Re checked (E.11).

5. Magnetic Measurements

Magnetic susceptibilities of essentially all of the compounds made to date have been measured. These measurements are comprehensively discussed subsequently (Section VII) together with *para-hydrogen conversion* studies.

6. Nuclear Magnetic Resonance Measurements

Several short notes on nuclear resonance studies have appeared, but so far no substantial paper has been published.

High resolution n.m.r. measurements and chemical shifts for ferrocene and a few other π-cyclopentadienyl compounds have been given (F.27). It was found possible to distinguish between π-C_5H_5 and σ-C_5H_5 derivatives, the former giving a proton resonance on the high field side relative to the latter. The apparent relatively high diamagnetic shielding of protons in π-C_5H_5 rings (1.5–3.2 p.p.m. vs. phenyl protons in toluene) may be due to fields in filled metal d orbitals rather than to high electron density on the ring protons.

Wide line n.m.r. measurements have been made on ferrocene (G.33); the narrow line width (4.0 gauss) at 273°K. was said to be consistent with free rotation, or at least with considerable motion of the rings. The line was reported to decrease in width to 2.2 gauss at 194°K., perhaps owing to a second-order phase transition, and to broaden

again to 4.2 gauss at 77°K. In contrast to this report of a minimum at about 194°K., other work (G.27) indicates that the line width and second moment remain constant over the range 300–110°K., suggesting no marked change in structure; the strong signals at low temperatures (a 10-fold increase in signal:noise ratio from 190 to 110°K.) were attributed to a pronounced reduction in the spin lattice relaxation time, perhaps owing to an electron transfer process. This would be in line with the well-known thermochroism of ferrocene, which changes from orange at 200°K. through yellow to a pale yellow at 77°K.

N.m.r. measurements have been made on the solid paramagnetic species $(\pi\text{-}C_5H_5)_2Ni$ (G.28), $(\pi\text{-}C_5H_5)_2V$, -Cr, -and -Co (H.10) and on manganese cyclopentadienide (H.10). In $\pi\text{-}Cp_2Ni$ a shift of the proton resonance of 0.032% to higher fields is attributed to charge-transfer bonding between the metal atom and the carbon atoms of the ring. Negative charge having spin polarization opposite to that of the nickel ion is transferred from the ring to the metal. The positive spin density thus produced on the carbon atoms in turn produces negative spin density on the protons, accounting for the anomalous proton shift to higher fields. The observed shift suggests that each unpaired electron in $\pi\text{-}Cp_2Ni$ is localized on the rings for a fraction of the time ($\sim$50%). For $\pi\text{-}Cp_2V$ and $\pi\text{-}Cp_2Cr$, shifts of the proton resonance to *lower* applied fields were observed. This suggests spin transfer processes which leave negative spin density on the carbon atoms in this case.

The integrated spin density on the carbon atoms is estimated to be +0.14 in $(\pi\text{-}C_5H_5)_2Ni$, −0.12 in $(\pi\text{-}C_5H_5)_2Cr$, and −0.06 in $(\pi\text{-}C_5H_5)_2V$. Shifts to higher fields in $Mn(C_5H_5)_2$ and $(\pi\text{-}C_5H_5)_2Co$ are smaller and are comparable to bulk demagnetization effects. These observations on the paramagnetic species have been stated by McConnell* to be incompatible with the predictions of any of the theoretical treatments (Section VIII-B) of the bonding in $(\pi\text{-}C_5H_5)_2M$ compounds given so far.

7. *Paramagnetic Resonance Measurements*

While paramagnetic resonance signals have been quoted as being observed in $(\pi\text{-}C_5H_5)_2Ni$ (G.27), no data have yet been published.

* 133rd National A.C.S. Meeting, San Francisco, April, 1958.

Paramagnetic resonance studies on π-Cp$_2$V have recently been described (I.13). In benzene solution, a *g* value of 2.00 was found with a V^{51} isotropic hyperfine splitting equal to 77 mc. This work is discussed in Section VII-B-1.

8. X-ray Absorption Edge Measurements

Numerous compounds have been studied by this technique. While attempts have been made to interpret the data as showing complete filling of the available metal orbitals to give an inert gas configuration, this interpretation is suspect. This topic is discussed in more detail and references to the literature are given in Section VIII.

9. Ultraviolet and Visible Absorption Spectra

Numerous and scattered measurements have been made. References to the literature are given in Table II for solution measurements. Measurements on single crystals (D.14,E.5) have also been reported, but at the present time no theoretical interpretation of the spectra of any of the compounds has been accomplished.

It may be noted, however, that the original observation (B.4) that the spectrum of ferrocene in carbon tetrachloride is different from that in hydrocarbon or alcoholic solvents with a band at 325 mμ in inert solvents, apparently increasing intensity and shifting slightly to shorter wavelengths, has been studied in detail (G.43). It was shown that a new band at 307 mμ, not connected with the band at 325 mμ in inert solvents, appeared in the ferrocene spectrum in halogenated solvents and that this could be attributed to dissociative charge transfer (eq. 7). The ferricenium ion was indeed observed to

$$(\pi\text{-}C_5H_5)_2Fe + CCl_4 \xrightarrow{\ h\nu\ } (\pi\text{-}C_5H_5)_2Fe^+ + Cl^- + CCl_3 \cdot \qquad (7)$$
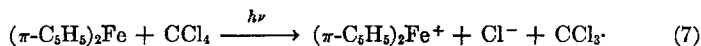
be formed on allowing solutions of ferrocene in carbon tetrachloride to stand in light. The electron transfer spectrum absorption was found in halocarbons in alkyl halides with low C-X dissociation energies. Ferrocene and iodine showed no charge transfer spectrum but were shown to be in thermal equilibrium (eq. 8), for which

$$(\pi\text{-}C_5H_5)_2Fe + {}^3/_2\,I_2 = (\pi\text{-}C_5H_5)_2Fe^+I_3{}^- \qquad (8)$$

equilibrium constants were obtained in benzene, chloroform, and dichloromethane. This work provides an explanation for previous

observations (O.6,O.19) on the reaction of ferrocene with iodine, in which it was claimed that ferrocene did not react and can be recovered unchanged after an hour's boiling with iodine in acetic acid (O.19) and that the addition of iodine in *any* quantity to ferrocene in a solvent gives a black powdery precipitate of stoichiometry $C_{10}H_{10}FeI_{20}$. Crystallization of the latter from acetone gave $C_{10}H_{10}FeI_6$. Both these products decomposed thermally to ferrocene and iodine; they are probably ferricenium polyiodide mixtures.

A comparison of the absorption spectrum of the ferricenium ion in solutions containing chloride ion with that in perchlorate solution showed deviations from Beer's law (G.42), which was interpreted as indicating the presence of chloride complexes such as π-Cp_2FeCl and π-$Cp_2FeCl_2^-$. This may be so, but the fact that Beer's law is not followed may also be due to the well-known hydrolytic decomposition of ferricenium salt solutions, even when quite strongly acid, to give ferrocene and other decomposition products.

10. Infrared and Raman Spectra

Infrared spectra have been widely used for routine characterization of C_5H_5 derivatives, since bands characteristic of a π-C_5H_5 ring, substituted π-C_5H_5 rings, σ-C_5H_5 groups, etc., have been recognized. These designations have been rather useful in organic studies of ferrocene derivatives (see, e.g., E.20,O.32,O.54). References to routine infrared measurements are included in Table II.

Lippincott and Nelson have made the only comprehensive studies for ferrocene (and ferrocene D-10), ruthenocene, and nickelocene. These were reported preliminarily (C.5,E.12), and recently the data have been collected in a complete vibrational analysis (H.19).

11. Thermochemical Data

The vapor pressure and heats of sublimation of ferrocene have been measured and heats of combustion using standard bomb calorimetry of $(\pi$-$C_5H_5)_2Fe$ and -Ni have been determined. The vibrational spectral data referred to in the preceding paragraph have allowed the calculation of other thermodynamic constants (E.12).

The available data and references are collected in Table V. Specific heat measurements from 17 to 300°K. by G. L. Kington, Imperial College, London, have shown a transition at 164°K. This may

TABLE V
Thermodynamic Properties[a]

Ferrocene

Heat of sublimation (solid)   (B.4)   16.81 kcal./mole
Heat of vaporization (liquid) (B.4)   11.3 kcal./mole
Heat of fusion   (B.4)   5.5 kcal./mole
Normal b.p., 230°[b]; triple point, 173° (B.4 is in error on this.)
Vapor pressure (liquid) log $p_{mm.}$ = 7.615 − 2470/T (B.4)
Vapor pressure (solid) log $p_{mm.}$ = 10.27 − 3680/T (B.4)
Standard heat of formation from elements of π-Cp$_2$Fe (s)
   (combustion) (B.5,D.5) ΔHf^0_{298} =   33.8 kcal./mole
   The following were obtained from spectroscopic data
      for π-Cp$_2$Fe (g) (E.12) $\Delta Hf^0_{298\cdot16}$ =   50.61 kcal./mole
                                          $\Delta Ff^0_{298\cdot16}$ =   75.97 kcal./mole
                                          $\Delta Sf^0_{298\cdot16}$ =   −85.07 cal./mole
                                          ΔHf^0f^0 =   57.5 kcal./mole
   For Cp°, $H^0 − E_0^0/T$, $−F^0 − E_0^0/T$ and S^0 from 298.16 to 1500°K., see E.12.

Ruthenocene

   For Cp^0, $H^0 − E_0^0/T$, $−F^0 − E_0^0/T$ and S^0 from 298.16 to 1500°K., see E.12.

Nickelocene

   Standard heat of formation from elements of π-
      Cp$_2$Ni(s) (combustion) (D.5) ΔHf^0_{298} =   62.8 kcal./mole
   The following were obtained from spectroscopic
      data for π-Cp$_2$Ni(g) (E.12) $\Delta Hf^0_{298\cdot16}$ =   79.61 kcal./mole
                                          $\Delta Ff^0_{298\cdot16}$ =   103.80 cal./mole
                                          $\Delta Sf^0_{298\cdot16}$ =   −81.10 cal./mole
                                          ΔHf^0f^0 =   85.9 kcal./mole (H.19)
   For Cp^0, $H^0 − E_0^0/T$, $−F^0 − E_0^0/T$ and S^0 from 298.16 to 1500°K., see E.12.

Dibenzenechromium

   Standard heat of formation from elements of
      (C$_6$H$_6$)$_2$Cr(s) (combustion) (I.9) ΔHf^0_{298} = 21 ± 8 kcal./mole
      (C$_6$H$_6$)$_2$Cr(s) (combustion) (I.23) ΔHf^0_{298} = 51 kcal./mole
Manganese cyclopentadienide
   Heat of sublimation (solid)   (F.23)   17.3 kcal./mole
   Heat of vaporization (liquid) (F.23)   12.0 kcal./mole
   Heat of fusion   (F.23)   5.3 kcal./mole[c]
   Vapor pressure (solid) log $p_{mm.}$ =   10.58 − 3780/T (F.23)
   Vapor pressure (liquid) log $p_{mm.}$ = −5.93 − 2615/T (F.23)

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[a] Some heats of sublimation recently reported by J. F. Cordes and S. Schreiner (*Z. anorg. u. allgem. Chem.*, *299*, 87 (1959)) appear to be in error because their experimental conditions make their use of the Knudsen equation inappropriate (G. L. Kington, private communication).

[b] The value of 249° in B.4 is in error (according to equilibrium still measurements—E. O. Brimm, private communication).

[c] F.23 is in error on this.