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THE ROLE OF CYCLOBUTADIENEIRON TRICARBONYL IN THE "CYCLOBUTADIENE PROBLEM"

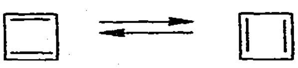
R. PETTIT

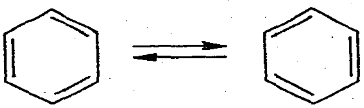
Department of Chemistry, The University of Texas, Austin, Texas 78712 (U.S.A.)

To a large extent the area of chemistry referred today as "organometallic chemistry", especially that of transition metals, owes its belated existence to the formal classification that has evolved in the teaching of chemistry. The areas of organic, physical, inorganic and biochemistry had been treated as almost separate subjects and research activities in interrelated fields, especially between the organic and inorganic fields, were minimal. Having been largely ignored for so long it is not surprising that when a significant number of people did become involved in the area (following the discovery of ferrocene), significant results came very quickly and the importance of organometallic chemistry as a field of study gained widespread and rapid acceptance. An organic chemist must now have knowledge of the field if he wishes to understand the "oxo" Process or the Ziegler—Natta polymerization of olefins for example, likewise an inorganic chemist must now also have knowledge of the area if he is to fully appreciate the chemistry of transition metals in low oxidation states. The recognition of the nature of vitamin B_{12} also serves to illustrate the importance of this interdisciplinary field of chemistry.

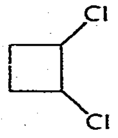
In the present paper we shall discuss the contribution that this area has made towards the solution of a classical problem of interest to organic chemists viz. the "cyclobutadiene problem".

In the early stages, interest in the cyclobutadiene molecule stemmed from the fact that, on paper at least, it was possible to write two equivalent structures for the molecule (formula I) just as it was for benzene (II) and the question was then asked as to whether the molecule should have aromatic properties as did benzene. This question was first posed during the period of Kékulé and his contemporaries and the importance of the system in view of the general nature of "aromaticity" has been apparent since that time. Over a period of about fifty years several attempts were made to prepare the compound, but all efforts end-


(I)


(II)

ed in failure. Time tested reactions leading to double bond formation, such as dehydrohalogenation and Hoffmann eliminations, failed to produce cyclobutadiene when applied to systems such as III [1], IV [2] and V [3]. From the failure of these and other experiments it became apparent that cyclobutadiene did not possess "aromatic stability" as might have been inferred from structure I.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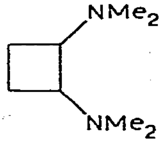
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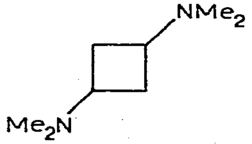
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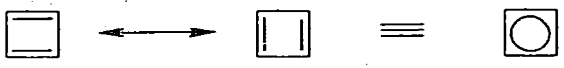
Theoretical support for the nonaromaticity of cyclobutadiene came from application of the simple Hückel Molecular Orbital method to the system. If one assumes in this calculation that the four carbon atoms lie at the corners of a square the orbital energy diagram shown in Fig. 1a is obtained. Likewise, if it is assumed that the carbon atoms lie at the corners of a rectangle then the energy levels shown in Fig. 1b are obtained. In each case it is calculated that the resonance energy of the system is zero (compared to 40 kcal for benzene) hence cyclobutadiene would not be expected to have aromatic resonance stabilization energy.

With the acceptance of its nonaromaticity the "cyclobutadiene problem" then changed in nature; the questions now posed were: "Does the molecule exist as a stable species or does it spontaneously decompose; if it does exist, is it, in its ground electronic state, a square triplet (VI) or a rectangular singlet (VII)?"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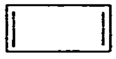
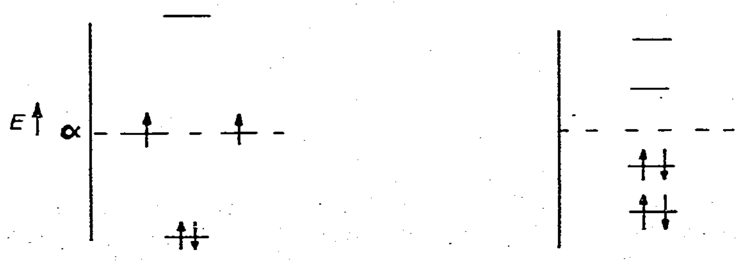

(VII)

It was at this stage of the problem then that organometallic chemistry played an interesting and significant role. In 1956 Lonquett-Higgins and Orgel proposed, on the basis of molecular orbital theory, that, despite the lack of stability of cyclobutadiene itself, there were reasons to believe that it nonetheless may form stable complexes with transition metals [4]. The basis for this prediction being

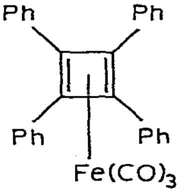


(a) (b)

Fig. 1. Hückel orbital energies for (a) square and (b) rectangular cyclobutadiene.

that the molecular orbitals of cyclobutadiene (assuming a square form) were of the appropriate symmetry to allow for interaction with transition metal atomic orbitals giving rise to the forward coordination and back donation type interactions that had become recognized as being the dominant bonding characteristics present in olefin—metal complexes.

Within a very short span of time the ideas expressed by these authors were shown to be essentially correct. Hubel and Braye reported [5] the isolation of tetraphenylcyclobutadieneiron tricarbonyl (VIII) and Criegee and Schroder [6] reported a stable complex of tetramethylcyclobutadienenickel chloride (IX). The cyclobutadiene nature of the ligand (rather than being bis-acetylenic for example) was clearly indicated from X-ray analysis of these two complexes. There being no obvious reason why the four substituents should play any important role in the bonding scheme, the isolation of these species then provided critical evidence for the validity of the concept that cyclobutadiene—transition metal complexes should be stable.



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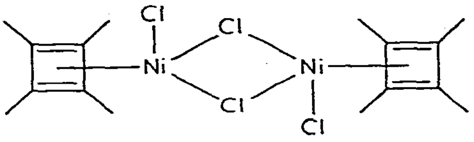
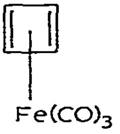
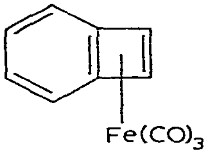


(IX)

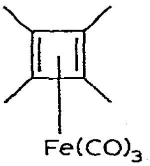
The first cyclobutadiene—metal complex of the parent hydrocarbon, viz. cyclobutadieneiron tricarbonyl (X) was prepared in 1965 through the reaction of dichlorocyclobutene with $Fe_2(CO)_9$ [7]; similar reactions between other dihalocyclobutenes and $Fe_2(CO)_9$ also afforded the corresponding cyclobutadieneiron tricarbonyl complexes e.g. the benzo derivative XI and the tetramethyl derivative XII, and the reaction appears to be fairly general [8]. The complexes are generally yellow-to-orange, crystalline, stable solids and, once prepared, present no problem in so far as handling is concerned.



(X)



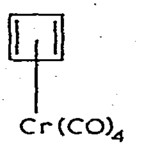
(XI)



(XII)

A second method for the preparation of complex X involves treatment of dichlorocyclobutene with the salt, $Na_2Fe(CO)_4$. This method is less convenient than the one mentioned above for preparation of the iron complex X, however, the method is useful for the preparation of cyclobutadiene complexes of transition metals other than iron; thus reaction of dichlorocyclobutene with $Na_2Ru(CO)_4$ and $Na_2Mo(CO)_4$ give rise to cyclobutadiene-ruthenium tricarbonyl and -molybdenum tetracarbonyl respectively [9].

A third method of preparation of cyclobutadienemetal carbonyl complexes consists of irradiation of a metal carbonyl in the presence of a dihalocyclobutene derivative. Thus irradiation of $Fe(CO)_5$ with dichlorocyclobutene affords X, likewise, irradiation of $Cr(CO)_6$ with dichlorocyclobutene and dibromobenzocyclobutene gives rise to cyclobutadiene- and benzocyclobutadiene-chromium tetracarbonyl, XIII and XIV, respectively [10]. It is of interest to note that similar irradiation of $Fe(CO)_5$ and $Cr(CO)_6$ with chloromethylallyl chloride (XV) also gives the trimethylenemethane complexes XVI and XVII as do the reactions of $Na_2Fe(CO)_4$ and $Na_2Cr(CO)_5$ with XV [10,11].



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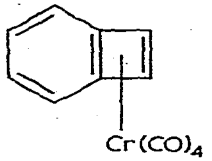

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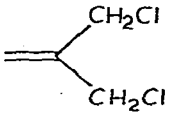

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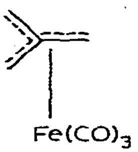

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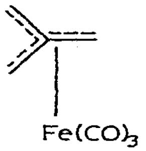
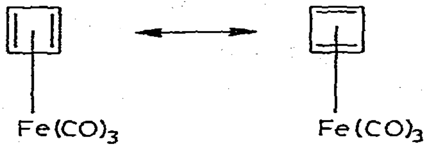


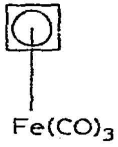
(XVII)

The mechanisms of the formation of the cyclobutadiene complexes in the reactions given have not been established; it seems extremely unlikely however that any of them involves "trapping" of free cyclobutadiene by some metal component; in each case it is much more probable that the cyclobutadiene ring is developed while the C_4 fragment is already bound to the metal in a *dihapto* or *trihapto* fashion.

Because of its relative accessibility the cyclobutadieneiron tricarbonyl complex X has been most extensively investigated and studies with this material have certainly contributed most to the "cyclobutadiene problem". Accordingly, we shall restrict our discussion primarily to the chemistry of this system, though it must be noted that a larger number of substituted cyclobutadiene complexes of various transition metals are now known [12].



(Xa) (Xb)

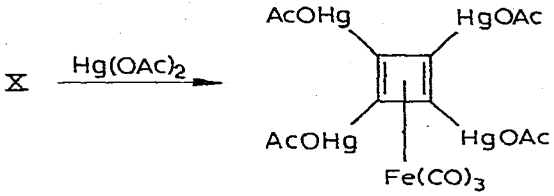


(Xc)

Electron diffraction studies on the parent complex X reveal that the four carbon atoms of the carbocyclic ligand are situated at the corners of a square, having bond distances of 1.46 Å. Therefore, while it is a ligand attached to iron, the cyclobutadiene ring must be considered as a resonance hybrid Xa↔Xb or, by analogy with the modern representation of benzene, the equivalent structure Xc. The complex can therefore be categorized as being "aromatic" in the physical sense of this term. This raises a very interesting point for, as we shall see presently, we believe that when it is not complexed to a metal, cyclobutadiene adopts a rectangular structure having alternating short double bonds and long single bonds.

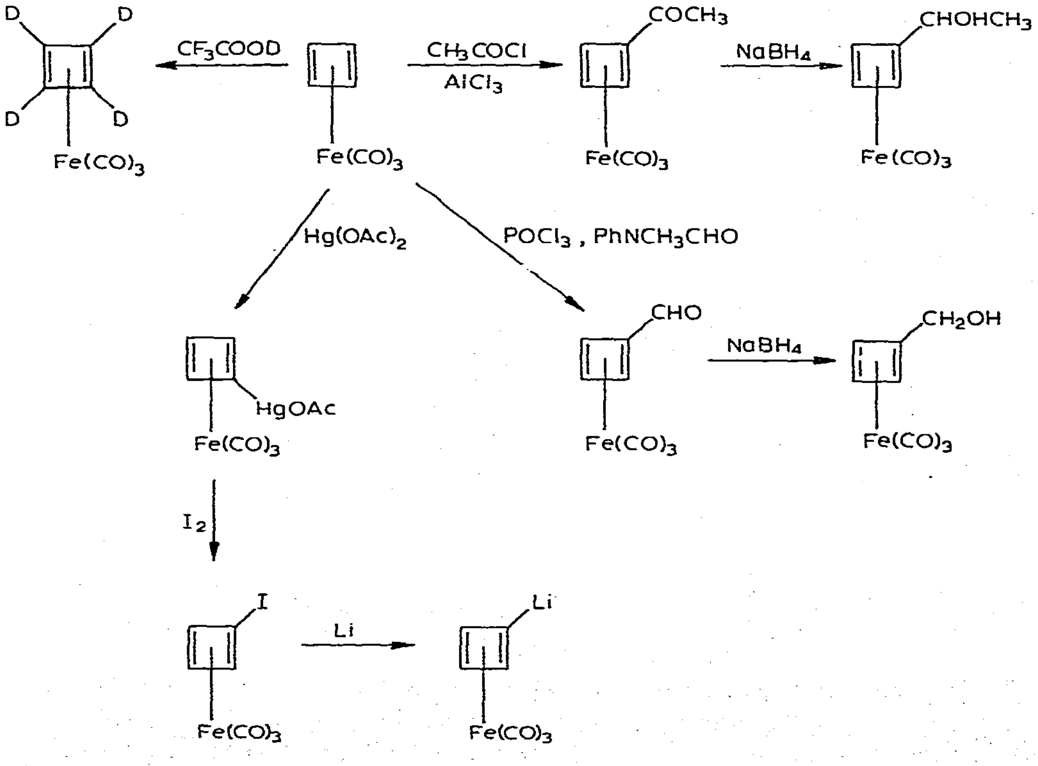
Also indicative of the "aromatic" nature of the cyclobutadiene ligand in the $Fe(CO)_3$ complex X is the fact that the molecule readily enters into electrophilic substitution reactions such as, for example, a Friedel—Crafts type reaction with an acyl halide and aluminum chloride giving rise to substituted derivatives of X [13].

Acetoxymercuration is a particularly interesting case of this electrophilic substitution; treatment of complex X with excess mercuric acetate readily leads to the formation of all possible acetoxymercury derivatives including the tetra-substituted complex XVIII [14]. With the possible exception of thiophene this is, to the author's knowledge, the only example of permercuration to be reported.

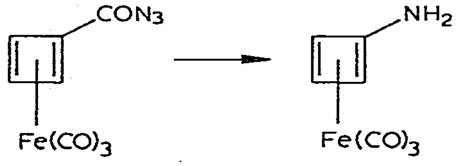


(XVIII)

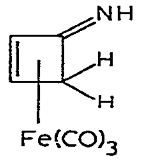
SCHEME 1



It is also found that functional groups in the side chain of a substituted cyclobutadieneiron tricarbonyl complex can be successfully transformed into other functionality, via standard reagents used in organic synthesis, without affecting the C_4-ring—metal bonding. The combination then of electrophilic substitution and subsequent chemical transformation allows for the preparation of a large and varied array of cyclobutadieneiron tricarbonyl complexes. In Scheme 1 are listed several typical reactions, individually they are of no particular interest in so far as carbon—metal chemistry is concerned and, except for the following case, this aspect of the chemistry of cyclobutadiene and its metal complexes will not be elaborated further. Aminocyclobutadieneiron tricarbonyl (XIX) can be prepared via a Curtius rearrangement of the acid azide derivative XX followed by hydrolysis. It is interesting here to note that the derivative exists in the ene-amine form XIX, as do other atomatic amines such as aniline, rather than the tautomeric imine form XXI which would be certainly expected for the case of aminocyclobutadiene, free of bonding to a metal.

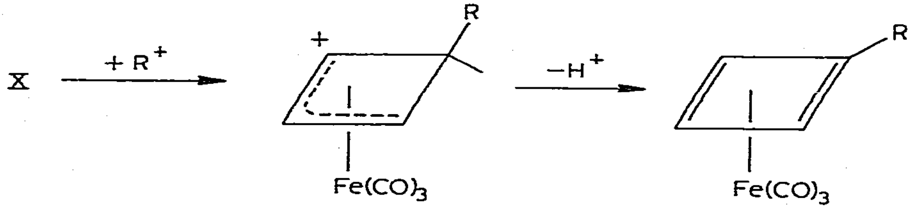


(XX) (XIX)



(XXI)

The mechanism of electrophilic substitution reactions on cyclobutadieneiron tricarbonyl have not been established but it would seem reasonable to suggest that they proceed in a manner closely related to those which occur on a benzene ring. Thus an electrophile is presumed to attack the ring to generate a π-allyliron tricarbonyl cationic species XXII which, upon ejection of a proton, regains the EAN rule* about iron and formation of the substituted derivative. Whether XXII is a metastable intermediate or a true transition state is not known, but the relative stability of species resembling XXII would be readily anticipated (stable salts of π-allyliron tricarbonyl cations have indeed been isolated) and it is then easy to rationalize the very facile manner in which the substitution reactions occur; competitive reactions between the complex X and benzene indicate that complex X is much more reactive.



(XXII)

This mechanism for electrophilic substitution on the ring also affords a somewhat satisfactory explanation for the curious orientation effects noted when methoxycyclobutadieneiron tricarbonyl (XXIII) is deuterated. Through a simple "arrow pushing" technique as shown in XXIII it could be concluded that the methoxy substituent should direct an electrophile to the 2-position. Con-

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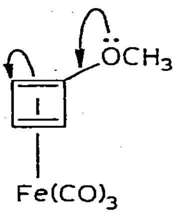
* EAN rule = effective atomic number rule.



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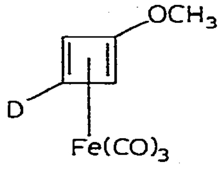

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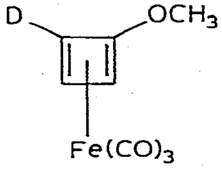
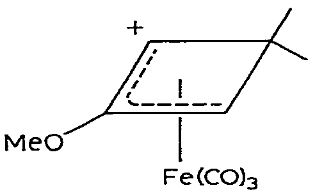


(XXV)

trary to this expectation however, it is found that upon dissolution in CF_3COOD or D_2SO_4 the deuterium cation attacks the 3-position leading exclusively to the deuterated product XXIV rather than XXV. The intermediate state in the formation of XXIV would be the π-allyl cation XXVI and one explanation for the greater stability of this system compared to the alternative species XXVII might be that conjugation of the methoxyl group with the allyl fragment decreases the energy of the back-donation bond from iron to the ligand in the latter case. In the species XXVI the methoxy group is cross conjugated with the allyl system and would therefore not compete with the iron atom in the back-donation process. An alternative explanation, invoking a special stability of XXVI through an oxatrimethylenemethane type structure XXVIII has received no experimental support [15].



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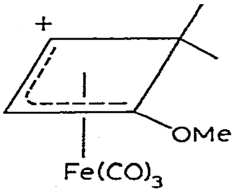

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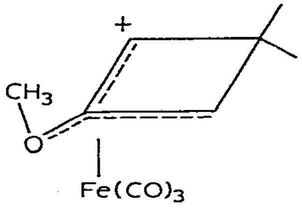
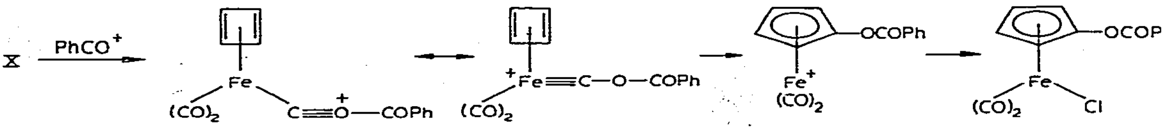


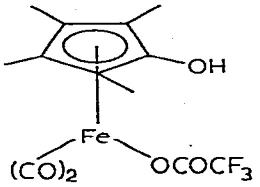
(XXVIII)

An interesting by-product was observed during the acylation of cyclobutadieneiron tricarbonyl with benzoyl chloride and aluminum trichloride. In addition to the expected product, benzoylcyclobutadieneiron tricarbonyl, there was obtained a red crystalline material which, from its NMR spectrum, clearly no longer contained a cyclobutadiene ligand. An X-ray structural study revealed the new material to be benzoyloxycyclopentadienyliron dicarbonyl chloride (XXIX) in which a ring expansion of the cyclobutadiene ring has occurred through incorporation of one of the original CO ligands and formation of a five-membered carbon ring [16]. The formation of the complex XXIX can be rationalized as follows: initial attack of the benzoyl cation at the terminal oxygen atom of a carbonyl ligand of X would produce the species XXX which, from the resonance structure indicated, may be considered as a benzoyloxycarbyne complex; insertion of the carbyne ligand to give the cation XXXI followed by attack of chloride ion could then provide for the observed product. A similar such ring expansion of a cyclobutadiene ligand has been observed in two other instances, and we presume these also involve initial attack of an electrophile at the oxygen atom of a coordinated CO group to generate a carbyne ligand which then undergoes insertion into the ring. Thus, tetramethylcyclobutadieneiron



(XXX) (XXXI) (XXIX)

tricarbonyl (in which the substitution pathway is of course blocked) reacts with CF_3COOH to give the hydroxycyclopentadienyl derivative XXXII [17]. Similarly, cyclobutadienemolybdenum tetracarbonyl reacts with acetyl chloride and aluminum trichloride to afford the ring expanded complex XXXIII [18]. This latter case is instructive because for some time it had been difficult to understand why cyclobutadienemolybdenum tetracarbonyl did not undergo electrophilic substitution reactions as did the iron complex. Now it would appear that the difference in this reactivity is simply associated with the fact that the molybdenum system shows a greater propensity for the insertion process and the lack of observed substitution reactions is not due to any fundamental difference in the nature of the cyclobutadiene ligands in the two systems.



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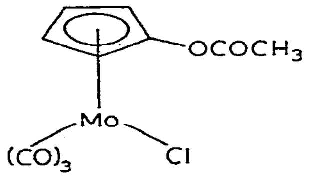
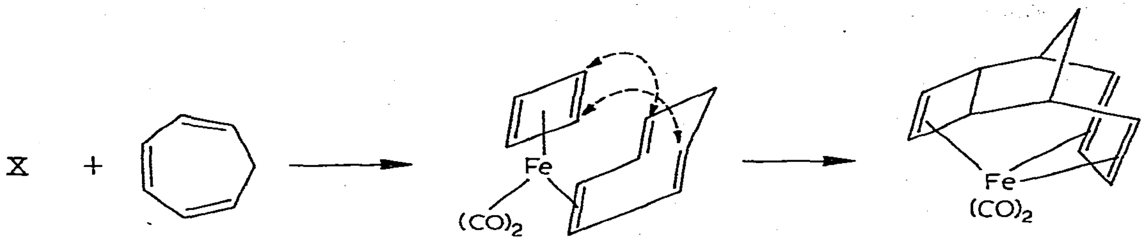


(XXXIII)

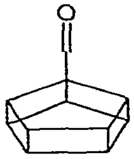
Contrary again, to what might surely be predicted for cyclobutadiene itself, is the fact that complex X does not react with reagents which typically add to olefinic bonds, e.g. as in catalytic hydrogenation or treatment with alkaline $KMnO_4$. With addition reagents which are also strong oxidizing agents, e.g. chlorine and bromine, the complex suffers extensive degradation presumably arising from initial oxidation of the metal. This also constitutes a restriction on electrophilic substitution reactions where the electrophile is also an oxidizing agent, for example the nitronium ion (NO_2^+) in attempted nitration reactions causes only oxidative destruction of the complex.

Under certain circumstances however, it seems that addition reactions can occur between the cyclobutadiene ring and a second organic unsaturated molecule when the latter is also coordinated to the iron atom. For example, irradiation of a mixture of cyclobutadieneiron tricarbonyl and cycloheptatriene leads to the formation of complex XXXIV in which cycloaddition between the cyclobutadiene and cycloheptatriene rings has obviously taken place [19]. The stereochemistry of the adduct XXXIV, which was determined by X-ray analysis, suggests that its formation involves initial photolytic replacement of a CO ligand by cycloheptatriene to give the intermediate complex XXXV and this is followed by an intramolecular cycloaddition between the coordinated ligands leading to the observed product. It should be noted that in this addition step i.e. XXXIV→XXXV the EAN rule about iron is maintained. Both oxepin and the ethylene ketal of

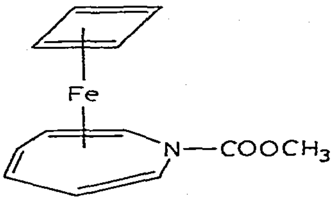


(XXXV) (XXXIV)

tropone behave in a similar manner as does cycloheptatriene in this reaction and advantage has been taken of the latter case in providing a novel synthesis of the highly caged ketone, homopentaprismanone (XXXVI) [19]. The cyclic triene, azapine carboxylic ester, behaves in a different manner, the irradiation in this case leads to replacement of all carbonyl ligands and the formation of the sandwich complex XXXVII.

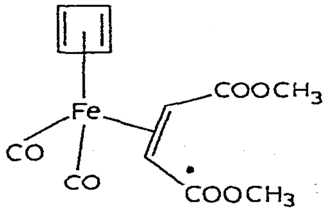


(XXXVI)

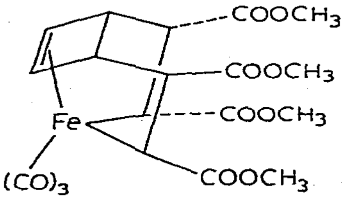


(XXXVII)

A second type of addition reaction is observed upon irradiation of complex X with dimethyl maleate. Two new complexes have been identified as products of this reaction; the first which is the major product when the reaction is conducted in ether as solvent, is simply the product resulting from replacement of a CO ligand by dimethylmaleate i.e. XXXVIII. The second compound which is the



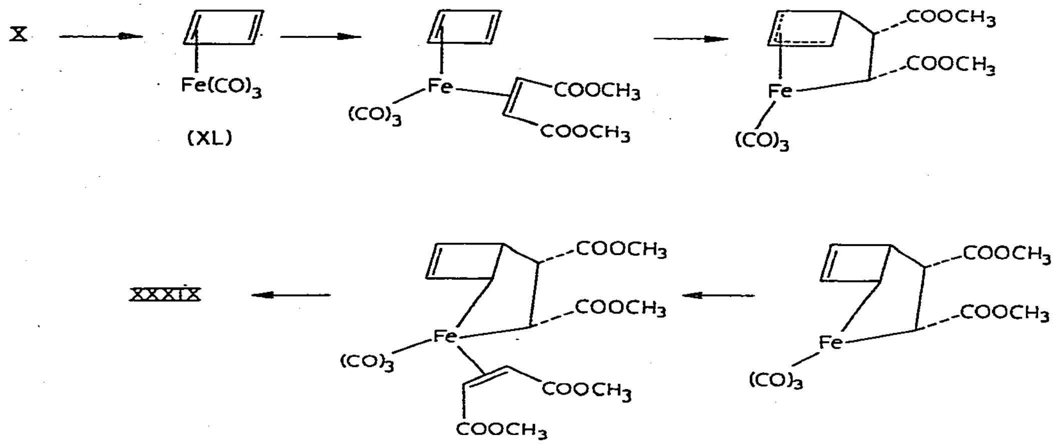
(XXXVIII)



(XXXIX)

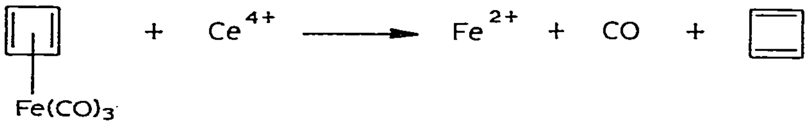
major product when the irradiation is conducted in pentane; has structure XXXIX as shown by X-ray analysis [20]. The latter product has retained all of the original CO groups and, as indicated in the following proposed reaction scheme for its formation, the initial activation of complex X perhaps involves loss of a carbon—carbon double bond ligand with formation of the electron deficient *dihapto*-cyclobutadieneiron tricarbonyl species XL. The remaining steps in the proposed Scheme 2, i.e. olefin insertion and π—σ-allyl interconversion have precedence.

SCHEME 2



dihapto-Iron complexes of cyclobutadiene have recently been isolated and although the EAN rule about the metal atom is maintained in these species, their isolation makes the formation of XL upon photolysis more plausible [21].

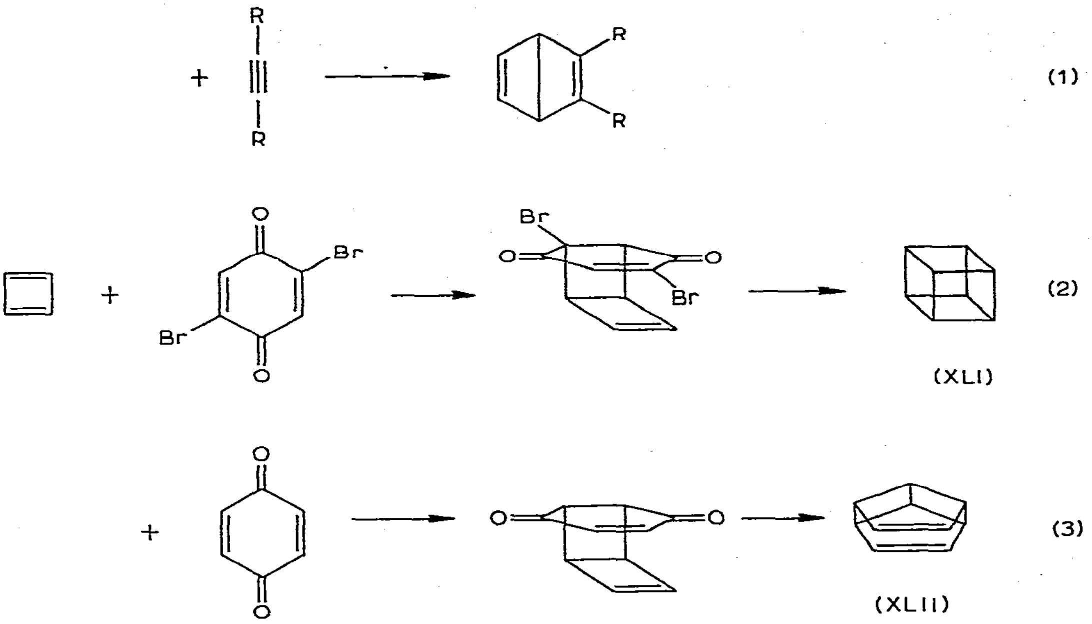
In common with other diene—iron tricarbonyl complexes, cyclobutadiene-iron tricarbonyl undergoes facile oxidative decomposition with liberation of the ligands when treated with electron transfer oxidizing agents such as Fe^{3+} or Ce^{4+}:



This simple reaction, although of little note as far as organometallic chemistry per se is concerned, is nonetheless of great interest with respect to the chemistry of cyclobutadiene for it afforded for the first time conditions under which the cyclobutadiene molecule could be generated and studied in a systematic manner. Through oxidative degradation of its iron carbonyl complex X, cyclobutadiene is now available as a reagent in organic synthesis; an indication of the utility of the reaction in this connection is given below. It is expected that cyclobutadiene would act as an excellent diene in a Diels—Alder reaction and in the reactions of Scheme 3 the initial addition of cyclobutadiene to the various dienophiles is accomplished in good yield through addition of ceric ammonium nitrate to a solution containing complex X and the dienophile.

The addition of cyclobutadiene to acetylenes (eqn. 1) constitutes an extremely simple and useful synthesis of Dewar benzene derivatives [22]. Equations 2 and 3 show that the addition of cyclobutadiene to cyclic dienophiles occurs to give the "*endo*" product as would be expected if cyclobutadiene were to act as a normal, but very reactive diene. The initial adduct in eqn. 2 has been converted via a sequence of standard organic transformations to cubane XLI [23], while that in eqn. 3 has likewise been transformed to give the novel structure "hypostrophene" (XLII) an amusing system which is found to undergo an endless sequence of degenerate cope rearrangements [24].

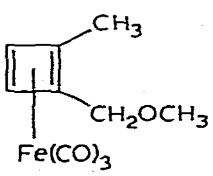
SCHEME 3



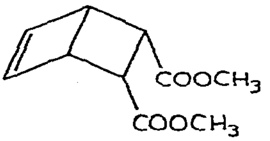
These examples by no means constitute a complete list, but they do illustrate the utility of complex X as a source of cyclobutadiene.

The evidence, from various experiments, that free cyclobutadiene is being generated in the oxidative degradation of X is largely circumstantial, but nonetheless very compelling. For example, evidence has been found showing that at least trace amounts of cyclobutadiene can be transferred in the gas phase from such a reaction; furthermore, only reagents having strongly electron withdrawing groups readily attack the C_4-diene, this would not be expected if the cyclobutadiene were reacting while still bound to some iron species bearing a positive charge. The observed *endo* stereochemistry also is inconsistent with a metal-bound cyclobutadiene species being involved as the principal reactant. The observation that a Diels—Alder adduct from oxidative degradation of the optically active complex XLIII is optically inactive provides especially convincing support for the argument that the ligand is free from the metal at the time of cycloaddition [25].

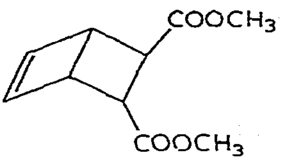
Cyclobutadiene is found to add to dimethylmaleate, dimethyl formate and cyclopentadiene to give exclusively the adducts XLIV, XLV and XLVI, respectively. The nature of the stereoselectivity of these adducts very strongly implies that these reactions are proceeding in a concerted manner involving a normal diene having a singlet electronic ground state [26]. If such is the case then theoretical arguments conclude that cyclobutadiene must have a rectangular ground state, i.e. XLVII; it then follows that there should exist two isomeric *ortho* disubstituted cyclobutadienes, for example the two diphenyl derivatives, XLVIII and XLIX. Evidence consistent with the existence of the two interconvertible isomers XLVIII and XLIX has been obtained [8a] through oxidative liberation and trapping of the ligands from 1,2-diphenylcyclobutadieneiron tricarbonyl (L)



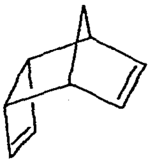
(XLIII)



(XLIV)

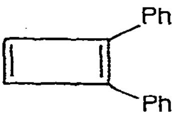


(XLV)

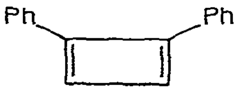


(XLVI)

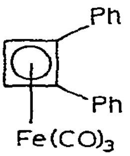
(XLVII)



(XLVIII)



(XLIX)

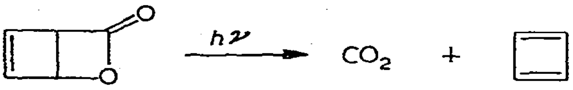


(L)

(because cyclobutadiene has a square configuration while acting as a ligand, only one isomer of complex L exists).

The conclusions then deduced from the reactions of cyclobutadiene generated from complex X is that the hydrocarbon is a rectangular singlet ground state having the double bond alternation that is seen in other non-aromatic conjugated polyenes, e.g. cyclooctatetraene; as such it then obeys Hückel's rules for aromaticity and non-aromaticity. Recently the X-ray structures of two very highly hindered cyclobutadiene derivatives have been obtained and these also reveal a rectangular disposition of the four carbon atoms in the ring [27,28]. The presence of the three or four tertiary butyl type substitutents in the ring which are responsible for the chemical stability of these systems, would not, alone seem likely to impose the rectangular disposition of the ring. There is thus a considerable body of evidence to suggest that cyclobutadiene is rectangular.

In contrast to these conclusions, however, is the observation that a cyclobutadiene species, prepared at very low temperatures through photolysis of photo-α-pyrone (LI) has a square configuration as determined by infrared spectroscopy [29,30]. The nature of the electronic state of the C_4H_4 species (i.e. singlet or triplet) has not yet been determined. If it is found that this square species is indeed a triplet state then all of the data discussed above will be consistent with the results of recent theoretical calculations [31], which indicate that the ground state of cyclobutadiene is a singlet rectangular state with a low barrier of interconversion of one rectangular form to another; in addition, there is found in these calculations, a metastable triplet state which has a square configuration and which could account for the product obtained from LI.



(LI)

The final answer to the "cyclobutadiene problem" is therefore still not at hand, however, the situation is now very much clearer than it was ten years ago and solutions to the remaining problems would seem to be within reach. There are now several methods, not involving organometallic species, which are available for the generation of cyclobutadiene [32]; some of these are more amenable for the isolation of the molecule and for the application of direct physical methods upon it and with such techniques the remaining questions concerning the precise nature of cyclobutadiene should be answered. Nonetheless, the comment can be fairly made that organometallic chemistry has played a very major role in our current knowledge of the chemistry of cyclobutadiene and has been an important factor in the attempts to solve the "cyclobutadiene problem".

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