Advances in
ORGANOMETALLIC CHEMISTRY

F. G. A. Stone and Robert West

Volume I

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Preface

During the past decade the study of organometallic chemistry has grown rapidly. Expansion of this area of scientific endeavor has been fostered by the discovery of several classes of compounds possessing remarkable structures, by the development of valence theory to account both for the existence of these novel compounds and for the nature of carbon–metal bonds in general, and by the growing use of organometallics in industrial processes. Organometallic chemistry now seems well on its way toward establishing its identity as an important domain of science, representing a convergence of inorganic, organic, and physical chemistry where the respective disciplines can benefit by interaction with each other.

In the volumes of this series, which we expect to have published at approximately twelve-month intervals for several years, we plan to include reviews of recent developments in all of organometallic chemistry, broadly defined as the science of substances containing organic groups bonded to metals. Included will be not only discussions of recent advances in the synthesis, properties, and reactions of organometallic compounds, but also articles on the application of modern structural techniques to organometallic problems, and on new technological applications of organometallic substances. We hope that chemists with a general interest in this field will, by turning to these volumes, be able to find recent information about many of the most active areas in organometallic chemistry.

No series of this sort could be successful without the cooperation of authors willing to undertake the demanding task of reviewing their fields of special competence. Users of these volumes, as well as the Editors, owe a debt of gratitude to the many busy scientists who are taking time from other labors to write these articles. The Editors also wish to thank the two members of the editorial advisory board for this series, Professors Henry Gilman and Harry J. Emeléus, whose advice and encouragement, in the initial planning stages, has been of vital importance.

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January, 1964

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Diene-Iron Carbonyl Complexes and Related Species

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I

# INTRODUCTION

A. Scope

In recent years a large number of compounds have been isolated in which an olefin or some other unsaturated hydrocarbon species is bonded to an iron carbonyl residue. As far as the general type of bonding of the unsaturated ligand to iron is concerned, these materials may be somewhat related to the well-known ferrocenes. However, the chemical behavior of the materials

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suggests that a separate classification is justified. The present review does not include compounds which possess the ferrocene-type structural unit. Furthermore, although many of the transition metals other than iron are known to form analogous olefin-metal complexes, the present review is restricted to discussion of the iron complexes. These are certainly the most numerous and varied. It is also apparent that each metal is associated with its own peculiarities as far as chemical properties are concerned and a comprehensive discussion of comparative and speculative chemical behavior of all the related organometallic species is far beyond the aim of this review.

B. Historical Aspects

The olefin-iron carbonyl complexes were first introduced by two entirely different synthetic methods. In 1930 Reihlen and co-workers (1) obtained butadiene-iron tricarbonyl by a reaction of butadiene with iron pentacarbonyl and in 1953 Reppe and Vetter (2) reported organoiron compounds, since shown to be diene-iron carbonyl complexes, following reaction of acetylene with iron carbonyls.

The first workers, while attempting to elucidate the structure of iron pentacarbonyl, treated $Fe(CO)_5$ with butadiene in a sealed tube at 150° C for several hours and obtained a product which analyzed as $C_4H_6Fe(CO)_3$. Although they were not able to assign a definite structure to this material they considered that the iron atom was bonded to the terminal carbon atoms of the diene and to three carbonyl groups. The cyclic structure (I) was proposed; however, they stated that the alternative structure (II) could not be ruled out.
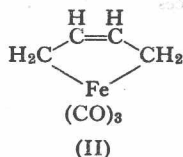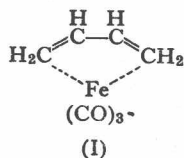
They also obtained organoiron complexes with isoprene and $Fe(CO)_5$ but the reaction apparently failed in the case of isobutylene.

Apart from a patent (3) which appeared in 1947 no further work was published on this particular reaction until Hallam and Pauson (4) extended the study in 1958. These latter workers investigated further the product obtained from butadiene and $Fe(CO)_5$. The diene complex was found to resist hydrogenation and not to undergo Diels-Alder-type reactions. Ozonolysis

of the material was found to produce some formaldehyde while vigorous reaction with LiAlH$_4$ led to the formation of some butadiene. This, together with some spectroscopic evidence, led them to suggest that the butadiene molecule remained essentially intact in the organoiron complex. Furthermore, they showed that an analogous compound, 1,3-cyclohexadiene-iron tricarbonyl, could be prepared in a similar manner from 1,3-cyclohexadiene and Fe(CO)$_5$. They therefore concluded that the diene system adopted a *cis* arrangement of double bonds as in (IIIa), rather than a *trans* one (IIIb) within the complex. The structure then proposed is shown by formula (IV).

(a)   (b)

(III)   (IV)
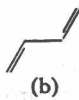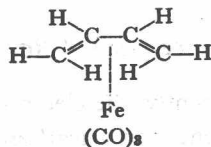
The butadiene moiety in (IV) is presumed to be planar, or nearly so, and the iron atom lies below this plane and approximately equidistant from the four carbon atoms of the diene system. The nature of the diene–iron bonding was presumed to involve interaction of the Fe atomic orbitals with π molecular orbitals of the diene system as a whole and was therefore more analogous to the π bonding in ferrocenes, rather than the σ type implied in Reihlen's structure (II). The conjugated nature of the diene system was considered to be an essential feature necessary for the formation of iron derivatives of this type.

At about the same time Hallam and Pauson published their work, the recognition of the diene-Fe(CO)$_3$ grouping as a stable system was independently made by several groups of workers who were then extending the field introduced by Reppe and Vetter (5–10). The chemistry associated with the reactions of acetylene is, by and large, an entity in its own and, for convenience, we have retained this separation in our discussion.

Since 1958 a considerable amount of research activity has centered around these systems, both in the acetylene-iron carbonyl reactions and the direct reactions of olefins with iron carbonyls. The types of unsaturated ligands which are now known to occur in stable iron carbonyl complexes include substituted and nonsubstituted cyclic, acyclic, and nonconjugated dienes as well as some aromatic systems. Furthermore, what may be formally regarded as dienyl cations as well as allyl cations and radicals are found to

occur as ligands in certain stable iron carbonyl systems. Heterocyclic diene-iron carbonyl complexes are now known and several monoolefin-iron tetracarbonyl complexes have also recently been reported. Finally, more complex systems, possessing two or more iron atoms per molecule, are now well known.

II

STRUCTURAL CONSIDERATIONS

A. Evidence from X-Ray Data

Until recently, the electronic structure proposed by Hallam and Pauson for the diene-iron tricarbonyl complexes seems to have been generally accepted. However, since 1960, several significant X-ray studies have been
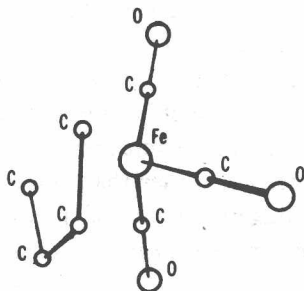
FIG. 1. The structure of butadiene-iron tricarbonyl, after Mills and Robinson. The bond lengths of the C—C bonds are 1.45 and 1.46 Å.

made which tend to indicate that the nature of the bonding is more complex than this. Mills and Robinson (11) in 1960 first published the X-ray data obtained for butadiene-iron tricarbonyl. The salient features of this study are given in Fig. 1.

The carbon atoms of the butadiene are found to be *cis* and coplanar. The bond angles are 118° for C_1—C_2—C_3 and approximately 70° for Fe—C_1—C_2. The iron atom lies below the plane of the diene carbon atoms and is approximately equidistant (2.1 ± 0.04 Å) from these four carbons. The plane of the butadiene carbons is not quite parallel to that defined by the three carbon atoms of the carbonyl groups. These data certainly tend

to support Hallam and Pauson's formulation over that of the two possible structures mentioned by Reihlen and co-workers.

It should be mentioned at this point that in 1959 Green and co-workers (12) introduced another interesting structure for butadiene-Fe(CO)₃. These workers found that the NMR spectrum of butadiene-iron tricarbonyl displayed two clearly different proton types. Four of the hydrogens appeared in the region of aliphatic hydrogens while the remaining two protons appeared at lower fields nearer the region of normal olefinic hydrogens. This data suggested structure (V).

$$HC=CH$$
$$H_2C \diagup \quad \downarrow \quad \diagdown CH_2$$
$$\diagdown Fe \diagup$$
$$(CO)_3$$

(V)
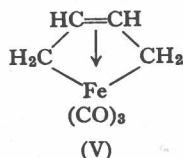
The same authors pointed out, however, that the infrared stretching frequencies of the C—H bonds were more like those associated with sp^2 rather than with sp^3 hybridized carbon–hydrogen bonds. In view of the unknown effect the Fe(CO)₃ grouping might have on the local magnetic field in the diene moiety they considered the infrared evidence, favoring (IV), to be more diagnostic.

Dickens and Lipscomb, in 1961, obtained the X-ray data for cyclooctatetraene-iron tricarbonyl (13, 14) and cyclooctatetraene-diiron hexacarbonyl (14, 15). These two complexes, which will be discussed again in a later section, had aroused considerable interest and speculation concerning the structural features. Chemical evidence for the first of these had indicated no free olefinic double bonds to be present and NMR data indicated only one type of hydrogen present and it was widely assumed that the C_8H_8 ring in this complex was planar rather than having the tub conformation present in the free hydrocarbon. Two molecular orbital calculations, using symmetry orbitals based upon a planar configuration of the C_8H_8 ring, had purported to have rationalized the chemical binding of the complex (16, 17).

However, the X-ray data showed clearly that, in the crystalline state at least, the Fe(CO)₃ grouping is attached to the C_8H_8 ring through a diene unit rather than a tetraene.

The structure found by X-ray studies is shown in Fig. 2.

The C_8H_8 ring is found to lie in two planes, the angle between them being 41°. From the interatomic distances it is clearly seen that the Fe(CO)₃ group

is associated with only one pair of conjugated double bonds with the remaining pair forming a second plane and having relative positions very similar to those in butadiene. The iron atom is at about the same position with respect to the four carbons of the diene unit to which it is bonded as was reported for the butadiene complex, though it possibly lies closer to the central carbons of the diene. The carbon–carbon distances involved in the coordinated diene unit are again equal though a little shorter than those found in the butadiene complex.

On the basis of the size of overlap integrals of various orbitals of the atoms having these relative positions Dickens and Lipscomb considered
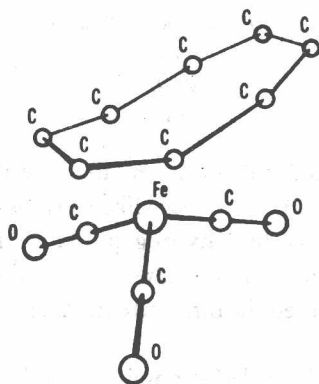

FIG. 2. The structure of cyclooctatetraene-iron tricarbonyl, after Dickens and Lipscomb. The C—C bond distances of the diene-Fe(CO)$_3$ unit are each 1.42 Å.

that both structural types, (IV) and (V), appeared reasonable, with some bias in favor of the latter. The true structure, they thought, might lie somewhere between these two representations.

The second complex, $C_8H_8Fe_2(CO)_6$, had also aroused considerable speculation concerning its structure (16–21), all of which was shown to be incorrect. The pertinent data of the X-ray studies are shown in Fig. 3.

The main point here is that the C_8H_8 ring adopts a chair conformation in the complex with each iron atom again clearly associated with a diene unit. In this conformation little π-type interaction is to be expected between the two diene units bonded to iron. It is also of interest that the disposition of the three carbonyl groups about each iron atom is the same as observed in the earlier studies.

Recent experiments involving the Mössbauer resonance of the two iron

atoms in this complex are in agreement with the X-ray studies insofar as the two iron nuclei are found to be equivalent. Furthermore a similarity in chemical environment of the two iron atoms with that in the $C_8H_8 \cdot Fe(CO)_3$ complex is also suggested (22).

Similar results have been found by Smith and Dahl who showed, from X-ray studies, that in the complex 2,4,6-triphenyltropone-iron tricarbonyl the tropone ring was no longer planar (23). The arrangement of the atoms of the tropone ring and the $Fe(CO)_3$ are as shown in Fig. 4.

It is clear again that the $Fe(CO)_3$ group is attached to a diene unit rather than to the fully conjugated ring as a whole, as might have been anticipated
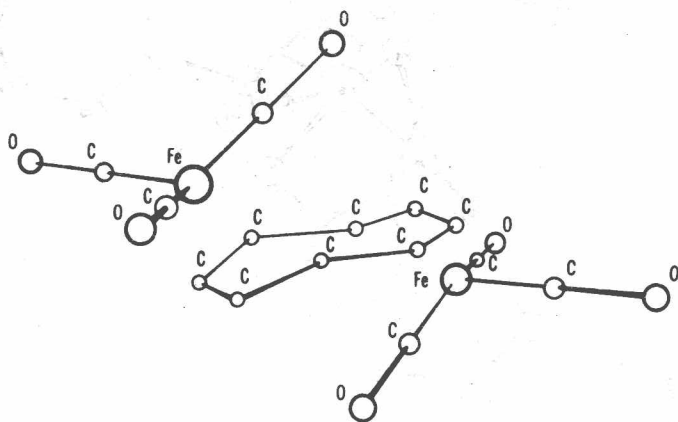

FIG. 3. The structure of cyclooctatetraene-diiron hexacarbonyl, after Dickens and Lipscomb. The C—C bond distances of the diene-$Fe(CO)_3$ units are 1.44, 1.40, and 1.44 Å.

from molecular orbital considerations (24). The two planes of the tropone ring are found to intersect at an angle of 139°. Of particular significance in this study is the fact that carbon atom number 4 (see Fig. 4) is found not to lie in the plane of the three other carbon atoms to which it is attached, but is displaced from this plane by approximately 0.22 Å. This is almost one-half the distance it would be displaced if C_4 were a normal sp^3 hybridized carbon atom. Carbon atom number 6 on the other hand does lie in the plane defined by the three carbon atoms to which it is attached.

On the basis of these results Smith and Dahl proposed that the distorted octahedral-type structure (VI) was preferred as a representation, provided that recognition was made of the contribution provided by structure (VII) to the actual electronic state of the molecule.