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PREVIEW

REACTIONS OF TRICARBONYL(PI-HYDROCARBON)IRON COMPLEXES
WITH TRIMETHYLAMINE OXIDE

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AND HUSBAND

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REACTIONS OF TRICARBONYL(PI-HYDROCARBON)IRON COMPLEXES
WITH TRIMETHYLAMINE OXIDE

by

LI-JANE CHEN

THESIS

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PREVIEW

TABLE OF CONTENTS

I.	INTRODUCTION	1
II.	HISTORICAL SURVEY	5
	A. Structures and Bonding in Tricarbonyl(buta- diene)iron	5
	B. Chemical Behavior of The Diene-Iron Tricarbonyl Complexes	10
	C. Disengagement of Organic Ligands from Iron Tricarbonyl Complexes	15
III.	THEORETICAL SURVEY	18
	A. The Applicability of The 18-Electron Rule to Kinetic Stability	18
	B. Kinetic Application of Crystal Field Theory ..	18
	C. Valence Bond Theory of π -Hydrocarbon-Iron Tricarbonyl Complexes	22
IV.	EXPERIMENTAL SECTION	26
	A. Materials and Syntheses	26
	B. Kinetic Procedures and Analyses	29
V.	RESULTS AND DISCUSSION	86
VI.	REFERENCES	93
	APPENDIX I	96
	APPENDIX II	97
	VITA	99

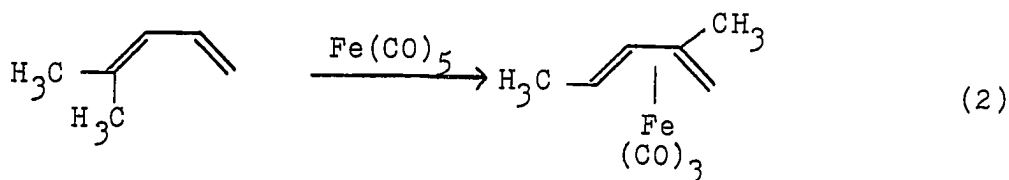
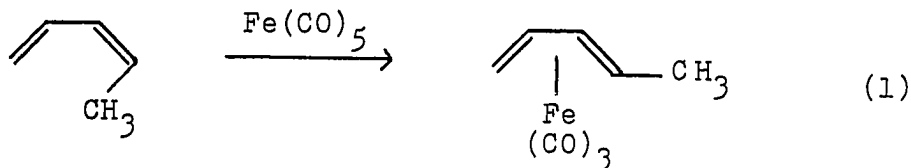
INTRODUCTION

Organometallic chemistry is one of the most vigorously developing fields in all of chemical science. During the last few years alone, organometallic systems have been central in the development of new theoretical insights, new laboratory syntheses, and even new industrial processes. One of the most interesting subfields in this area is that of the organometallic hydrocarbon complexes. Organometallic complexes are of considerable structural interest as well as of importance industrially as catalysts and as reagents in new synthetic routes to organic molecules. In recent years a large number of organometallic complexes have been isolated in which an olefin or some other unsaturated hydrocarbon species is bonded to an iron carbonyl residue. This type of bonding is general and well known in chemistry, and many of the transition metals other than iron are known to form analogous olefin metal complexes.¹ However, this thesis is mainly concerned with the tetrahapto iron tricarbonyl complexes (diene and aromatic hydrocarbon π -ligands).

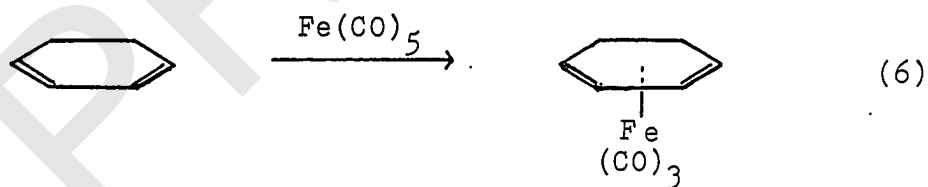
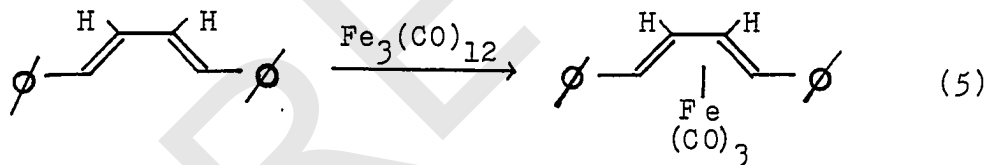
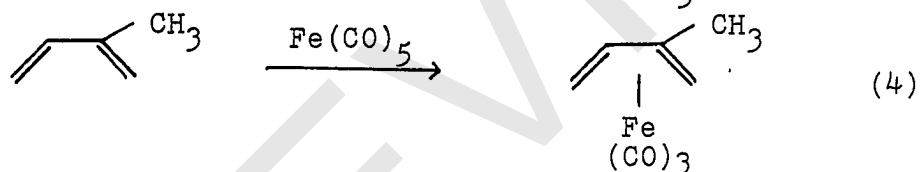
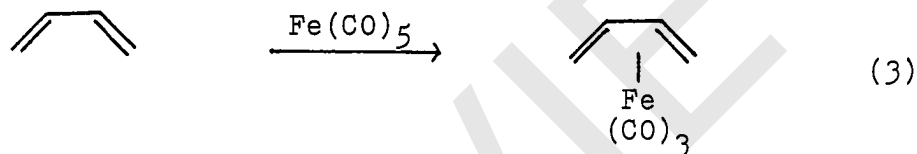
Tricarbonyl(diene)iron complexes are compounds in which both carbon monoxide and diene are bonded to a central iron atom. The nature of the diene-iron bonding can be presumed to involve interaction of¹ the iron atom valence orbitals with π -molecular orbitals of the diene system as a whole.

The iron atom is in a low oxidation state and the diene possess vacant π -orbitals that can stabilize low oxidation states. The conjugated nature of the diene system is considered to be an essential feature necessary for the formation of iron derivatives of this type² and back-bonding from metal to olefin is also considered to be important. The Dewar-Chatt-Duncanson bonding model incorporates these theoretical features and is generally accepted as a good first-order explanation for the bonding in these complexes.^{3,4}

The great majority of diene-iron tricarbonyl complexes have been made by direct action between diene and one of the three common ironcarbonyl reagents ($\text{Fe}(\text{CO})_5$, $\text{Fe}_2(\text{CO})_9$, $\text{Fe}_3(\text{CO})_{12}$), either by simply heating the reagents together or by means of a photochemical combination.⁵ There exists a limitation to this direct method of synthesis in the case of acyclic dienes having cis-alkyl substituents. Although these compounds may react with $\text{Fe}(\text{CO})_5$ to form diene-iron tricarbonyl complexes. The π -ligand in the complex invariably has the structure of a rearranged diene.⁶ As for examples in Eq. (1) and Eq. (2).



Conjugated diolefins that are known to form diene-iron tricarbonyl complexes include butadiene, isoprene, and 1,3-cyclohexadiene. The simple derivatives of butadiene which have been converted to the corresponding $\text{Fe}(\text{CO})_3$ complexes utilizing the direct reaction with $\text{Fe}(\text{CO})_5$ or $\text{Fe}_3(\text{CO})_{12}$ are given in Eqs. (3-6).



The diene-iron tricarbonyl complexes are relatively stable compounds; the stability depends on the nature of the π -ligand. This stability is reflected in the difficulty of removing the iron tricarbonyl moiety to regenerate the uncomplexed π -hydrocarbon. It has been found that the iron carbonyl residue can be conveniently removed by the action

of tertiary-amine oxides.²⁰ Removal of the iron residue by trimethylamine oxide in the presence of an additional reactant therefore allows a study of the reactions of the uncomplexed ligand. This is a very convenient technique for examining the chemistry of highly reactive and elusive species.⁷

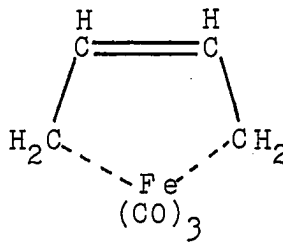
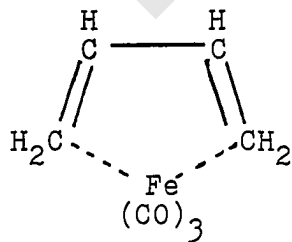
The main subject of the work described in this thesis is the kinetic stability of diene-iron tricarbonyl complexes in the presence of trimethylamine oxide. Consequently, the reactivity of diene-iron tricarbonyl complexes will be reviewed in the second chapter of this thesis, and the application of theory to kinetic stability will be surveyed. Kinetic experiments carried out by this author will then be used to establish the rate, order, and activation energies for decomposition of a typical complex, i.e. tricarbonyl-(1,4-diphenyl-1,3-butadiene)iron. Some previous data on other complexes, obtained and described in a previous thesis by Lin,⁸ will also be reanalyzed. A short description of a valence-bond theory for complexes of this type⁹ will be presented and it will be applied to yield explanations of the rate parameters.

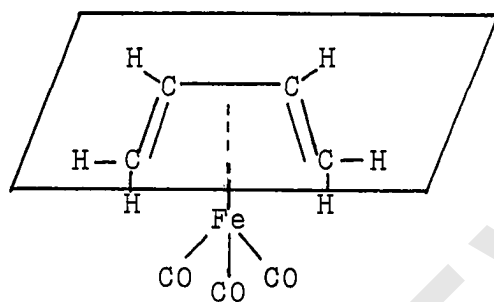
HISTORICAL SURVEY

A. Structures and Bonding in Tricarbonyl(butadiene)iron.

Buta-1,3-diene is a readily accessible and technically versatile diolefin which made a very early entry into π -complex chemistry. Tricarbonyl(butadiene)iron represents not only the first, but also the most thoroughly investigated, of the 1,3-diene-metal complexes.

In 1930 Reihlen and co-workers¹⁰ obtained butadiene-iron tricarbonyl by a reaction of butadiene with iron pentacarbonyl. These first workers, while attempting to elucidate the structure of ironpentacarbonyl, treated $\text{Fe}(\text{CO})_5$ with butadiene in a sealed tube at 150°C for several hours and obtained a product which analyzed as $\text{C}_4\text{H}_6\text{Fe}(\text{CO})_3$. They considered that the iron atom was bonded to the terminal carbon atoms of the diene and to three carbonyl groups. The cyclic structure (1) was proposed; however, they stated that the alternative structure (2) could not be ruled out.





(3)

In a reinvestigation in 1958, Hallam and Pauson¹¹ proposed a more delocalized type (3) of bonding between the olefinic ligand and the metal. They suggested that (a) the C_4H_6 is present in the planar cis configuration, (b) the iron atom is roughly equidistant from the four carbon atoms of the butadiene, and (c) the π -electrons of buta-1,3-diene are completely delocalized over the four carbon atoms. The overall molecular model used is shown in Figure 1.¹²

The interaction between iron tricarbonyl and diene involves the delocalization of electron density over an orbital system involving both iron tricarbonyl and diene. The molecular orbitals¹³ of butadiene and their possible interactions with iron orbitals are illustrated in Figure 2.

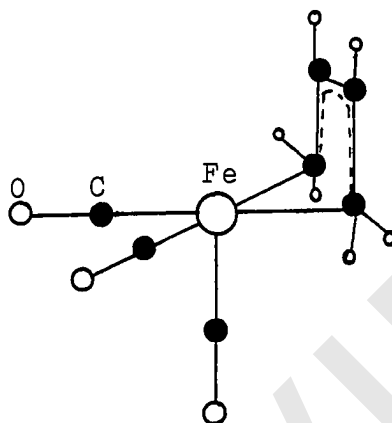


Fig. 1. Butadiene tricarbonyliron, $C_4H_6Fe(CO)_3$.

$$r(Fe-CO) = 1.798 \pm 0.015 \text{ \AA}$$

$$r(Fe-C) = 2.074 \pm 0.015 \text{ \AA}$$

$$r(C-C) = 1.413 \pm 0.015 \text{ \AA}$$

$$r(C-O) = 1.137 \pm 0.010 \text{ \AA}$$

The OC-Fe-CO bond angle was found to be $100.5 \pm 5.0^\circ$.

Representation of The metal orbitals which are most likely
M.O.s of butadiene to be important in the diene-metal bond

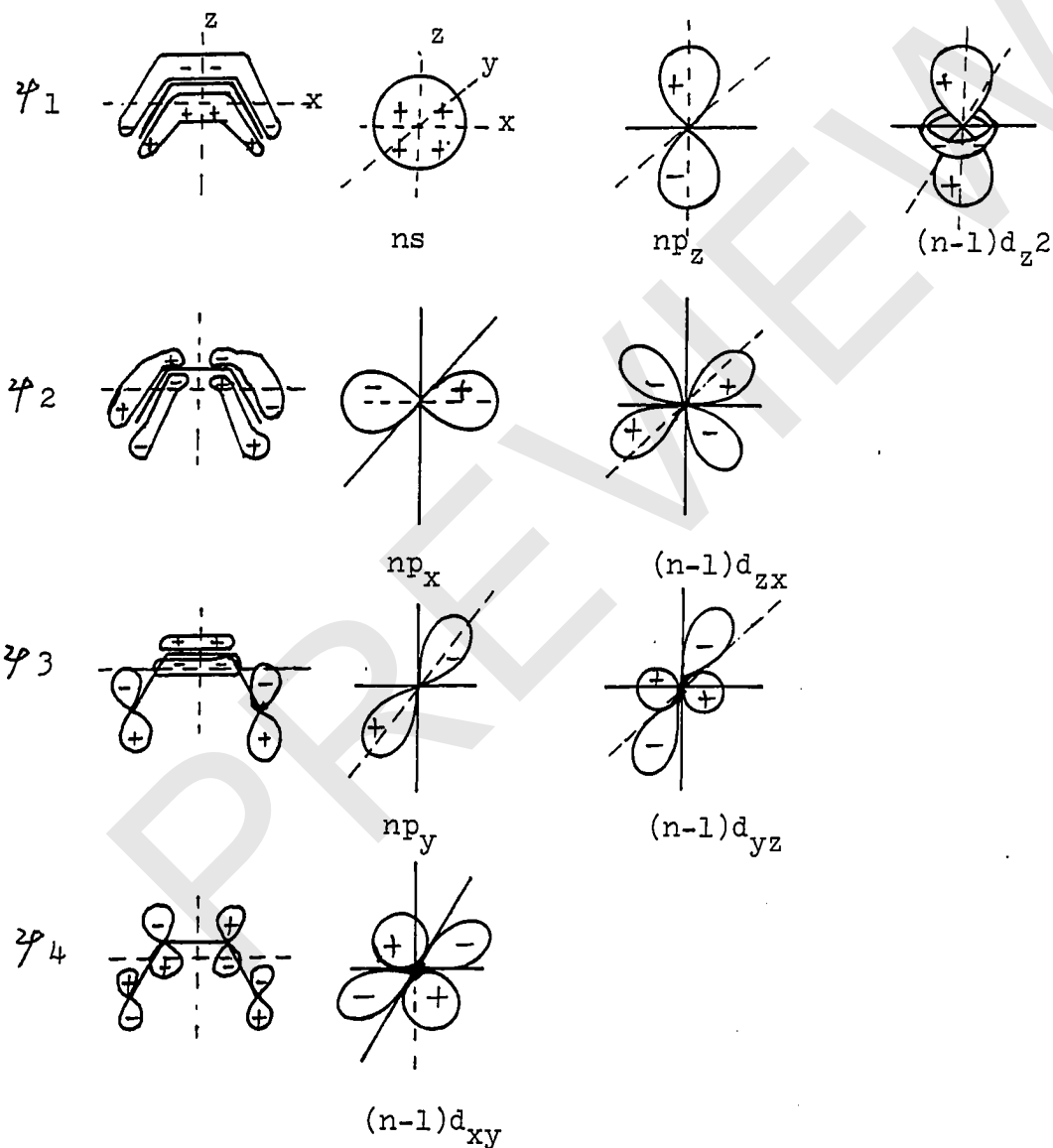


Fig. 2

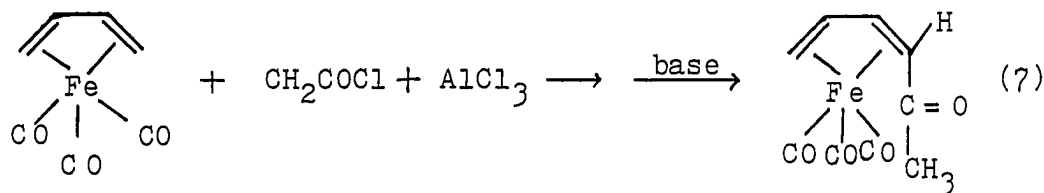
In the ground state of the free butadiene, ψ_1, ψ_2 will be occupied and ψ_3, ψ_4 unoccupied. On complexation overlap of ψ_1 with iron orbitals s, p_z and d_{z^2} ; and ψ_2 with p_x and d_{xz} corresponds to electron donation from butadiene to the iron orbitals. This is called "forward coordination". In addition, the lowest unoccupied level of the butadiene can overlap with the p_y and d_{zy} orbitals of the iron and would correspond to back donation from iron to butadiene. The extent of back coordination into ψ_3 depends on the nature of the other ligands on iron (the carbonyl groups).¹⁴ If the electron acceptor power of these groups is greater then back coordination into ψ_3 is diminished. Many compounds of the type $\text{Fe}(\text{CO})_3$ (conjugated diolefin) have an intense carbonyl absorption band at ν_a . 1980 cm^{-1} . With $\text{Fe}(\text{CO})_3(\text{C}_4\text{H}_6)$ the low frequency absorption is resolvable into two bands at 1985 and 1975 cm^{-1} .¹¹ With electro-negative substituents on the diene system the bands move to higher frequencies. It should be noted that back-bonding takes place by a conjugative electron displacement and involves electrons that are polarised fairly easily.¹⁵ Consequently, although in a specific metal complex there may only be a low degree of back-bonding to a particular ligand, this back-bonding will be increased under the influence of polarising forces. For example, it will be increased if a positive charge is generated in the ligand as the result of attack by an electrophile. This increased back-bonding would serve, of course, to stabi-

lize the positive charge and hence lower the energy of the transition state of the reaction. Therefore, we conclude that back-bonding is promoted by:

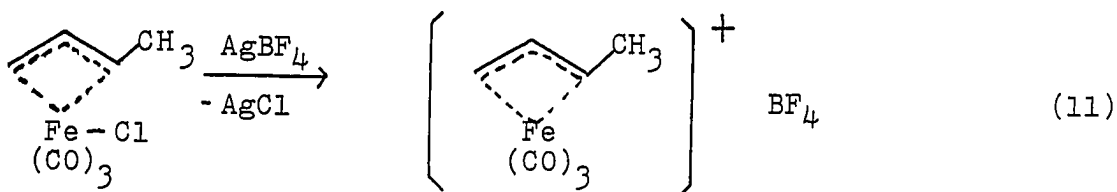
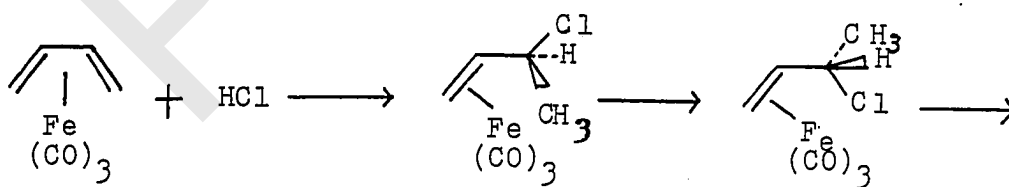
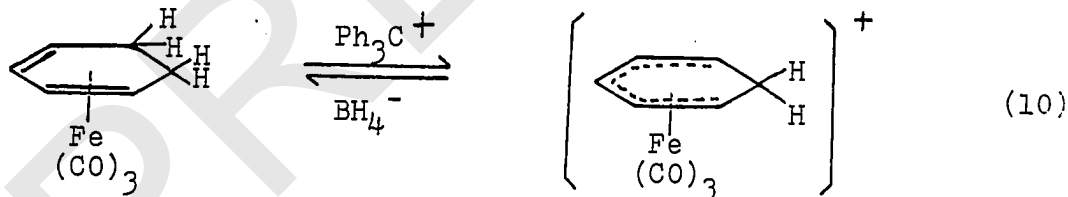
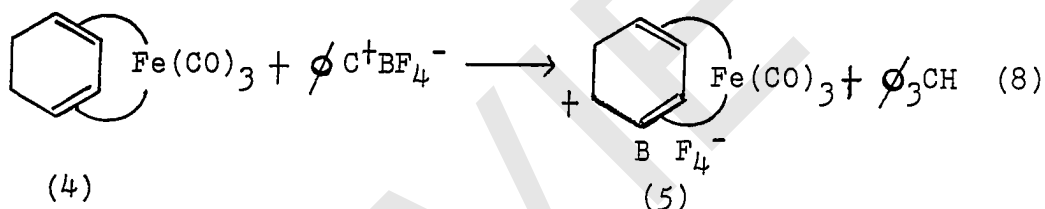
- (a) The metal being in a low oxidation state.
- (b) Strong σ -donor but weak π -acceptor ligands on the metal.
- (c) Electron-withdrawing substituents on the ligands.

B. Chemical Behavior of The Diene-Iron Tricarbonyl Complexes.

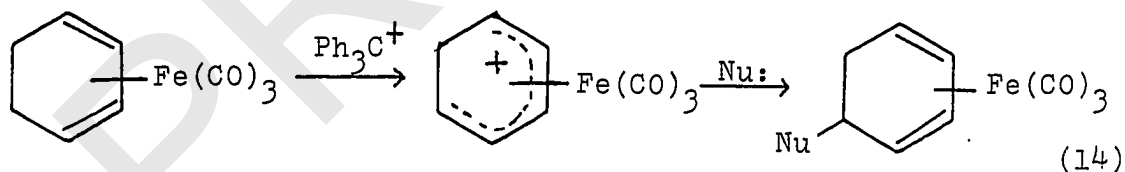
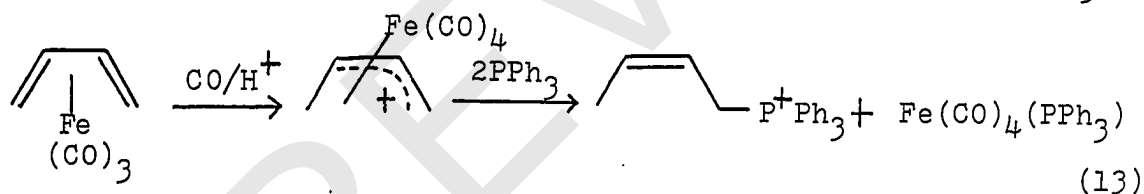
The chemical behavior of a diene- $\text{Fe}(\text{CO})_3$ complex is quite different from that of the free diene itself. A major problem is that the metal complex may not be stable enough to withstand the reaction conditions necessary to effect reactions at the π -bonded ligand. In cases where the complexes are stable, the usual kinds of organic reaction may be carried out, but the reactivity of the ligand is usually greatly modified by coordination with the metal. Some examples illustrate this point. 1,3-Butadienetricarbonyliron can be acetylated with acetyl chloride and aluminum chloride to form the 1-acetyl derivative,¹⁶ while the free ligand would be polymerized under the reaction conditions.



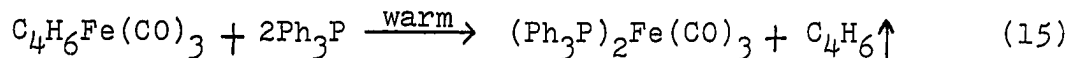
Fischer et al. have found that reaction of cyclohexadiene-iron tricarbonyl (4) with triphenylmethyl tetrafluoroborate¹⁷ produces cyclohexadienyliron tricarbonyl tetrafluoroborate (5) and triphenylmethane. The driving force for the hydride abstraction reaction stems largely from the stability of salts of the type (5). Some other examples are given in Eq. (9-11).¹⁸



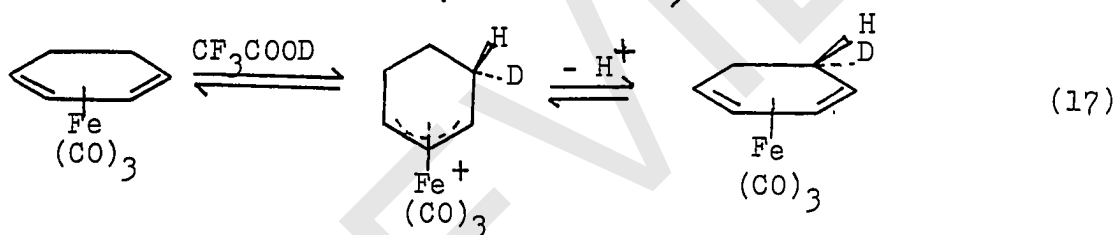
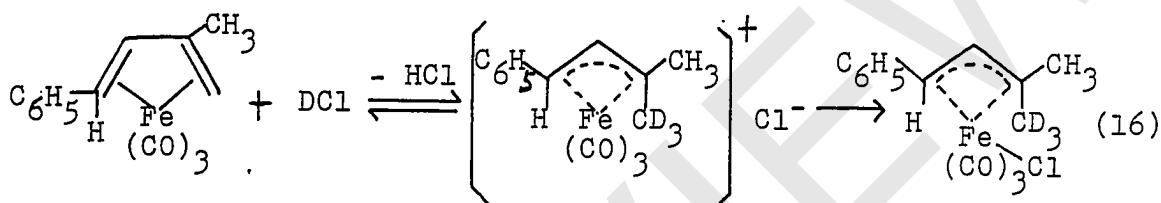
A useful feature of these metal-stabilised carbonium ions is that they can often be generated by reactions other than those involving the departure of conventional leaving groups from saturated carbon, e.g. by hydride abstraction or protonation of an unsaturated ligand. In some cases the ions are sufficiently stable for them to be isolated and stored in the form of salts which may subsequently be subjected to attack by nucleophiles.¹⁹



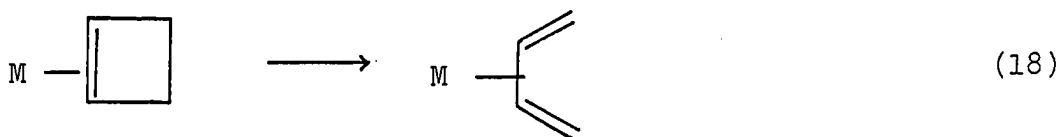
The iron tricarbonyl residue can easily be removed from the product of nucleophilic attack by mild oxidation.²⁰ Thus allowing the synthesis of many compounds difficult to obtain by other routes. Frequently the diene ligands may also be replaced by donor-acceptor molecules such as tertiary phosphines:²¹

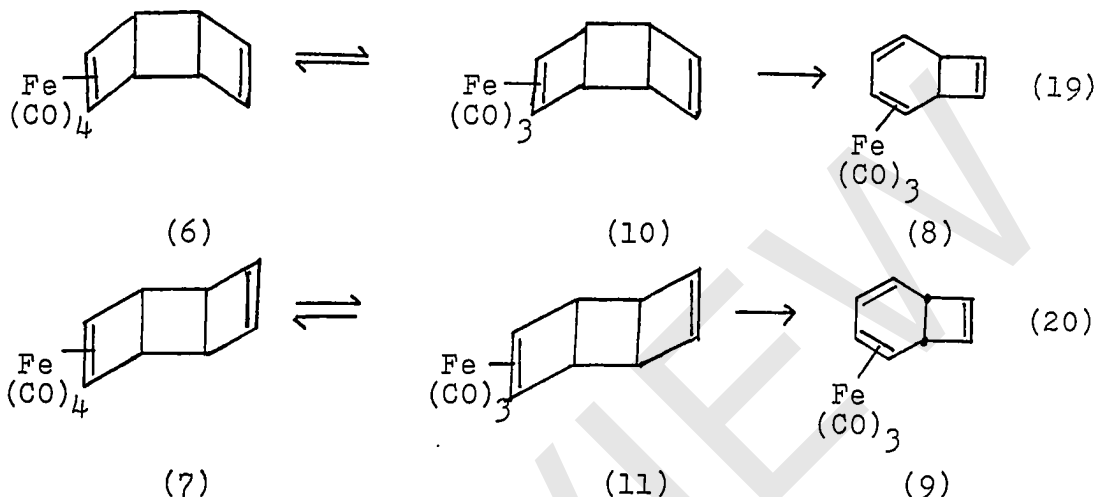


Treatment of tricarbonyl- π -1-phenyl-3-methyl butadiene iron with deuterium chloride in pentane produces the anti-trideuterated π -allylic product. The reversible deuteration of tricarbonyl- π -1,3-cyclohexadieneiron with deuterotrifluoroacetic acid likewise is specific.²²



In earlier experiments it was found that silver ions catalyzed the isomerization of strained cyclobutene derivatives to the corresponding butadiene derivatives.²³ The basic reaction involved the ring opening of a cyclobutene metal olefin complex Eq. 18.

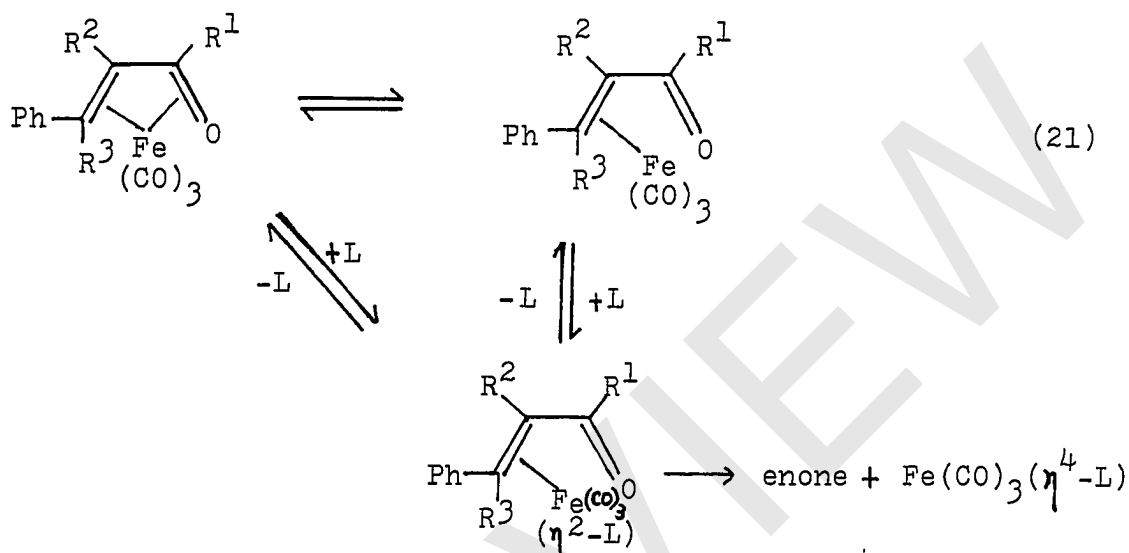




The iron-tetracarbonyl complexes of syn- and anti- tricyclooctadiene (6 and 7 respectively) were prepared. Each complex is readily converted to isomeric iron tricarbonyl complexes of bicyclooctatriene (8 and 9) upon heating in hexane.²⁴ The reactions involve thermal loss of a carbonyl ligand to generate the olefin-iron tricarbonyl complexes (10) and (11) and these undergo disrotatory cyclobutene ring opening reactions leading to the butadiene-Fe(CO)₃ complexes (8) and (9). These results support the assertion that strained cyclobutene-olefin metal complexes readily isomerize to butadiene-metal complexes via a disrotatory ring opening process as depicted in Eq. 18.

Some transition-metal-catalysed reactions of olefins and polyolefins involve olefin as a substituting ligand at a metal center. Burkinshaw and Howell²⁵ have investigated the displacement of enone from complexes with cyclohexa-1,3-diene

and 1,4-diphenylbutadiene.

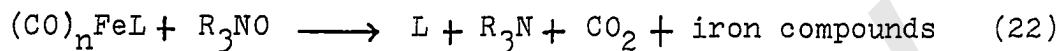


L = Cyclohexadiene, 1,4-Diphenylbutadiene.

C. Disengagement of Organic Ligands from Iron Tricarbonyl Complexes.

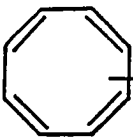
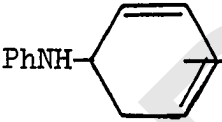
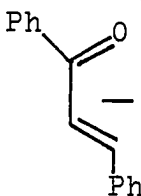
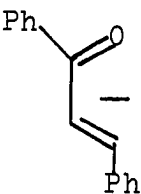
The disengagement of an organic ligand (L) from an iron carbonyl complex may be achieved by oxidizing the complex with ceric ammonium nitrate or ferric chloride in acetone or ethanol solution.²⁰ The inherent disadvantage of this method is the instability of the π -electron-rich organic ligands under the oxidative reaction conditions. Several years ago²⁰ it was discovered that trimethylamine oxide induced the release of the organic ligands (L) from the iron tricarbonyl complexes in good yields and without any detectable deterioration of the organic product. The nature of the reaction

is expressed in Eq. 22.



The results and conditions determined by Shvo and Hazum²⁰ for these disengagements are presented in Table 1. In each case the iron-free organic ligand of the listed complex was obtained.

Table 1.

Compound	yield %	Reaction, (Time/h.)	Solvent (Temp)
 -Fe(CO) ₃	95	1	Benzene (reflux)
 -Fe(CO) ₃	45	24	Acetone (25°C)
 -Fe(CO) ₃	70	12	Benzene (reflux)
 -Fe(CO) ₃	71	24	Benzene (25°C)

An intermediate compound in the decomplexation of a tricarbonyl iron complex using trimethylamine oxide has recently been demonstrated by Eekhof, Hogeveen, and Kellogg.²⁶ They isolated a dimethylamine substituted compound from the reaction of trimethylamine oxide with the tricarbonyl iron complex of 2,5-dimethylthiophen SS-dioxide. The structure of (12) was established from the ^{13}C n.m.r. spectral data and from the mass spectrum. A possible mechanism leading to the formation of (12) has been suggested by other workers.^{27,28} No additional mechanistic work on these disengagement reactions has been reported.

