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The Organic Chemistry of Iron

Volume 1

edited by

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E8063733



Academic Press

New York

San Francisco

London

1978

A Subsidiary of Harcourt Brace Jovanovich, Publishers

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ACADEMIC PRESS, INC.
111 Fifth Avenue, New York, New York 10003

United Kingdom Edition published by
ACADEMIC PRESS, INC. (LONDON) LTD.
24/28 Oval Road, London NW1 7DX

Library of Congress Cataloging in Publication Data

Main entry under title:

The Organic chemistry of iron.

(Organometallic chemistry series)

Includes index.

1. Organoiron compounds. I. Koerner von
Gustorf, 1932-1975. II. Fischler, Ingrid.
III. Grevels, Friedrich Wilhelm.

QD412.F4073

547'.05'621

77-16071

ISBN 0-12-417101-X (v. 1)

PRINTED IN THE UNITED STATES OF AMERICA

The Organic Chemistry of Iron

Volume 1

ORGANOMETALLIC CHEMISTRY

A Series of Monographs

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To the memory of

Ernst A. Koerner von Gustorf

(1932–1975)

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Foreword

The large body of information that today forms organo-transition metal chemistry can be classified and discussed in two ways. The properties and reactivities of given ligands when attached to different metals can be emphasized; alternatively, the chemistry of one metal can be defined in terms of the effect it has on differing ligands. A complete understanding requires both approaches and one long-term aim of the Organometallic Chemistry Monograph Series is to provide this.

In addition to books on specific ligands and on more general topics, some years ago we inaugurated the survey of the organic chemistry of individual transition metals. Volumes on organo-titanium, -zirconium, -hafnium, -chromium, -nickel, -palladium, and -platinum chemistry have already appeared, and monographs on organo-molybdenum, -tungsten, -cobalt, -rhodium, -iridium, -ruthenium, and -osmium chemistry are in preparation.

We were particularly pleased, at the time that these volumes were being planned, that Dr. Ernst A. Koerner von Gustorf of the Institut für Strahlenchemie im Max-Planck-Institut in Mülheim agreed to undertake *The Organic Chemistry of Iron*. Koerner von Gustorf was an ideal choice; he had established himself as a very innovative organometallic chemist, particularly in respect to his work on the photochemical syntheses of organo-iron complexes, and he also had access to the archives of the Max-Planck-Institut in Mülheim with their reference files on organometallic chemistry.

Even with this background, the task of organizing and compiling all the knowledge of organo-iron chemistry was impossible for one man to accomplish within a reasonable space of time, and Koerner von Gustorf wisely enlisted the help of a number of other distinguished experts to author specific chapters of the work.

The organization of all this material was just beginning at the time of Koerner von Gustorf's untimely and tragic death in September 1975 at the age of 43. It accordingly fell to his collaborators, Dr. F. W. Grevels and Dr. Ingrid Fischler, to actually undertake the onerous task of collating and editing the final manuscripts. This task was greater than it had been for other volumes in the series since it had been decided to print directly from camera-

ready typescript and the work of editing as well as of organizing both the typing and the drawing of the diagrams and the formulas was a very extensive one. We are very grateful to Dr. Grevels and Dr. Fischler for having succeeded so well.

From our knowledge of the scope of the topic we had expected a large volume; in the event the project has grown beyond our original estimate and has, owing to Koerner von Gustorf's death, taken longer. We hope that this first of two volumes will be well received and that the extra material that has gone into it will make it even more useful. We would also like to thank all the individual authors for their carefully and comprehensively organized contributions and also for their patience with the delays that have occurred. Doctors Grevels and Fischler have been able to ensure that all the contributions have been updated and in most cases the literature has been covered up to and including the year 1975.

It was not possible to adhere entirely to the order that Koerner von Gustorf had planned for the material, but the reader will see that a logical arrangement has been followed. Volume 1 covers the structures and bonding and the applications of a variety of physical techniques to organo-iron compounds, optically active compounds, as well as chapters on σ -bonded, η^2 -, η^3 -, and η^4 -organo-iron compounds. Volume 2 will be developed in a similar manner and will include further chapters on spectroscopy, both electronic and vibrational (Poliakoff and Turner), metal-metal bonded compounds and iron cluster chemistry (Dahl and Sinclair; Chini), complexes of polyenes (Kerber), arenes (King), and those derived from acetylenes and cumulenes (Müller), complexes with N-bonded ligands (tom Dieck and De Paoli), as well as a short discussion of ferrocene chemistry (Eagar and Richards).

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THE ORGANIC CHEMISTRY OF IRON, VOLUME 1

STRUCTURE AND BONDING IN ORGANIC IRON COMPOUNDS

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I. INTRODUCTION

SCOPE OF THE SURVEY.

This article is concerned with the results of structural analyses, and to a lesser extent, with the bonding principles of organometallic iron compounds. The aim is to survey as completely as possible structural details presently available on these compounds, and to indicate problems which are still under discussion. Literature has been searched up to 1975, and all relevant structural results are summarized by tables referred to by each section of the article. However, due to delays in the editing, the discussion part of this review only covers those reports published up to 1972. Data quoted in these tables represent published values, including non-significant digits. The outline of this review follows the editorial arrangement of this volume.

For each class of compounds discussed, one or more typical examples were selected for computer drawings. The selected illustrations are not intended to reflect the accuracy of the individual structural determinations.

The author wishes to caution the uninitiated reader of structural publications from uncritical acceptance of accuracy of crystallographic data. Neither a low R-value (residual index, defined as

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

thus describing the fit of a molecular model (F_c) to a given data set (F_o) nor low standard deviations are alone an absolute measure for the accuracy of an X-ray structural determination. A low R-value, which represents good precision and not necessarily good accuracy, could describe an excellent fit of a distorted structural model to a poor data set, hence giving rise to erroneous interpretations. Systematic, but not obvious errors in intensity measurements, can give rise to underestimates of standard deviations. These values are obtained from the inverse error matrices of the usual least-squares refinement, and decrease with the increasing symmetry of the crystal system. Therefore one should avoid overly interpreting crystallographic data. If these data are the basis for theoretical computations, the advice of a specialist in the field should be sought.

However, the precision of structural work increased tremendously during the last decade with the introduction of diffractometers and better mathematical formalisms and computational techniques. The estimated errors in bonding distances between the non-hydrogen atoms may now be in the range of

0.005 to 0.01 Å, and those of the bonding angles 0.5° to 2°. Hopefully some of the earlier, but fundamental, work will be repeated with the accuracy presently possible. Despite the limitations mentioned above, X-ray diffraction methods still yield the most accurate information about the geometry of complex molecules.

II. σ -BONDED IRON CARBON COMPOUNDS

BONDING

Compounds containing iron-carbon bonds are sensitive to homolytic cleavage, producing a free organic radical and the metal in a lower oxidation state. This instability is explained by small energy differences between the filled d orbitals and the valence s and p orbitals of the metal used in bonding to the carbon. As a result, high energy d electrons can transfer to antibonding orbitals of the Fe-C bond. In compounds of higher oxidation state, electrons of the Fe-C bond may move into vacant metal d orbitals. Both formalisms result in a weakening of the metal-carbon bond.

From this scheme, Fe-C bonds may be stabilized in two ways. Often ligands with acceptor properties (such as carbon monoxide, η^5 -cyclopentadienyl, phosphines, arsines, etc.) are attached to the metal, along with additional ligands to complete a stable electronic configuration. Secondly, the Fe-C bond may be strengthened by altering the effective electronegativity of the carbon by using different hybridization states of the carbon (sp^3 - sp^2 - sp). Attaching strongly electronegative substituents to the carbon (e.g. fluorine) gives similar results.

All effects mentioned are reflected in the observed Fe-C bond lengths. In addition, the geometry, the oxidation state of the iron, as well as the steric arrangement and the electronic properties of the other ligands, may influence the observed bond lengths. Average values stated below should only be accepted within the limits of these considerations.

STRUCTURAL DETAILS OF FE-C σ -BONDS

Few X-ray structures containing Fe-C(sp^3) bonds have been reported so far. The observed bond lengths range from 2.08 to 2.16 Å (see Table 1), with the average value being 2.11 Å.

Introducing fluorine substituents at the bonded carbon (e.g. Fe-CF₂-) shortens this value remarkably to 2.07 Å (131). A similar value (2.06 Å) has been reported for an acetic acid

dicarbonylcyclopentadieneiron complex, the acetic acid being the σ -bonded group via the α -carbon (23,330) (see Figure 1). In the latter compound, an interaction between Fe and the C atom of the carboxylic group (Fe-C : 2.85 Å) is suggested. This is supported by the unusually low pK value of the acid and correspondingly lengthened C-O bonds (1.32 Å) in the carboxylic group.

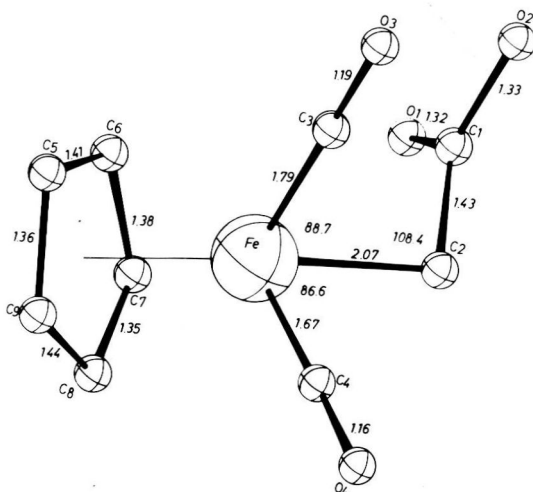


Fig. 1: The molecular structure of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CH}_2\text{COOH}$

Interestingly, perfluorobutadiene is found to be σ -bonded to a tetracarbonyliron moiety (359). The average Fe-C distance in this planar ring system (see Table 1, Nr. 3) is 2.00 Å.

Among the earlier published structures containing Fe-C (sp^2) and Fe-C(sp) bonds are those of hexamethylisocyanidoferrous chloride (537) and β -tetramethyl ferrocyanide (379). This class of compounds, which include iron- σ -olefin, iron- σ -arene, iron-carbene and ferracyclopentadiene moieties, is listed in Table 2. The observed Fe-C(sp^2) distances in these compounds range from 1.89 Å to 2.11 Å, clustering around 1.98 Å. A typical example of this class, the structure of *trans*-1,4-bis[dicarbonyl-(η^5 -cyclopentadienyl)iron]buta-1,3-diene, determined independently by two groups, is shown in Figure 2.

The olefinic bond in the butadiene system is not altered by the end-on bonding to the transition metal (C=C in 1,3-butadiene: 1.337(5) Å).

Examples of structures containing Fe-(C=C) groups coordinated to a *second* iron atom within one molecule are also known

(see Table 2). The reported Fe-C distances range from 1.96 to 2.09 Å in these compounds. The participation of the iron atom

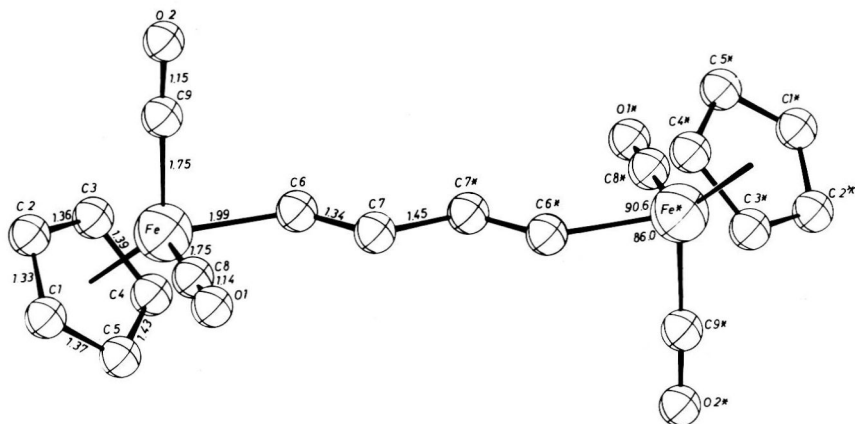


Fig. 2: The molecular structure of *trans*-1,4-bis[dicarbonyl-(η^5 -cyclopentadienyl)iron]buta-1,3-diene (Refs. 141,238).

in an η^3 -ferra-allylic system, implying a partial multiple bond order of the Fe-C bond (see Figure 3), has been suggested in a compound where this Fe-C distance has been reduced to 1.89 Å.

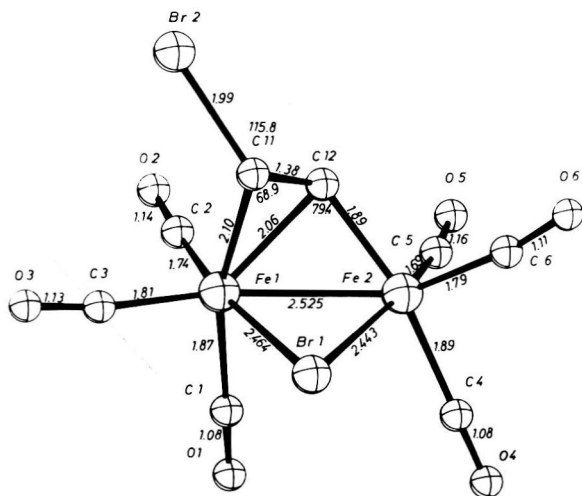


Fig. 3: The molecular structure of μ -[1- η :1,2- η (*trans*-2-bromovinyl)]- μ -bromo-bis(tricarbonyliron)-(Fe-Fe) (Ref. 430).

Multiple bond character within iron- σ -vinyl linkages has been claimed even when the vinyl group is not π -bonded to a second Fe atom (130,154).

Ferracyclopentadienes, in which an iron atom replaces one carbon atom of a cyclopentadienyl system (see below), are stabilized by being coordinated to a second iron atom. The C-Fe-C angles within the five-membered ring range from 81° to 82.3° . Substituents at the carbon atoms of the *cis*-diene fragment of the ring system do not significantly deviate from the best plane of the diene, suggesting a conjugated character of this system. The ring iron atom is displaced by 0.10 to 0.28 Å from the basal plane defined by the terminal diene carbon atoms and two carbonyl carbon atoms. A typical ferracyclopentadiene structure is shown in Figure 4.

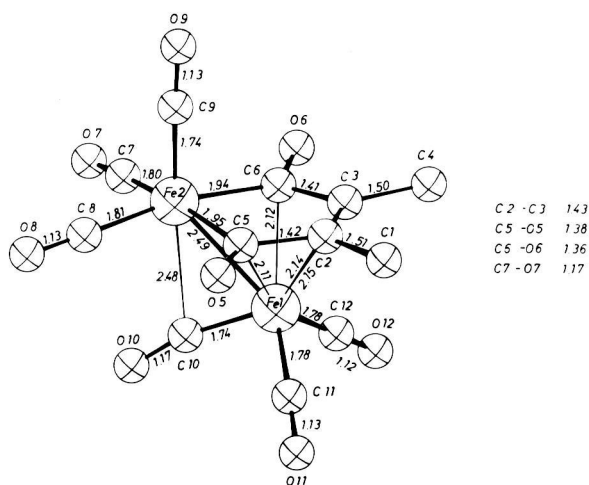


Fig. 4: The molecular structure of (2,5-dihydroxy-3,4-dimethyltricarbonylferracyclopenta-2,4-diene) tricarbonyliron (Refs. 364,363).

X-ray structural analyses of two binuclear iron carbene complexes have been completed (293,449,488). The structure of μ -diphenylvinylidene-bis(tetracarbonyliron)-(Fe-Fe) (see Table 2, Nr.37) is shown with its molecular dimensions in Figure 5. The sp^2 -hybridized atom C(9) bridges two iron atoms symmetrically. The system Fe(1)-Fe(2)-C(9)-C(10) is planar and twisted slightly with respect to the moiety C(9)-C(10)-C(11)-C(17). The structure of bis(μ -phenyloxycarbene)-bis(tricarbonyliron)-(Fe-Fe) (see Table 2, Nr.25) is shown in Figure 6. The atomic arrangement possesses a crystallographic mirror plane passing