

MYRON ROSENBLUM

CHEMISTRY
of the IRON GROUP
METALLOCENES

PART 1

Chemistry of the iron group metallocenes:

ferrocene, ruthenocene, osmocene

Part One

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Chemistry of the iron group metallocenes:
ferrocene, ruthenocene, osmocene

Part One

This is a volume in the series

THE CHEMISTRY OF ORGANOMETALLIC COMPOUNDS

THE CHEMISTRY OF ORGANOMETALLIC COMPOUNDS
A Series of Monographs

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Introduction to the Series

In 1937 all that was known about organometallic chemistry was summarized most excellently by E. Krause and A. von Grosse in their book, *Die Chemie der metallorganischen Verbindungen*. In the intervening years and, in particular, since about 1950, organometallic chemistry has undergone a tremendous growth in depth and in breadth. Not only have organosilicon, organotin, organoboron, organoaluminum, and organolithium chemistry grown almost explosively, but the whole new area of transition metal-organic chemistry has come into being and has grown to impressive proportions. Since the publication of Krause and von Grosse's book, no treatment of comparable scope has appeared. Books such as those by Coates and by Rochow, Hurd and Wilson serve as a good introduction to the subject but do not give the comprehensive treatment required by those who are active in organometallic chemistry.

It is the purpose of this series to bring Krause and von Grosse's description of organometallic chemistry up to date. It is not possible to cover organometallic chemistry as exhaustively as Krause and von Grosse did twenty-five years ago. Indeed, complete coverage, in the sense that all known organometallic compounds and all references concerning this subject are listed, is not desirable, now that the literature on organometallic chemistry has become so voluminous. But it is hoped that by selective use of this literature it is possible to cover as completely as possible all that is known about the chemistry of organometallic compounds: the methods used for their preparation, their physical properties, their structures, and their chemical reactions. Included in the subject of "chemical reactions" is the field of organofunctional organometallic chemistry: the effect of a metal-carbon bond on the reactivity of an organic functional group in the same molecule, as well as the effect of an organic functional group on the properties of the metal-carbon bond. However, a discussion of the organic chemistry of organofunctional organometallic compounds when nothing can be said about the effects of the metal-carbon bond on the reactivity of the functional group would

not fall within the scope of this series. The emphasis is on the "metallic" part of organometallic chemistry.

A mere listing of the reactions of organometallic compounds as is given by Krause and von Grosse will be avoided. The reactions of organometallic compounds, as well as the reactions leading to their formation, will, wherever possible, be discussed in terms of what is known today about chemical bonding, structure, and reaction mechanisms. Physical properties in a similar manner will be related to our current knowledge of chemical bonding and structure. Organometallic chemistry is a borderline field, and for such a discussion it is necessary to make full use of what both inorganic and organic chemistry can offer in the way of theoretical and practical results. Correlations within periodic groups as well as between periodic groups will be stressed.

The following volumes, in addition to the present one, are in preparation: *Organolithium Chemistry* (G. L. Closs); *Organosodium and Organopotassium Chemistry* (R. A. Finnegan); *Organometallic Chemistry of the Group II Metals* (R. Dessy); *Organoaluminum Chemistry* (J. C. Snyder); *Organometallic Chemistry of Gallium, Indium and Thallium* (W. A. G. Graham); *Organogermanium Chemistry* (M. Lesbre, P. Mazerolles, and J. Satgé); *Organotin Chemistry* (D. Seyferth); *Organolead Chemistry* (H. Shapiro and F. Frey); *Organometallic Chemistry of Arsenic, Antimony, and Bismuth* (G. O. Doak and L. D. Freedman); and *Olefin and Acetylene Complexes of Transition Metals* (M. A. Bennett).

The authors, it will be noted, are all active in research in the areas about which they write.

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PREFACE

It is now barely thirteen years since the discovery of ferrocene, an event which marks the beginning of a period of unusual ferment and significant change in the field of organometallic chemistry.

The preparation of ferrocene, toward the end of 1951, was quickly followed by a recognition of its unique chemical structure and shortly thereafter by the discovery of its aromatic character. It was not long before cyclopentadienyl complexes of other transition elements as well as the lanthanides and actinides had been prepared, and to this growing number of progeny were soon added a multitude of new organometallic complexes in which cyclic and acyclic olefins as well as acetylenes were bound as ligands. The reformulation of Heine's long neglected and puzzling chromium compounds as arenechromium complexes, similar in structure to the biscyclopentadienyl metal complexes, brought even benzene within the purview of such metal coordinating groups. These developments have been accompanied by widespread interest in the chemistry and electronic structure of these substances, and by an increasing awareness of their potential use as intermediates in organic synthesis.

The present volume, the first of two, was written with the intent of providing a comprehensive and critical review of the chemistry of ferrocene and its congeners, ruthenocene and osmocene, the so-called iron-group metallocenes. The intensity of research activity in this field, largely generated by the discovery that ferrocene could be subjected to electrophilic substitution, may be judged by the fact that since 1952 almost 1000 papers have been published in this area alone. Although the task of providing an up-to-date review of these developments is therefore not a simple one, our knowledge of these substances has unquestionably matured to the point where such a review would appear to be both timely and useful. Every attempt has been made to provide as inclusive and up-to-date a bibliography as is possible. The literature references should be complete through 1962 and much of 1963. In addition, several literature citations in 1964 have been made possible through the cooperation of colleagues who were kind enough to provide me with preprints of their papers.

In general, the material is organized and treated according to metallocene derivative type. Although there are obvious shortcomings to such an arrangement, it nevertheless is one that lends itself readily to ordering a relatively large body of chemical information in a coherent and easily retrievable form. Each of the chapters dealing with acyl-, alkyl-, and arylmetallocenes is concluded by a table of these derivatives which, it is hoped, will supplement the more general treatment of material within each chapter with the specific kind of information and referencing that is often of great value.

In addition, one chapter has been devoted to a review of the physical properties of the metallocenes, and another to a summary, in largely descriptive form, of the electronic structures of these complexes. It is apparent that such information is useful, if not essential, for an understanding of much of the chemistry of these substances.

In Chapter I I have attempted to summarize, in historical form, those procedures developed for the synthesis of biscyclopentadienyl complexes, and also to provide a brief description of some of the reactions of monocyclopentadienyl iron complexes.

The work on this volume was begun in 1962 when I was on leave from Brandeis University, and it was supported in part by a grant from the National Institutes of Health. Grateful acknowledgement of this support and of assistance from Brandeis University is hereby made.

It is a pleasure to thank Professors R. H. Richards, K. L. Rinehart, and F. A. Cotton who read much of the early manuscript and made many valuable suggestions. I am particularly indebted to Professor P. L. Pauson and to Dr. G. R. Knox whose detailed and knowledgeable criticism of the entire manuscript was of the greatest assistance in removing many errors and in improving the treatment of the material.

In preparing the manuscript I was fortunate to have had the excellent secretarial services of Miss Ann Thompson and Mrs. Barbara MacDonald, and it is a pleasure to acknowledge my debt to them.

Finally, I owe a particular expression of gratitude to my wife Rachel whose encouragement and active help were so important in writing this book.

MYRON ROSENBLUM

Lexington, Massachusetts
February, 1965

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Part Two

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1 Preparation of metallocenes

Two general methods, exemplified in the synthesis of ferrocene, have been used for the preparation of cyclopentadienyl metal complexes. In the first of these, the cyclopentadienide ion and either a ferrous or ferric salt are brought into reaction, while the second employs cyclopentadiene and either iron powder, iron oxides, or iron carbonyls. These latter reactions are generally carried out at elevated temperatures. While the cyclopentadienide method is more suited to laboratory use, certain of the high-temperature methods, particularly those employing iron pentacarbonyl, find special application.

CYCLOPENTADIENIDE METHOD

Grignard reagent

Ferrocene was first prepared by Kealy and Pauson by the reaction of cyclopentadienylmagnesium bromide and ferric chloride in ether-benzene solutions (39).^{*} Subsequent attempts to extend the procedure to the synthesis of nickelocene and cobaltocene (13) were not satisfactory, largely due to the insolubility of the metal halides.

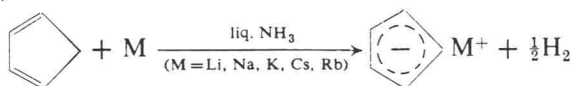
However, the more soluble tetrachlorides of titanium, zirconium, and vanadium were converted to their biscyclopentadienyl dihalide derivatives by this procedure (63). The metal acetylacetonates soon proved to be useful substitutes for the more insoluble metal halides, although an excess of the Grignard reagent is required since some is consumed by reaction with the β -diketone. Ruthenocene (61), nickelocene (63, 65, 66), and the cobaltocenium ion (62) were first made in this manner.

^{*} The use of high boiling ethers in this reaction has more recently been reported (58).

2 Chemistry of the Iron Group Metallocenes

Alkali metal salts

The alkali metal salts of cyclopentadiene have been used with considerable success in the synthesis of a wide variety of cyclopentadienyl complexes. In one of the first variants of this procedure, cyclopentadiene in liquid ammonia is converted to the ion by treatment with an alkali metal (14).



Subsequent addition of the anhydrous transition metal nitrate or thiocyanate salt, as for example $\text{Ni}(\text{SCN})_2$, gives the insoluble complex metal ammine cyclopentadienide.



These, in turn, lose ammonia on heating *in vacuo* to give the corresponding metallocene.



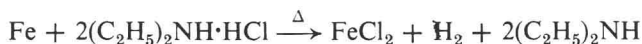
Fischer's group has employed this technique for the preparation of cyclopentadienyl complexes of cobalt (15), nickel (14), chromium (15, 16), manganese (15), and iron (19). Of the alkali metals, sodium and lithium are to be preferred, since their cyclopentadienide salts are more soluble in liquid ammonia than the others (15).

The use of sodium or potassium cyclopentadienide in tetrahydrofuran, or ethylene glycol dimethyl ether in place of liquid ammonia, constituted an advantageous preparative modification. The procedure is the most generally applicable and, besides ferrocene (69, 70), many transition metal, lanthanide, and actinide cyclopentadienyl complexes have been synthesized by this method (6, 24, 25, 36, 64, 67, 68, 69). The patent literature abounds with variations of this technique for the synthesis of ferrocene in ether (74, 79, 80, 86), ethylene glycol dimethyl ether (83), tetrahydrofuran (88), benzene or toluene (79, 80), ethanol (87), and liquid paraffin (80, 81). Both ferric and ferrous salts have been used, although the latter give higher yields since part of the cyclopentadienide is not consumed in reduction of the metal salt (70). The cyclopentadienide may be generated either by exchange reactions with sodium acetylide, hydride (74, 80, 81, 86), or ethoxide (3, 35, 42, 87), or directly from the metal (69, 70, 80, 81).

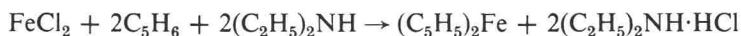
Ammonium salts

A further simplification in procedure, which avoids the necessity of preparing the cyclopentadienide in a separate step, was first introduced by Birmingham, Seyferth, and Wilkinson in 1954 (3) and has since been greatly improved (69, 70). It is by far the most expeditious procedure for the synthesis of ferrocene. The method consists simply in treating a solution of cyclopentadiene in diethylamine* with either anhydrous ferric or ferrous chloride.† The acidity of cyclopentadiene is sufficiently great ($\text{p}K_a$ 16) (10) that in the presence of excess amine a small but significant proportion is converted to the anion. The method has also been applied successfully in the synthesis of nickelocene (70), cobalticinium perbromide (60) and, on a microscale, in the preparation of iron isotopes of ferrocene (11). Several recent patents relating to the preparation of cyclopentadienyl complexes of nickel, zirconium, titanium, and cobalt, as well as iron, have been described (91–95).

A somewhat more direct and commercially applicable modification of this synthesis, which dispenses with the need for anhydrous ferric chloride, has recently been described by Pruett and Morehouse (53). In this procedure, ferrous chloride is prepared from diethylamine hydrochloride and iron powder in the melt,



so that the over-all reaction leading to ferrocene,



requires essentially only iron and cyclopentadiene as the raw materials, since the amine and its hydrochloride may be recycled.

Other cyclopentadienides

Cyclopentadienyl complexes, possessing a ferrocene-like molecular structure, but in which the metal-ring bonding is partially or largely ionic, may serve as a source of the anion. Thus, biscyclopentadienyl-magnesium, prepared directly from cyclopentadiene and magnesium at

* Other amines such as triethylamine and pyridine were found to be less effective.

† The use of solvents, other than tetrahydrofuran or dioxane (60), for the preparation of anhydrous ferrous chloride from iron powder and ferric chloride does not appear to offer any particular advantage (59). Anhydrous ferrous chloride may also be conveniently prepared by heating ferric chloride in chlorobenzene solution (40).