Cyclobutadienemetal Complexes

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I. Introduction

Cyclobutadiene (C_4H_4) is a deceptively simple organic molecule which has captured the imagination of generations of chemists for over 100 years. Kekulė[1] was the first to turn his attention to cyclobutadiene ("diacetylene") while attempting a total synthesis of a benzene derivative from aliphatic components. Around the turn of the century, Willstätter and Schmaedel[2] reported an unsuccessful synthesis which was specifically directed at the obtainment of cyclobutadiene. Subsequent synthetic efforts, until 1965, to isolate the parent cyclobutadiene molecule or some of its simply substituted derivatives had been met with bitter disappointment,[3] although in the meantime considerable evidence for their intermediacy in certain reactions had been accumulated.[3-5] A crucial breakthrough in resolving the "cyclobutadiene problem" was achieved in 1965 when Pettit and his co-workers reported the first successful generation and trapping of the parent cyclobutadiene[6] from its iron tricarbonyl complex.[7] This dramatic development was made possible owing to the impact of organometallic chemistry and in particular the increased awareness that fixation of unstable molecules could be achieved by complexation to transition elements.[8,9] Meanwhile, a whole series of organic precursors has become available for the generation of the parent as well as substituted cyclobutadienes, and these synthetic aspects have been dealt with in several recent reviews.[10,11] Among these synthetic procedures, noteworthy in particular is that which has led to the generation of the parent molecule by the irradiation of photo-α-pyrone in noble gas matrices at temperatures of 8–20 K and the recording of its infrared spectrum. This important achievement, reported independently by Krantz[12] and Chapman[13] and their co-workers, was accomplished primarily by the refinement of the matrix-isolation technique, since Rosenblum and his co-workers had demonstrated the utilization of photo-α-pyrone in the preparation of cyclobutadiene complexes[14,15] some 5 years earlier.

The theoretical aspects of the "cyclobutadiene problem" have been examined rather extensively. In the early 30's, Hückel's rule[16] of $(4n + 2)$ π electrons as a criterion for aromaticity provided a basis for the contrasting properties of benzene and cyclobutadiene. According to this rule, benzene is the simplest representative in the series of $4n + 2$ aromatic systems, whereas cyclobutadiene is the prototype of the $4n$ class of molecules which exhibit no particular stabilization in spite of the conjugated arrangement of its double bonds. Application of the simple Hückel MO treatment[17] to square-planar (D_{4h}) cyclobutadiene affords four molecular orbitals: one bonding, two nonbonding, and one antibonding. The filling of electrons into these energy levels can be accomplished in a number of ways, two of which, a square triplet (ST) and square singlet (SS) ground states, are depicted in Figure 1. Hund's rule suggests that the former arrangement with parallel spins will be of lower energy. More recently, numerous theoretical studies by ab initio[18] and semiempirical[19] SCF as well as by MINDO/3[20] procedures have mostly agreed in predicting a rectangular (D_{2h}) singlet (RS) to be the ground state of cyclobutadiene. These various methods also mostly concur in predicting the ST to be energetically favored over the SS. A view contrasting with the above has been expressed in a recent paper,[21] in which it was shown that when

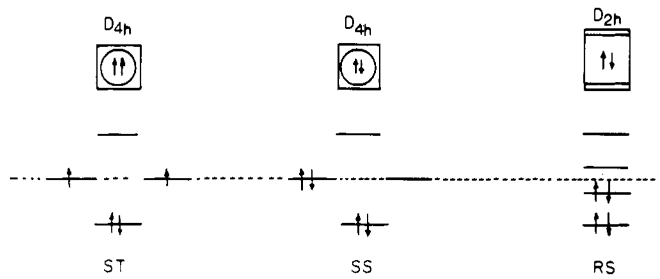


Figure 1. Filling of electrons into the energy levels of square triplet (ST), square singlet (SS), and rectangular singlet (RS) free cyclobutadiene.

cognizance is taken of the importance of the effects of electron repulsion in open-shell systems in MO calculations, a square or effectively square singlet can, in fact, be the ground state of cyclobutadiene. In view of the theoretical aspects, noteworthy in particular is the growing body of experimental results on related issues. The infrared spectra of the matrix-isolated cyclobutadiene[12,13,22] and its dideuterio derivative[23] indicate strongly in favor of square ground state. Implication of current theory[18,19,22] would seem to require this to be ST, although the possibility of an excited square triplet has also been raised.[20] The stereospecific addition of cyclobutadiene, generated from its iron tricarbonyl complex, to dienophiles[24] is consistent with the free molecule being either RS or SS; the former possibility is particularly appealing in view of the behavior of the vicinal diphenyl derivative of cyclobutadiene which appears to exist as two valence tautomers separated by a quite high activation barrier.[25]

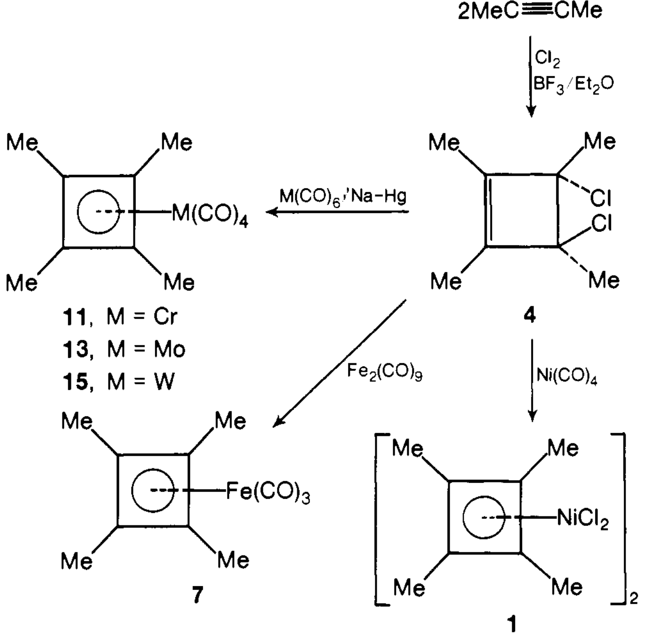
The significant role played by organometallic chemistry in resolving some of the aspects of the "cyclobutadiene problem" has already been cited, briefly, earlier. The field of cyclobutadienemetal complexes started with the 1956 theoretical prediction by Longuet-Higgins and Orgel,[26] who pointed out that the presence of two unpaired electrons in the nonbonding orbitals of the ST, which are of proper symmetry to permit overlap with suitable metal orbitals, would lead to stabilization of cyclobutadiene by complexation to a metal. Some specific types of complexes, such as $C_4H_4AuCl_2^+$ and $C_4H_4Ni(CO)_2$, whose plausible formation was predicted have not yet been synthesized. Nonetheless, the main aspects of this remarkable prediction soon after materialized with the preparations, in 1959, of $[Me_4C_4NiCl_2]_2$ (**1**) by Criegee and Schröder[27] and $Ph_4C_4Fe(CO)_3$ (**2**) by Hübel and his co-workers.[28,29] The x-ray crystal structures of **1**[30] and **2**[31,32] have subsequently confirmed the presence of a substituted cyclobutadiene ligand in these complexes. Beyond the initial discoveries, it would perhaps be pertinent to mention at this stage some of the highlights in the development of the chemistry of cyclobutadienemetal complexes.[8] In the early 60's, Maitlis and his co-workers discovered the π-cyclobutadiene ligand transfer reaction which led to the preparation of a considerable number of novel tetrasubstituted cyclobutadienemetal complexes.[33,34] The first complex with the parent cyclobutadiene ligand, $C_4H_4Fe(CO)_3$ (**3**), was synthesized in 1965 by Pettit and his co-workers and shown to behave as a typical aromatic system.[35] More recently, Giering and his co-workers have reported the generation and trapping of the first known examples of complexes containing η^2-cyclobutadienoid ligands.[36,37]

The area of cyclobutadienemetal complexes has previously been reviewed.[3,33,38] The large volume of work which has appeared in the literature during the last few years and the enormous interest in the utilization of certain cyclobutadienemetal complexes in organic synthesis[39] have prompted the writing of this current review.

The following abbreviations are used in this review:

Ac	acetyl
acac	acetylacetonate
amb	ambient temperature (~25 °C)
Cp	cyclopentadienyl
facac-	hexafluoroacetylacetonate
DMF	*N,N*-dimethylformamide
Fp	cyclopentadienyldicarbonyliron
phen	*o*-phenanthroline
py	pyridine
To	*p*-tolyl
Ts	tosyl
$\boxed{\textcircled{\pi}}$	schematic representation of cyclobutadieneiron tricarbonyl used in the description of certain organic reactions

SCHEME I



II. Syntheses of Cyclobutadienemetal Complexes

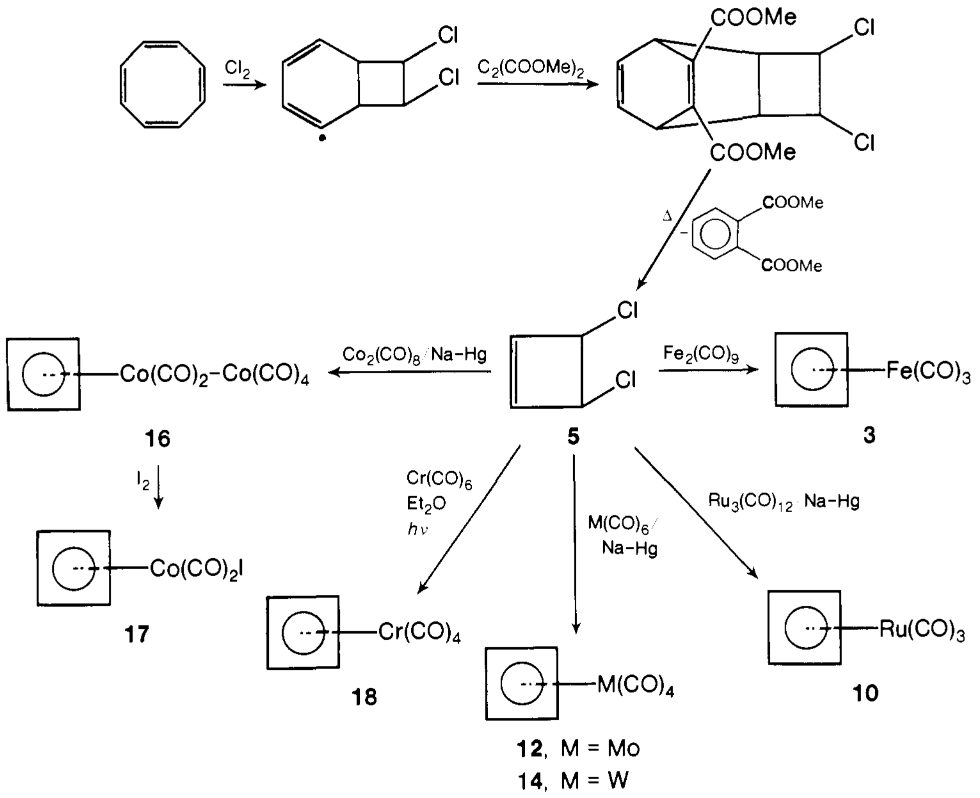
The various methods and procedures used in the preparation of *tetrahapto*cyclobutadiene (sections A–C) and *dihapto*cyclobutadiene (section D) complexes of the transition elements are discussed below. The free ligands, namely, the parent cyclobutadiene and its simply substituted derivatives, are extremely labile, and consequently they cannot be used directly in the syntheses of the complexes. All of the currently known synthetic routes to cyclobutadienemetal complexes involve indirect approaches. Noteworthy in particular are the organic precursors from which the coordinated cyclobutadiene ligands are constructed. For the benefit of the readers, the syntheses of some of the more common precursors will be cited in brief during the discussion in this chapter.

A. Preparation of *Tetrahapto*cyclobutadienemetal Complexes Starting from Cyclobutene and Cyclobutane Derivatives

1. Halocyclobutene Route

The dehalogenation of 3,4-dihalocyclobutenes in the presence of metal carbonyls is potentially the most straightforward route for the synthesis of cyclobutadienemetal complexes. The main disadvantage of this synthetic approach is the limited availability of suitable dihalocyclobutenes. In 1959, Criegee and Schröder[27] reported the preparation of **1** by the reaction of *trans*-3,4-dichloro-1,2,3,4-tetramethylcyclobutene (**4**)[40] with $Ni(CO)_4$. Incidentally, the nickel complex **1** is one of the original two cyclobutadienemetal complexes first to be reported. A similar reaction between the dibromo analog of **4** and $Ni(CO)_4$ gave

SCHEME II



$[Me_4C_4NiBr_2]_2$.[41] Modifications of the original synthesis which avoid the use of $Ni(CO)_4$ have also been reported. For instance, 3,4-diiodo-1,2,3,4-tetramethylcyclobutene on reaction with Raney nickel gave $[Me_4C_4NiI_2]_2$,[42] and treatment of **4** with a mixture of lithium naphthalenide and $NiBr_2$ at low temperature afforded a nearly quantitative yield of **1**.[43]

A significant development in this area came in 1965 when Pettit and his co-worker reported the synthesis of the parent cyclobutadieneiron tricarbonyl (**3**)[7,44] by the reaction of *cis*-3,4-dichlorocyclobutene (**5**)[45,46] with $Fe_2(CO)_9$. Alternative methods[39] for the preparation of **3** include the reaction of **5** with either $Na_2Fe(CO)_4$ or irradiation with $Fe(CO)_5$; however, these procedures are considerably less convenient than the one cited above[44] which utilizes $Fe_2(CO)_9$. The successful dehalogenation of other dihalocyclobutenes including **4**, 3,4-dibromo-1,2-diphenylcyclobutene, and dibromobenzocyclobutene (**6**)[47] with $Fe_2(CO)_9$ was shown to afford the respective complexes tetramethylcyclobutadieneiron tricarbonyl (**7**),[48,49] 1,2-diphenylcyclobutadieneiron tricarbonyl (**8**),[48] and benzocyclobutadieneiron tricarbonyl (**9**)[7] (see Schemes I–III) In some instances, the dehalogenation of dihalocyclobutenes with the sodium salt of metal carbonyls has been found to provide a more facile synthetic route to the desired complexes. For example, the sodium salts prepared by the treatment of $Ru_3(CO)_{12}$, $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, and $Co_2(CO)_8$ with sodium amalgam in tetrahydrofuran reacted with either **4** and/or **5** to afford the cyclobutadiene complexes of ruthenium (**10**),[49] chromium (**11**),[49] molybdenum (**12** and **13**),[49] tungsten (**14** and **15**),[49] and cobalt (**16** and **17**)[50] as appropriate. In a somewhat different procedure, the cyclobutadiene- and benzocyclobutadienechromium complexes **18** and **19** were obtained by the treatment of a previously photolyzed etherate solution of $Cr(CO)_6$ with the dihalocyclobutenes **5** and **6**, respectively.[51] In these instances, the active dehalogenating agent was presumed to be a chromium carbonyl etherate intermediate.

A noteworthy development which ultimately provided a variety of 1,2-dimethylcyclobutadienemetal derivatives came with the discovery that 1,5-hexadiynes (**20**) undergo thermal rearrangement to give **21**[52] (Scheme IV). The treatment of the latter with HCl affords a mixture of dichlorocyclobutene isomers (**22**)[53] with vicinal dimethyl substituents. Brune and his co-workers had employed the dichlorocyclobutenes (**22**), synthesized by the above cited procedure, in the preparation of an extensive series of iron (**23**) and nickel (**24**) cyclobutadiene complexes including **23** [$R_1 = R_2 = H$;[54] $R_1 = H$, $R_2 = Me$;[54] $R_1 = R_2 = Me$[54] (the same as **7**);[49] $R_1 = R_2 = Et$;[55] $R_1 = Me$, $R_2 = Et$;[55] $R_1 = R_2 =$ *i*-Pr;[56] $R_1 = Me$, $R_2 =$ *i*-Pr;[56] $R_1 = H$, $R_2 = Et$;[57] $R_1 = H$, $R_2 =$ i-Pr][58] and **24** [$R_1 = R_2 = H$; $R_1 = H$, $R_2 = Me$; $R_1 = Me$, $R_2 = Et$; $R_1 = Me$, $R_2 =$ *i*-Pr; $R_1 = R_2 = Et$; $R_1 = R_2 =$ *i*-Pr].[59] In one

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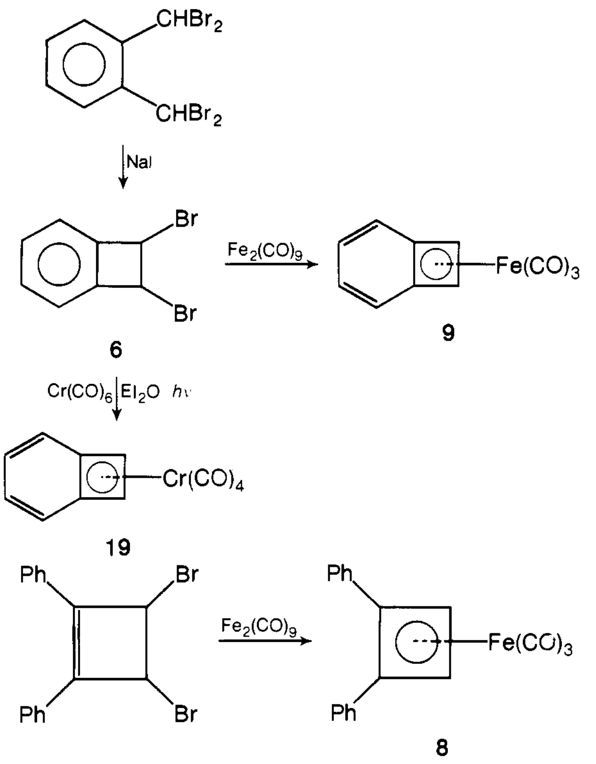
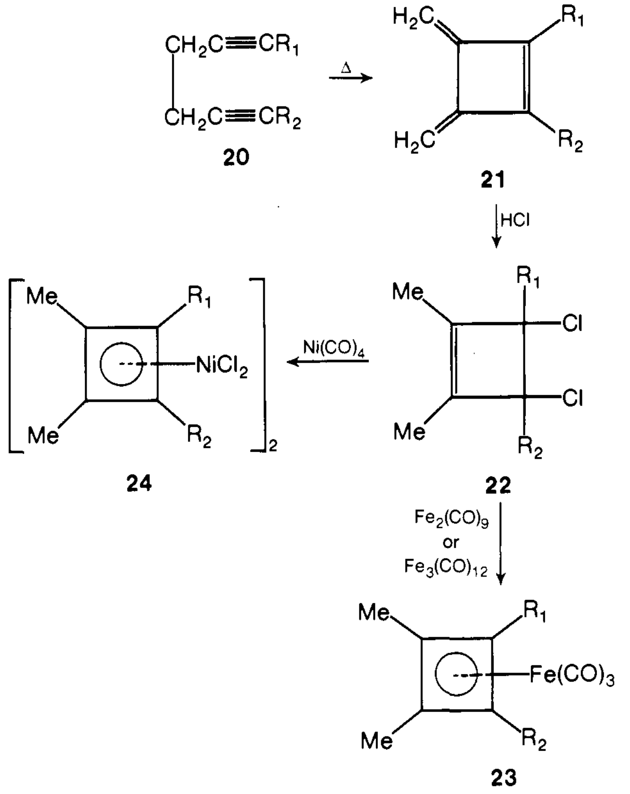
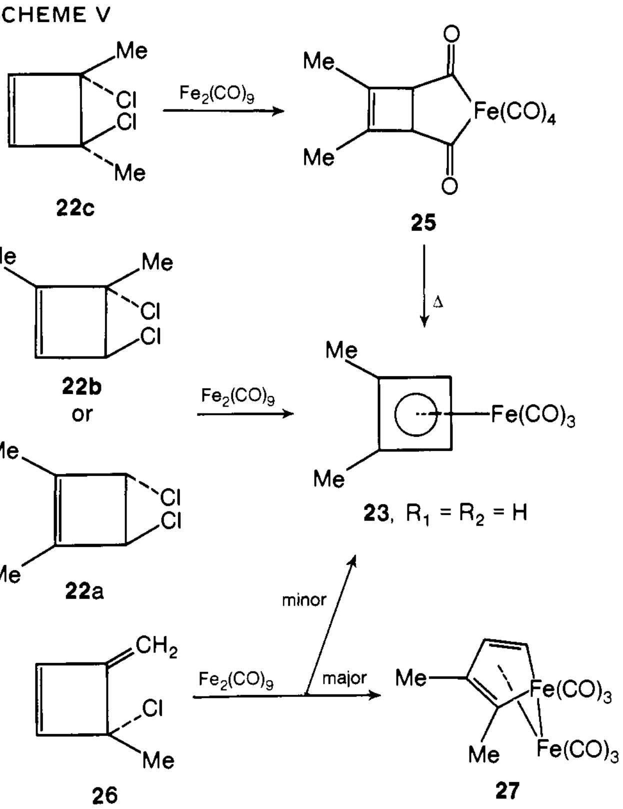


SCHEME IV



SCHEME V



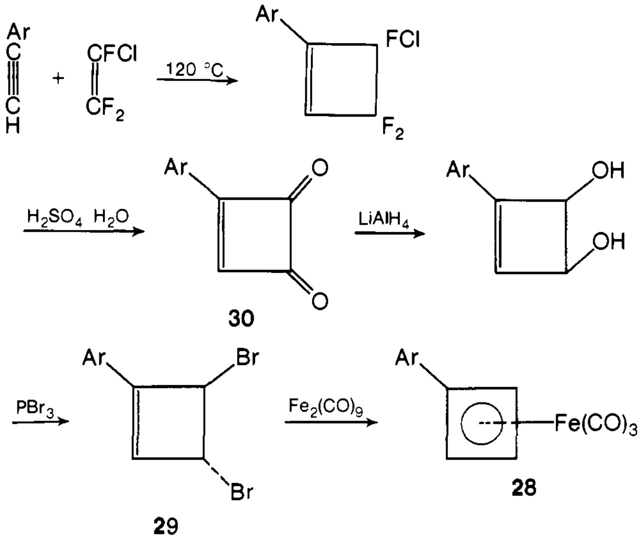
instance, the individual isomers of **22** ($R_1 = R_2 = H$) [*trans*-3,4-dichloro-1,2-dimethylcyclobutene (**22a**), *trans*-3,4-dichloro-2,3-dimethylcyclobutene (**22b**), and *trans*-3,4-dichloro-3,4-dimethylcyclobutene (**22c**)] were separated and their reactions with $Fe_2(CO)_9$ followed. It was found[60] that both **22a** and **22b** reacted with $Fe_2(CO)_9$ to afford **23** ($R_1 = R_2 = H$), whereas, the sole organometallic product from a similar reaction with **22c** was the dibridged acyl tetracarbonyliron complex **25** which under thermal conditions at 140 °C could be converted to **23** ($R_1 = R_2 = H$) (Scheme V). These results suggest that the dehalogenation of the 3,4-dichlorocyclobutene isomers does not necessarily proceed via the same mechanism, and furthermore, indicate the plausibility of acyl intermediates in certain such processes. A somewhat different reaction between 3-methyl-3-chloro-4-methylenecyclobut-1-ene (**26**) and $Fe_2(CO)_9$ was shown[61] to give the 2,3-dimethylferrole complex **27** as the major product (10% yield), in addition to small amounts (2% yield) of **23** ($R_1 = R_2 = H$).

The synthesis of para-substituted phenylcyclobutadieneiron tricarbonyl derivatives (**28**) was achieved by the reaction of 3,4-dibromo-2-arylcyclobutene (**29**),[62,63] prepared from arylcyclobutene-1,2-dione (**30**), with $Fe_2(CO)_9$ (Scheme VI). The dione **30** used in this synthesis was obtained by the thermal addition of arylacetylene to trifluorochloroethylene followed by hydrolysis with concentrated sulfuric acid.[64] The monoarylcyclobutadieneiron complexes prepared by this procedure include **28** [Ar = p-XC_6H_4; X = H,[62] CH_3,[63] F,[63] Cl,[63] Br[63]].

Among the halocyclobutenes whose reactions with $Fe_2(CO)_9$ have been examined, noteworthy are the trihalocyclobutenes. The reaction of *cis*-3,4-dichloro-1-chlorocyclobutene (**31**)[65] with $Fe_2(CO)_9$ at 60 °C gave the chlorocyclobutadieneiron complex **32**,[66] whereas, *cis*-3,4-dichloro-1-bromocyclobutene (**33**)[65] under similar conditions reacted[67] to afford the halogen-free bimetallic complex **34**, instead of bromocyclobutadieneiron tricarbonyl (**35**) (Scheme VII). The bromocyclobutadieneiron complex **35** was ultimately prepared[68] by the reaction of *trans*-3,4-dibromo-1-bromocyclobutene (**36**) with $Fe_2(CO)_9$ at 45 °C in pentane–hexane mixture.

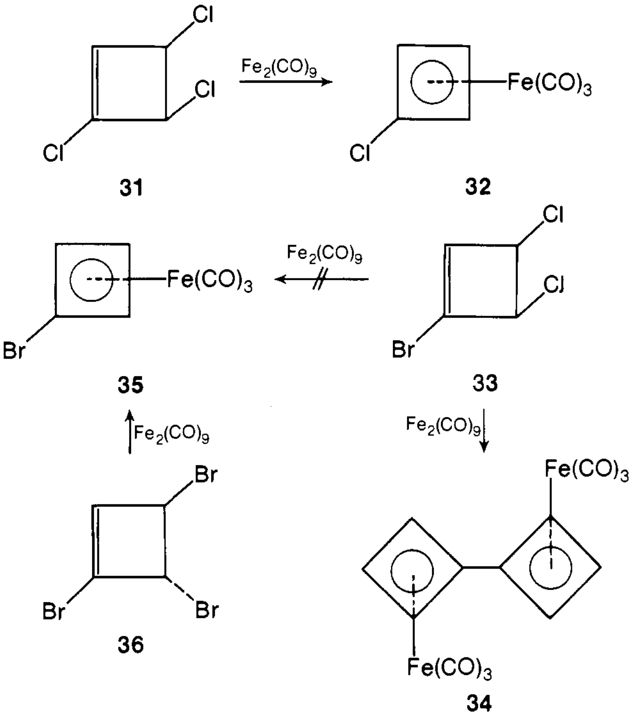
Another cyclobutadieneiron complex, whose preparation from the appropriate dichlorocyclobutene precursor and $Fe_2(CO)_9$ has also been reported in brief, is tri(*tert*-butyl)cyclobutadieneiron tricarbonyl.[69]

SCHEME VI

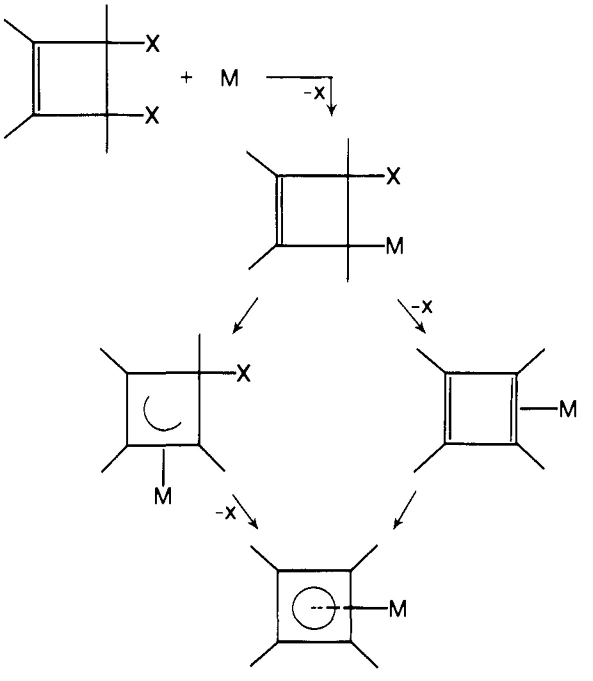


The mechanisms of formation of cyclobutadienemetal complexes from halocyclobutenes have not yet been established. It is almost certain that the complexation process does not proceed via a free cyclobutadiene ligand. Plausible intermediates involved in the construction of the complexed ligand are the metal bound *monohapto*cyclobutene, *dihapto*cyclobutadiene, and/or *trihapto*cyclobutenyl; numerous stable complexes with related ligands have already been synthesized and will be discussed at a later stage in this review. Possible sequences which depict the development of a coordinated cyclobutadiene by the dehalogenation of dihalocyclobutene with a metal (M) complex are shown in Scheme VIII. It should, however, be pointed out that

SCHEME VII



SCHEME VIII. Mechanism Proposed for the Formation of Coordinated Cyclobutadiene from Dihalocyclobutene

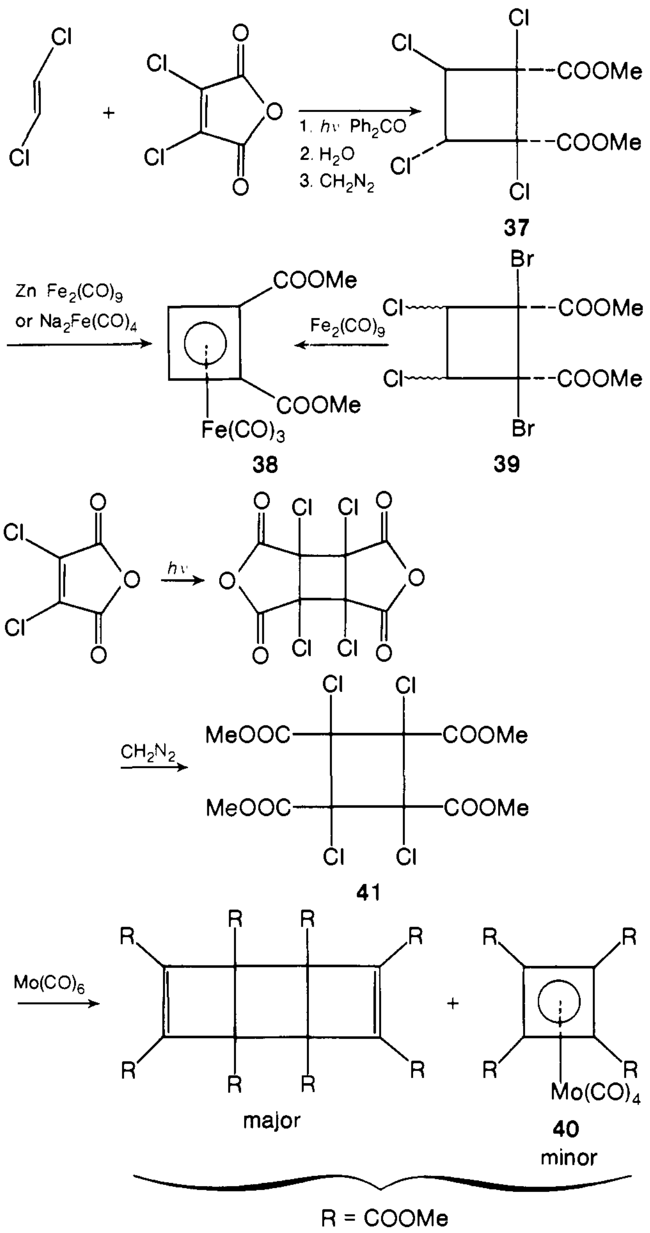


the participation of other intermediates, and in particular acyl intermediates, cannot be ruled out as was indicated earlier.[61] Another point of interest has to do with reactions between dihalocyclobutenes and metal carbonyl anion complexes which do not afford cyclobutadienemetal complexes; these reactions will be mentioned in conjunction with *dihapto*cyclobutadienemetal complexes (section II.D).

2. Halocyclobutane Route

In 1969, Roberts et al.[70] reported the synthesis of the dicarboxylate methyl ester of tetrachlorocyclobutane (**37**) by the photolysis of *trans*-1,2-dichloroethylene with dichloromaleic anhydride, using benzophenone as a sensitizer, followed by treatment of the hydrolyzed product with diazomethane. In the presence of $Fe_2(CO)_9$ and activated zinc dust, the tetrachlorocyclobutane **37** reacted to afford the diester iron complex **38** in 7-9% yield. Subsequently, it has been found[71] that by using $Na_2Fe(CO)_4$, instead of $Fe_2(CO)_9$, the yield of **38** could be improved to 35-40%. The same product **38** was also obtained[72] by a similar procedure from the dicarboxylate methyl ester of dichlorodibromocyclobutane (**39**) and $Fe_2(CO)_9$ (Scheme IX). Noteworthy also is the preparation of the tetra(carbomethoxy)cyclobutadienemolybdenum tetracarbonyl (**40**) which was obtained[73] as a minor product in the reaction between $Mo(CO)_6$ and the tetrachlorocyclobutane derivative **41**; the latter was synthesized by the self-dimerization of dichloromaleic anhydride in acetone under irradiation.

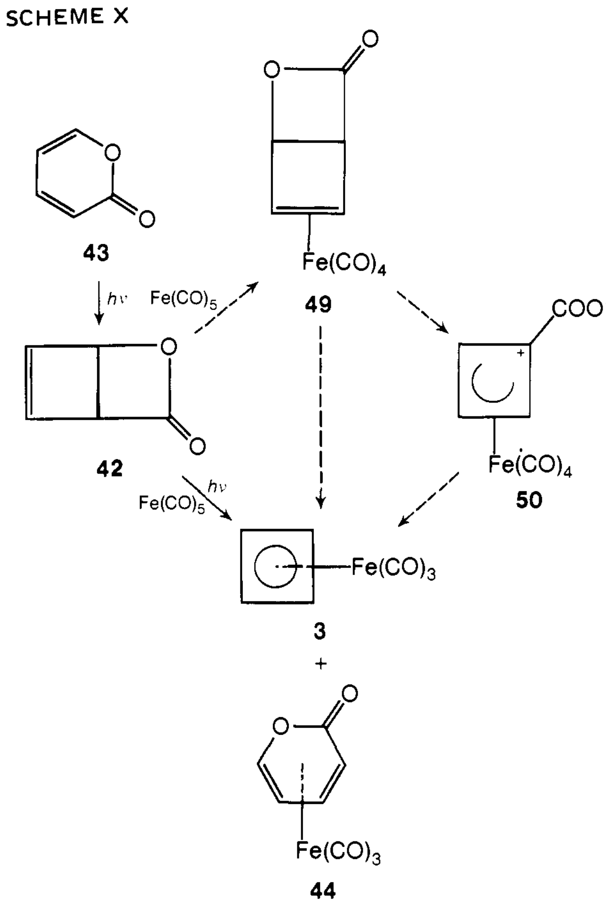
SCHEME IX



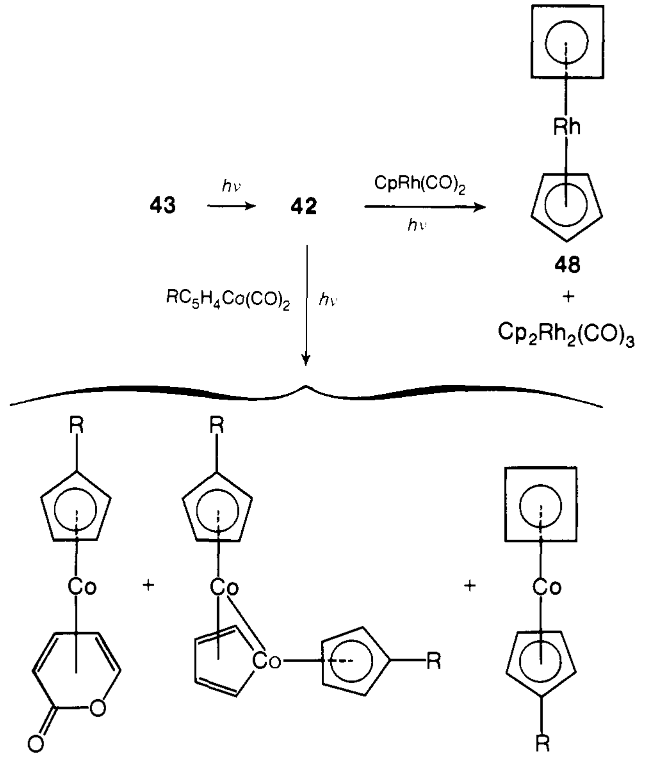
3. Photo-α-pyrone Route

Photo-α-pyrone (**42**), a molecule which contains a cyclobutene unit, is obtained in nearly quantitative yield by the photolysis of α-pyrone (**43**) (Scheme X).[74] In 1967, Rosenblum and Gatsonis reported[14] the synthesis of the parent cyclobutadieneiron complex **3** by the brief irradiation of **42** with $Fe(CO)_5$. A second product from this reaction is the α-pyroneirontricarbonyl (**44**). In a similar procedure, the photoproduct obtained by the irradiation of 3-carbomethoxy-2-pyrone was shown to react with

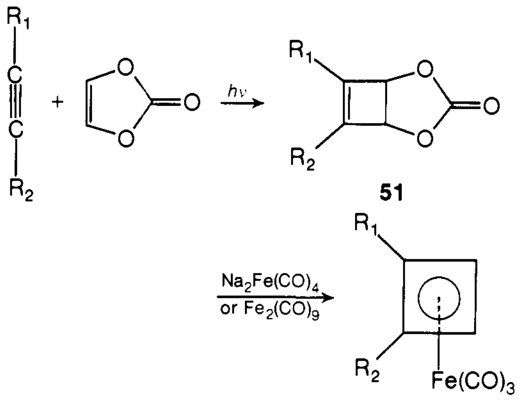
SCHEME X



SCHEME XI



46, R = H
47, R = COOMe



(1)

3, $R_1 = R_2 = H$
23, $R_1 = R_2 = Me$
52, $R_1 = H$; $R_2 = Bu$
53, $R_1 = H$; $R_2 = CH_2OMe$
54, $R_1 = Me$; $R_2 = CH_2OMe$

$Fe(CO)_5$ to afford carbomethoxycyclobutadieneiron tricarbonyl (**45**),[75] in 21% yield. This synthetic route was also extended to the preparation of cyclobutadiene complexes of cobalt **46**[15,76] and **47**[76] and rhodium **48**[77] (see Scheme XI). The mechanism of this reaction was presumed to involve the substitution of a carbonyl by photo-α-pyrone followed by the loss of CO_2 from the intermediate (e.g., **49**),[14] which may proceed either in a concerted fashion or stepwise (e.g., via **50**; see Scheme X).

4. *cis-3,4-Carbonyldioxycyclobutene Route*

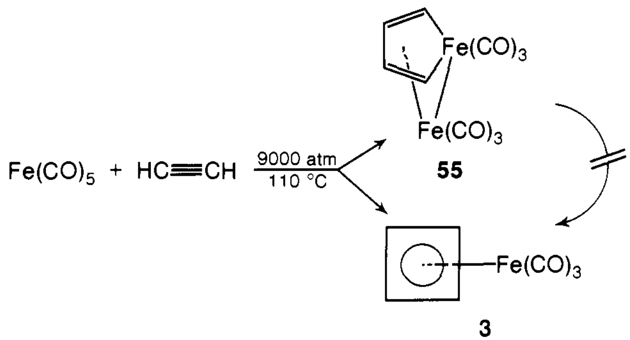
The treatment of *cis*-3,4-carbonyldioxycyclobutenes (**51**),[78] prepared by the irradiation of vinylene carbonate with alkynes, with either $Fe_2(CO)_9$ or, preferably, $Na_2Fe(CO)_4$ gave the parent cyclobutadieneiron tricarbonyl (**3**) as well as the iron tricarbonyl complexes with butylcyclobutadiene (**52**) and 1,2-dimethylcyclobutadiene (**23**)[54] ligands (eq 1). This procedure was ultimately extended to the synthesis of methoxymethylcyclobutadieneiron tricarbonyl (**53**)[79] and 1-methyl-2-methoxymethylcyclobutadieneiron tricarbonyl (**54**).[80] In general, this technique affords the respective iron complexes in yields ranging from 25 to 50% depending on the organic precursor (**51**) which is utilized in the reaction.

B. Preparation of *Tetrahapto*cyclobutadienemetal Complexes Starting from Alkynes and Alkadiynes

The reactions of alkynes with transition metal complexes in general and metal carbonyls in particular have been extensively studied during the last three decades.[81] These reactions are known to afford a large variety of organic and/or organometallic products. Reactions to be discussed in this section are those which directly or indirectly lead to the formation of cyclobutadienemetal complexes.

1. *Reactions of Alkynes with Metal Carbonyl Derivatives and Organometallic Compounds*

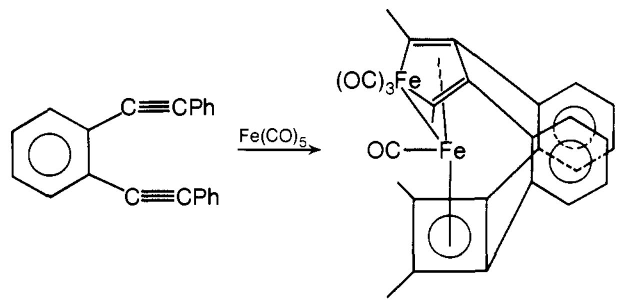
Tetraphenylcyclobutadieneiron tricarbonyl (**2**) was already prepared in 1959 by Hübel and his co-workers[28,29] from the high-temperature reaction between diphenylacetylene and $Fe(CO)_5$. The major product of this reaction was tetraphenylcyclopentadienoneiron tricarbonyl rather than **2**. A somewhat improved yield of **2** was claimed[82] from the reaction of Ph_2C_2 with $Fe(CO)_5$ which was carried out in a sealed tube at 240 °C. A low yield (~4%) of **2** was also obtained[83] from the reaction of Ph_2C_2 with cyclooctatetraeneiron tricarbonyl. Particularly noteworthy is the reaction of $Fe(CO)_5$ with HC≡CH, conducted at 110 °C and 9000 atm, which among other products gave[84] the parent cyclobutadieneiron complex **3** as well as the metallocycle complex **55** (eq 2). Significantly, the metallocycle **55** was reported not to be an intermediate in the formation of **3**, since



(2)

all attempts to affect the conversion of the former into the cyclobutadieneiron complex under the reaction conditions were apparently unsuccessful. It should be pointed out that the above cited reaction is the only known example for the formation of a parent cyclobutadienemetal complex by cyclodimerization complexation of acetylene.

An interesting metallocycle-cyclobutadiene complex of iron (**56**) was prepared[85] by the reaction of *o*-di(phenylethynyl)benzene and $Fe(CO)_5$ (eq 3). The crystal structure of this complex has subsequently been determined.[86]



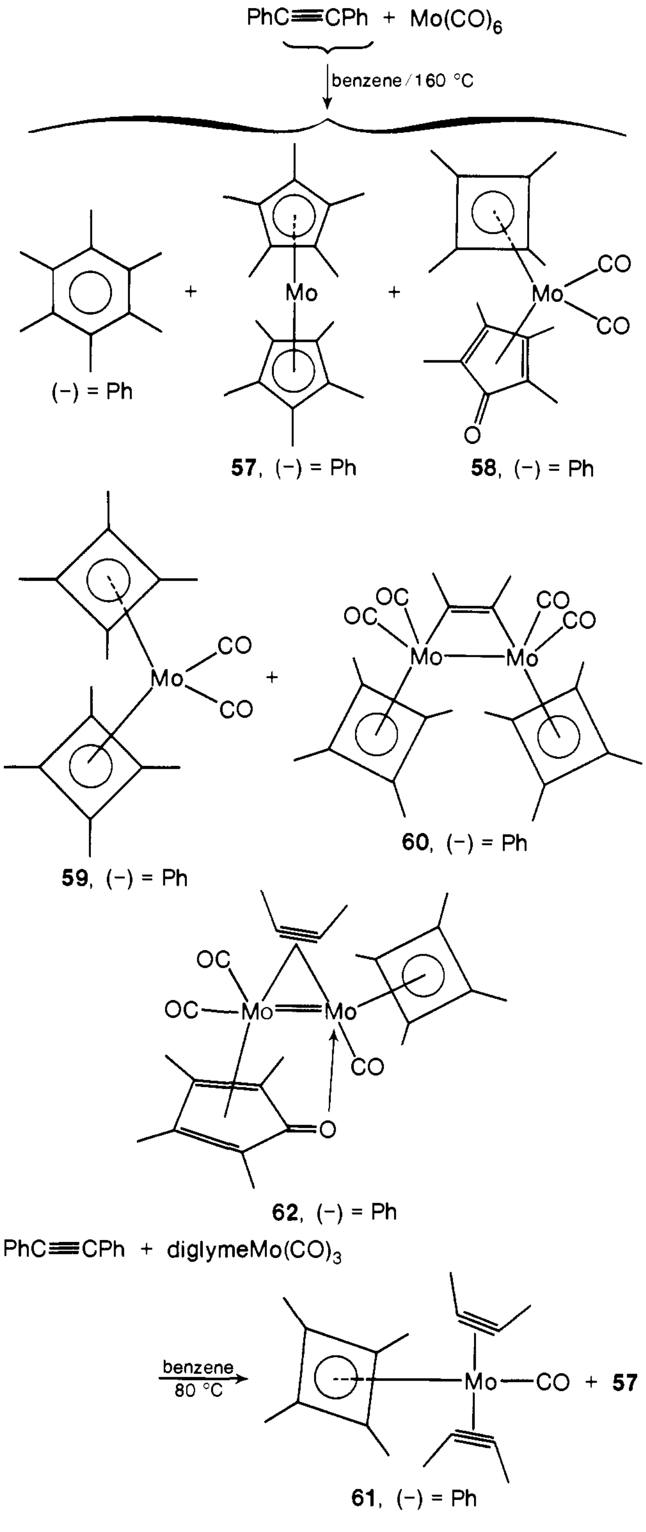
56, (-) = Ph

(3)

In 1964 Hübel and Merenyi reported[87] the reactions between diphenylacetylene and $Mo(CO)_6$ or (diglyme)$Mo(CO)_3$ which gave, among others, a variety of tetraphenylcyclobutadienemolybdenum complexes of the assigned structures **58, 59, 60,** and **61** (Scheme XII). Recently, the structures of two of the products, **59** and **60,** were examined by x-ray crystallography. The results of this investigation have confirmed the biscyclobutadiene geometry[88] of **59,** whereas the structure of the green complex was found to consist of **62,**[89] rather than the originally assigned structure **60.** Incidentally, complex **59** is the only known complex with a biscyclobutadiene geometry. It should also be mentioned that the asymmetric structure of **62** contains some rather unusual features such as a molybdenum-molybdenum double bond and π-bonded cyclopentadienone ligand which is also σ-coordinated via the oxygen atom to the adjacent molybdenum atom. These features will be examined in further details later on in a section devoted to the structures of cyclobutadienemetal complexes.

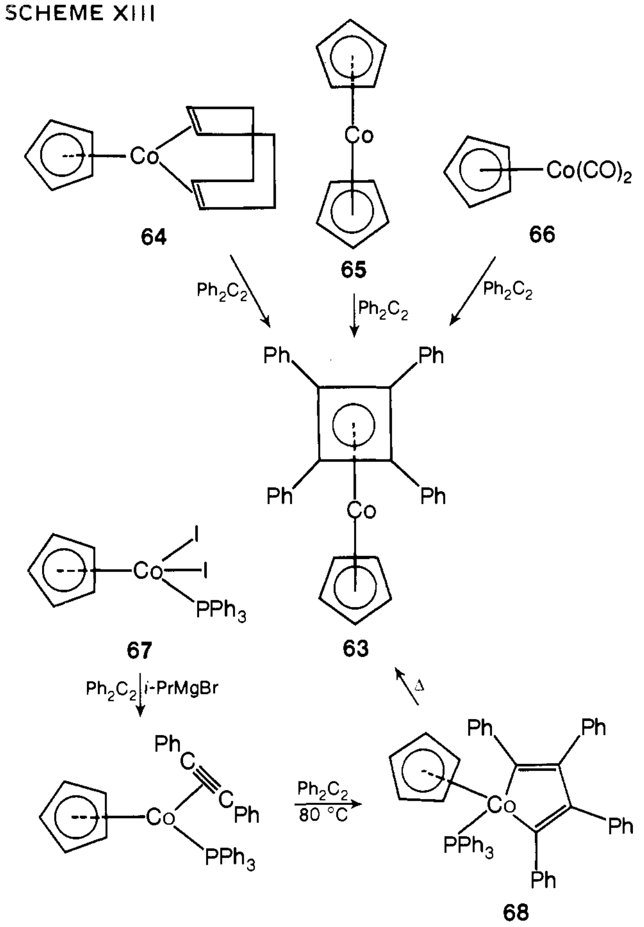
The first reported cyclobutadienecobalt complex, (cyclopentadienyl)(tetraphenylcyclobutadiene)cobalt (**63**), was prepared in 1961 by Nakamura and Hagihara[90,91] from the reaction of (cyclopentadienyl)(1,5-cyclooctadiene)cobalt (**64**) with diphenylacetylene. This cobalt complex **63** was also shown to be formed in the reactions of cobaltocene (**65**)[92] or cyclopentadienylcobalt dicarbonyl (**66**)[93] with Ph_2C_2; the major product in the latter reaction is (cyclopentadienyl)(tetraphenylcyclopentadienone)cobalt.[94] A sequence of reactions involving the reduction of cyclopentadienylcobalt triphenylphosphine diiodide (**67**) in the presence of Ph_2C_2 followed by the thermal addition of a second mole of Ph_2C_2 gave the metallocycle complex **68,** which then, on strong heating in the absence of Ph_2C_2, underwent isomerization with loss of Ph_3P to afford[95,96] **63** (Scheme XIII). The (monosubstituted cyclopentadienyl)(tetraphenylcyclobutadiene)cobalt complexes **69** and **70** were obtained[97] from the respective $RC_5H_4Co(CO)_2$ [R = Ph and $SiMe_3$] derivatives on reaction with Ph_2C_2 (Scheme XIV). A variety of (cyclopentadienyl)(disubstituted diphenylcyclobutadiene)cobalt complexes of the types **71** and **72** were obtained[98] by the reaction of PhC≡CR [R = $SiMe_3$, $SnPh_3$, Me, COMe, $CH(OEt)_2$, and CF_3] with either **64** or **65.** The silyl and stannyl derivatives of **71** and/or **72** reacted with HCl to afford the partially unsubstituted cyclobutadienecobalt complexes **73** and **74,** respectively.

SCHEME XII

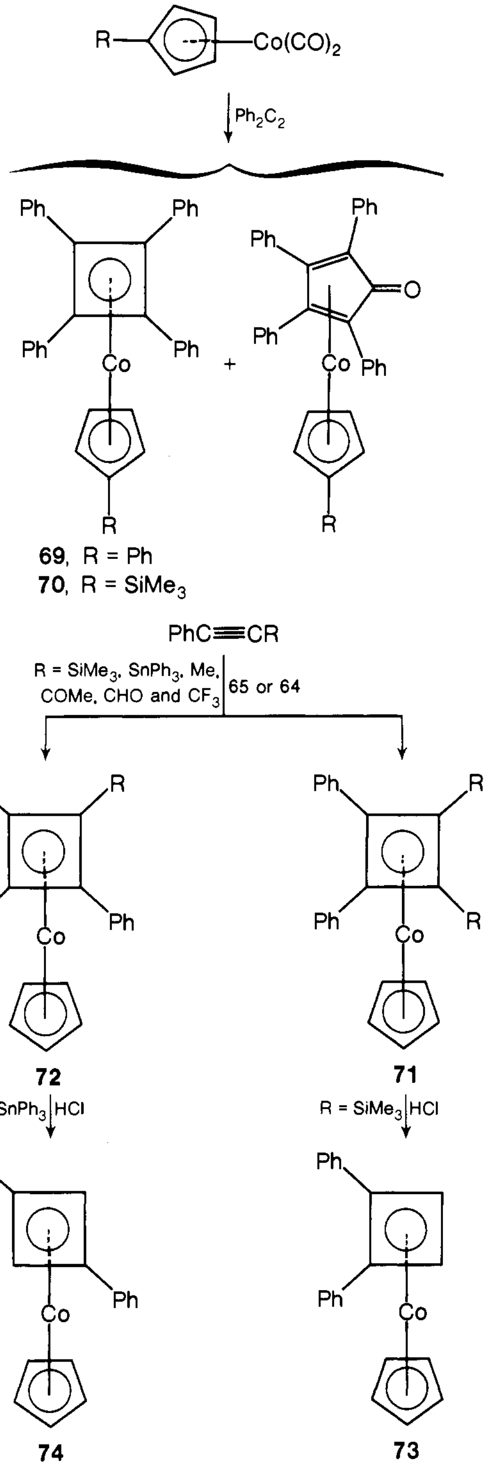


Other noteworthy cyclobutadienecobalt complexes whose preparations have recently been reported include **75,**[99] synthesized from the sandwich complex **76** and Ph_2C_2 (eq 4), and **77**[100] which was obtained as a yellow oil in small amounts (~3%

SCHEME XIII

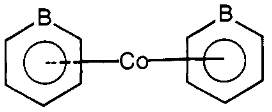


SCHEME XIV

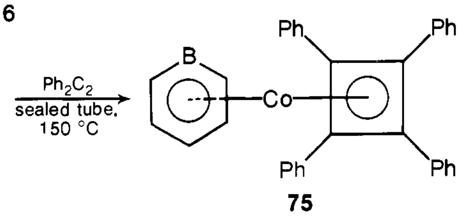


yield) from the $CpCo(CO)_2$ (**66**) catalyzed reaction of 1,5-hexadiyne (**20**) with bis(trimethylsilyl)acetylene (**78**) in refluxing *n*-octane (eq 5).

In an analogous reaction to that cited earlier between Ph_2C_2 and **64**, (cyclopentadienyl)(1,5-cyclooctadiene)rhodium (**79**) has been found to react with Ph_2C_2 to afford small amounts of (cyclopentadienyl)(tetraphenylcyclobutadiene)rhodium (**80**)[101] (eq 6). Interestingly, neither $CpRh(CO)_2$[102] nor $CpRh(PF_3)_2$[103] was found to afford cyclobutadienerhodium complexes on reaction with Ph_2C_2 or other alkynes. In contrast, $[RhCl(PF_3)_2]_2$ (**81**) has been shown to undergo a facile reaction with Ph_2C_2 to afford tetraphenylcyclobutadienerhodium chloride dimer (**82**)[103,104] in 50% yield (eq 7). The dimeric structure of **82** was assigned primarily on the basis of chemical evidence, since the complex has been shown to undergo typical bridge cleavage reactions (e.g., **82** reacted with CpTl, Tl(acac), and Tl(facac) to give **80**, $Ph_4C_4Rh(acac)$, and $Ph_4C_4Rh(facac)$, respectively).



76

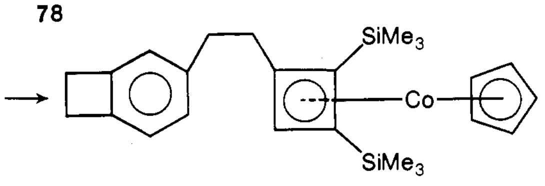


(4)

75

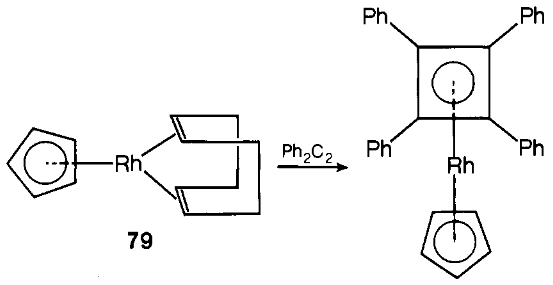
$Me_3SiC{\equiv}CSiMe_3$ + **20** + **66**

78



(5)

77

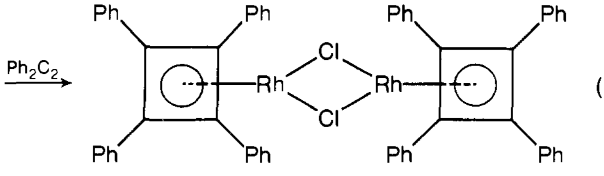


(6)

79

80

$[Rh(PF_3)_2Cl]_2$
81

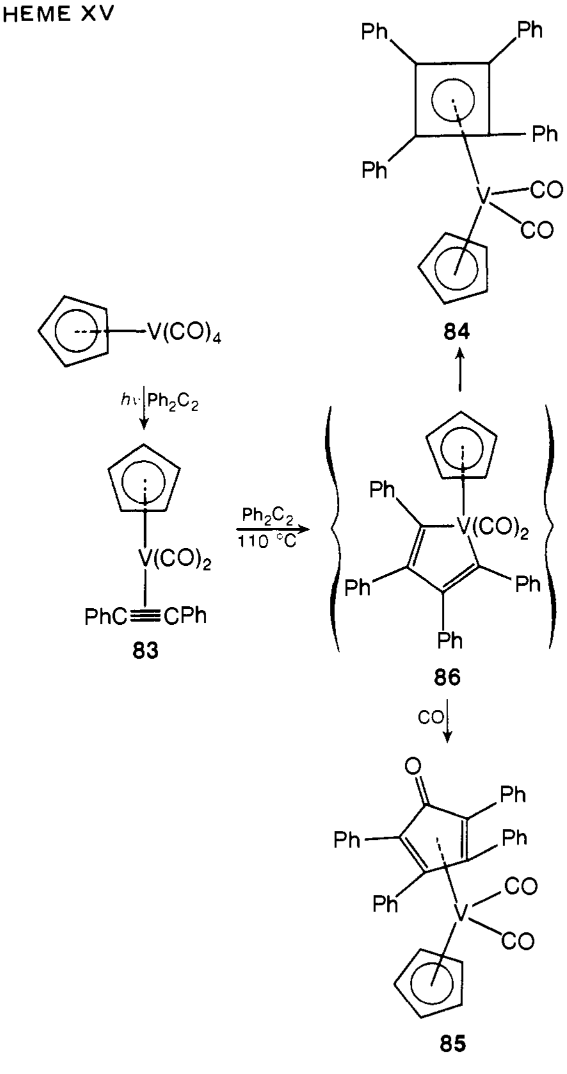


(7)

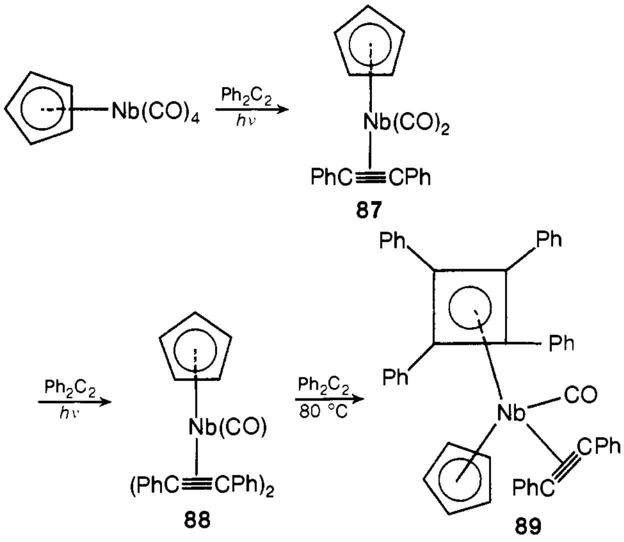
82

Some unusual tetraphenylcyclobutadiene complexes of group 5B transition element have been reported by Nesmeyanov and his collaborators[105] from their investigations of the reactions of $CpM(CO)_4$ [M = V, Nb, and Ta] with Ph_2C_2. The irradiation of $CpV(CO)_4$ in the presence of Ph_2C_2 gave the dicarbonyl monoacetylene complex **83**, which then underwent thermal addition of a second Ph_2C_2 without any loss of carbonyl groups to afford (cyclopentadienyl)(tetraphenylcyclobutadiene)vanadium dicarbonyl (**84**).[105] In the presence of carbon monoxide (40 atm), the reaction of **83** with Ph_2C_2 yielded the tetracyclone complex **85** (15% yield)[106] as well as **84** (50% yield). The metallocycle complex **86** was proposed to be an intermediate in these reactions[106] (Scheme XV). The tetraphenylcyclobutadienevanadium complex **84** was also prepared independently by the ligand transfer reaction between $[Ph_4C_4PdBr_2]_2$ and $CpV(CO)_4$. Similar reactions to those cited above have also been encountered with $CpNb(CO)_4$. The photochemical reaction of equimolar amounts of $CpNb(CO)_4$ and Ph_2C_2 gave **87**,[107] whereas, the bis(diphenylacetylene)monocarbonyl complex **88**[108,109] was obtained, under similar conditions, by using a 1:2 molar ratio of the respective reactants. The bis(acetylene)niobium complex **88** reacted with another mole of Ph_2C_2 in boiling benzene solution to afford a complex which was initially formulated as $CpNb(CO)(Ph_2C_2)_3$.[108] However, the crystal structure of this complex has ultimately shown it to be (cyclopentadienyl)(tetraphenylcyclobutadiene)diphenylacetylene)niobium carbonyl (**89**) (Scheme XVI).[110]

SCHEME XV



SCHEME XVI

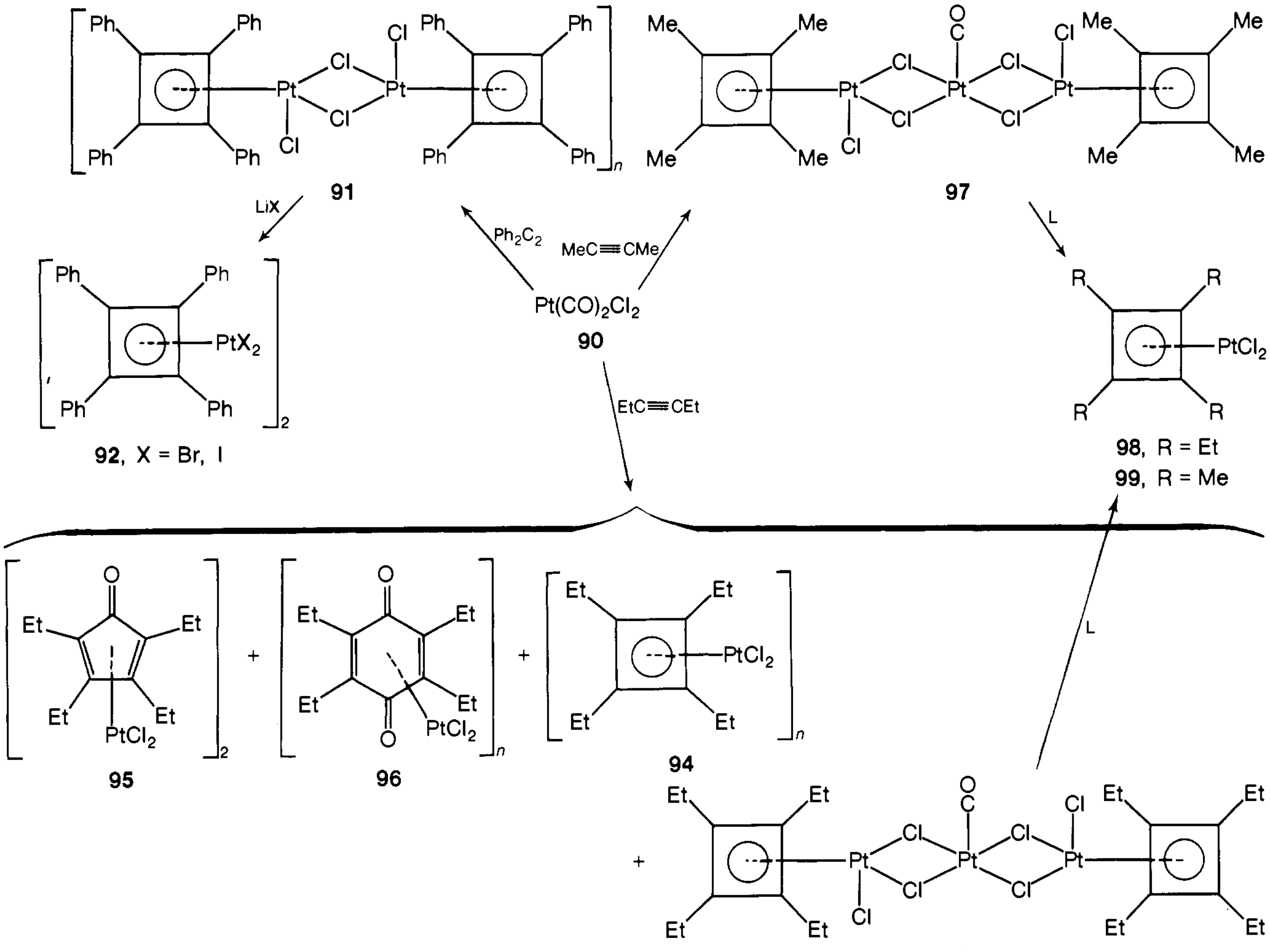


Recently, some attention has been given to the reactions of dichlorodicarbonylplatinum (**90**) with various alkynes. Complex **90** reacted with Ph_2C_2 in ether to afford hexaphenylbenzene, tetracyclone, and the tetraphenylcyclobutadieneplatinum complex **91**;[111] the latter was converted into the bromide and iodide dimeric derivatives **92** (X = Br, I) on refluxing in acetone with LiX (X = Br, I) (Scheme XVII). A similar reaction between **90** and 3-hexyne gave a mixture of products including the tetraethylcyclobutadieneplatinum complex **93** and **94** as well as the tetraethylcyclopentadienone- and tetraethyl(*p*-benzoquinone)platinum complexes **95** and **96**, respectively.[112] The reaction of **90** with 2-butyne afforded the tetramethylcyclobutadienetriplatinum complex **97** in ~64% yield. The triplatinum complexes **93** and **97** underwent facile reactions with Lewis bases (e.g., L = Ph_3P, Ph_2MeP, $p\text{-}CH_3C_6H_4NH_2$ and C_5H_5N) to afford the tetrasubstituted cyclobutadieneplatinum complexes **98** and **99**, respectively, whose structures based on molecular weight measurements were shown to be monomeric. In addition to the above cited reactions, the platinum carbonyl complex **90** has been shown to undergo facile reactions with other alkynes (e.g., C_2H_2, PhC≡CH, etc.); however, none of the products of these reactions was claimed to contain a cyclobutadiene ligand.[113]

2. Reactions of Macrocyclic Alkadiynes with Metal Carbonyl Derivatives

In 1970, King and Efraty reported[114] the intramolecular transannular cyclizations of macrocyclic alkadiynes (**100**) with $CpCo(CO)_2$ (**66**) to afford cyclobutadienecobalt complexes of the type **101** (Scheme XVIII). The macrocyclic alkadiynes employed in this investigation, which included 1,7-cyclododecadiyne (**100**, *n* = *m* = 4), 1,7-cyclotridecadiyne (**100**, *n* = 4, *m* = 5), 1,8-cyclotetradecadiyne (**100**, *n* = *m* = 5), 1,7-cyclotetradecadiyne (**100**, *n* = 4, *m* = 6) and 1,8-cyclopentadecadiyne (**100**, *n* = 5 5, *m* = 6), gave on reaction with **66**[115] in boiling *n*-octane, or cyclooctane, the respective cobalt complexes **101** (*n* = *m* = 4; 85% yield), **101** (*n* = 4, *m* = 5; 75% yield), **101** (*n* = *m* = 5; 2% yield), **101** (*n* = 4, *m* = 6; 40% yield), and **101** (*n* = 5, *m* = 6, 52% yield). In the instance of the reaction between

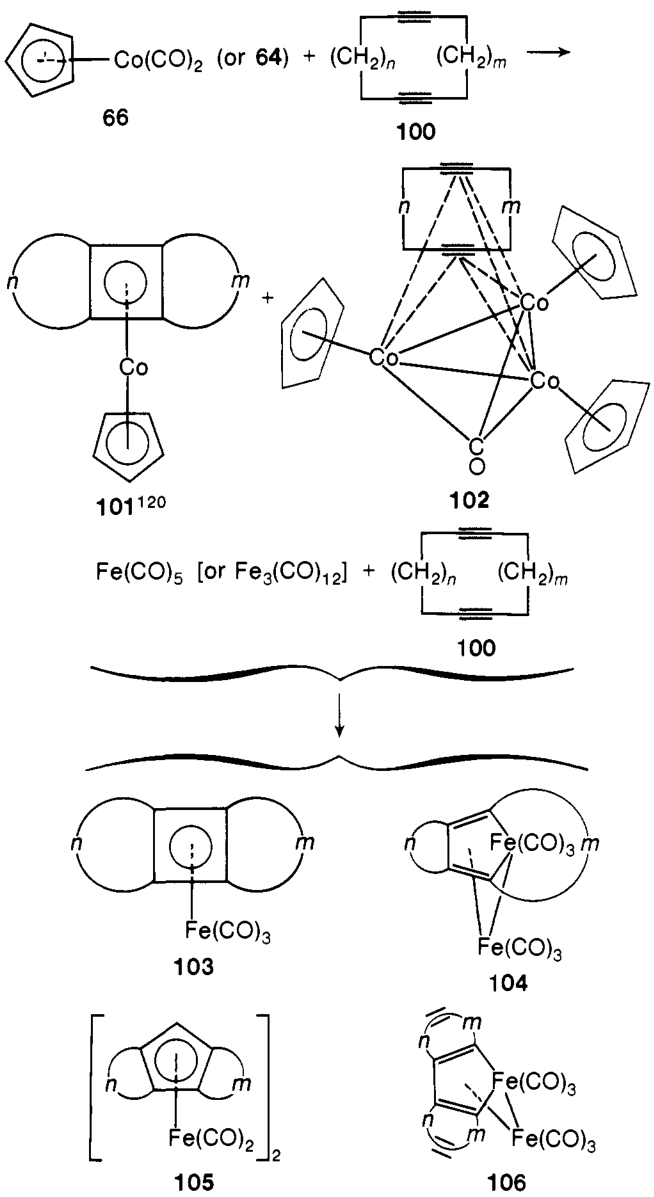
SCHEME XVII



100 (n = m = 5) and **66**, a second product of the assigned structure **102** was also isolated and characterized.[115] Two of the above cited complexes (**101**, n = 4, m = 5 and n = m = 5) also were obtained by the reaction of the 1,5-cyclooctadienecobalt complex **64** with the appropriate macrocyclic alkadiynes.[115] While the reactions of the macrocyclic alkadiynes with $Co_2(CO)_8$ and $[CpNi(CO)]_2$ gave alkadiyne-bridged complexes[116] of known types, their reactions with $Fe(CO)_5$ or $Fe_3(CO)_{12}$ have been shown to proceed with a considerably greater complexity to afford products, or mixtures of products, consisting of the iron complexes of the assigned structures[117-119] **103, 104, 105,** and **106**. In the context of the current review, especially interesting are the cyclobutadieneiron complexes **103** and the ferrole derivatives **104** which are presumed to be the precursors of the former.[118,119] The cyclobutadieneiron complex **103** (n = 4, m = 6) was the major product from the reaction between **100** (n = 4, m = 6) and $Fe(CO)_5$, whereas a similar reaction with **100** (n = m = 4) gave the ferrole complex **104** (n = m = 4) as the major product, and in addition, a very small yield of **103** (n = m = 4). Only trace amounts of the cyclobutadieneiron complexes **103** (n = 4, m = 5; n = m = 5; and n = 5, m = 6) were produced in the reactions of the respective macrocyclic alkadiynes and iron carbonyls.

The intramolecular transannular cyclization of macrocyclic alkadiynes with metal carbonyls has been proposed to proceed via metallocyclic intermediates of type **107**. The isolation of a stabilized intermediate-like complex of such nature (**104**, n = m = 4) was actually claimed[118,119] from the reaction of 1,7-cyclododecadiyne (**100**, n = m = 4) with $Fe(CO)_5$. However, a subsequent crystal structure analysis of the product from this reaction has revealed that the complex is structure **108**, n = m = 4,[121] namely, the "metathesized" form of the originally proposed structure (Scheme XIX). The formation of **108**, n = m = 4, could conceivably be explained by the initial production of **103**, n = m = 4, traces of which were actually found among the reaction products, followed by the insertion of a $Fe(CO)_3$ moiety into the cyclobutadiene ring upon further reaction with $Fe(CO)_5$. Recently, similar insertion processes have been encountered in the reactions of benzocyclobutadieneiron tricarbonyl (**9**) with $Fe(CO)_5$[122] and $Fe_3(CO)_{12}$,[123] an issue to be discussed elsewhere in this review. Molecular orbital calculations by Mango and Schachtschneider[124] have indicated that the formation of cyclobutadienemetal complexes by a concerted cyclization of coordinated bisacetylene on any single transition metal center is a symmetry forbidden process. According to this theory, two nonrestrictive-field transition metal centers sharing opposite faces of a plane containing a bisacetylene system remove the symmetry restrictions to a bisacetylene-cyclobutadiene interconversion.[125] Evidently, this theory does not conflict with the plausibility of metallocyclic intermediates in the nonconcerted bisacetylene-to-cyclobutadiene conversion. A direct implication of the theoretical treatment is the prediction of multimetal center intermediates in the concerted interconversion process. The foregoing would suggest that intermediates of the type $(CpCo)_3(CO)(alkadiyne)$, one of which, $(CpCo)_3(CO)(C_{14}H_{20})$, was actually isolated[115] and has tentatively been assigned the structure **102**, or of related nature might play a prominent role in the concerted transannular cyclization of macrocyclic alkadiynes (**100**) with $CpCo(CO)_2$ (**66**). This process is envisaged to occur either simultaneously with or instead of a second possible pathway involving the participation of metallocyclic intermediates of type **107**[119] in a nonconcerted cyclization process.

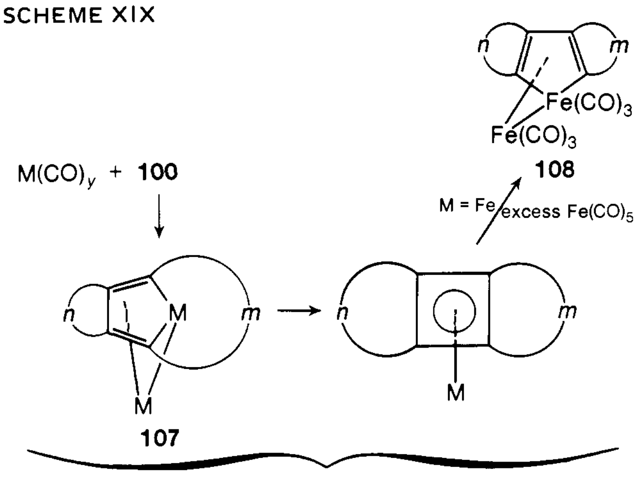
SCHEME XVIII



Similarly, the participation of ferrole intermediates of type **107** in nonconcerted processes leading to the formation of the cyclobutadieneiron complexes **103** cannot be ruled out entirely, although in this context it should be remembered that little, if any, evidence has so far been presented to substantiate the existence of such intermediates in the processes under consideration. Furthermore, the parent ferrole complex **55** was reported not to be an intermediate in the formation of **3**, although both complexes were apparently formed simultaneously[84] in the high-pressure reaction of $Fe(CO)_5$ and HC≡CH. Likewise, the tetraphenyl analogue of **55**, which was investigated rather extensively,[81] has not been reported to undergo either thermal or photolytic conversion to **2**. To date, the only concrete evidence of metallocycle-to-cyclobutadienemetal conversion has been reported by Yamazaki and Hagihara[95,98] in the reaction **68** (+Δ) → **63** + Ph_3P, although the postulation of metallocyclic intermediates in related processes has been widespread.[106,114,118,119,126]

3. Reactions of Alkynes with Coordination Complexes and Inorganic Salts

SCHEME XIX



M = Fe(CO)$_x$ or CpCo

The slow addition of diarylacetylenes to bis(benzonitrile)palladium chloride (**109**) in aprotic solvents (e.g., benzene, chloroform, etc.) led to the preparation of numerous palladium chloride bridged tetraarylcyclobutadienepalladium chloride complexes of type **110**,[127-129] which upon treatment with HCl or HBr gave the respective tetraarylcyclobutadienepalladium halide dimers **111**[128,129] (Scheme XX). The cyclobutadienepalladium halide derivatives prepared by this procedure included **110** and **111** (X = Cl, Br with Ar = Ph,[129] *p*-ClC_6H_4,[127] *p*-MeC_6H_4,[128] and *p*-$MeOC_6H_4$[128]). A similar reaction conducted between (*tert*-butyl)phenylacetylene and **109** followed by the treatment of the product with HCl in DMF afforded 1,2-di(*tert*-butyl)-3,4-diphenylcyclobutadienepalladium chloride dimer (**112**).[130] Complexes of type **111** were also synthesized by an indirect route involving the reaction of diarylacetylene with $PdCl_4^{2-}$ or **109** in the presence of protic solvents (e.g., EtOH, MeOH, H_2O, etc.), followed by the treatment of the product obtained with HX. The first step in this sequence was first reported by Malatesta and his co-workers[131] and was subsequently examined by other investigators.[132-135] Ultimately, a crystal structure analysis of the product $(EtOPh_4C_4PdCl)_2$ has revealed[136] an *endo*-ethoxy-η^3-cyclobutenyl geometry for the organic moiety in complex[136] **113** (R = Et, Ar = Ph). Incidentally, the *exo*-ethoxy-η^3-cyclobutenylpalladium isomer (**114**, R = Et, Ar = Ph) was prepared by the reaction of the appropriate cyclobutadienepalladium complex **111** with EtOH, and its reconversion to the latter achieved on treatment with HX. The cyclobutenyl–cyclobutadiene sequence represent a convenient route to a variety of cyclobutadienepalladium complexes of type **111**. This procedure was utilized, among others, in the synthesis of **112**;[137] however, in this instance the product was reported to be monomeric rather than dimeric as was indicated earlier.[130]

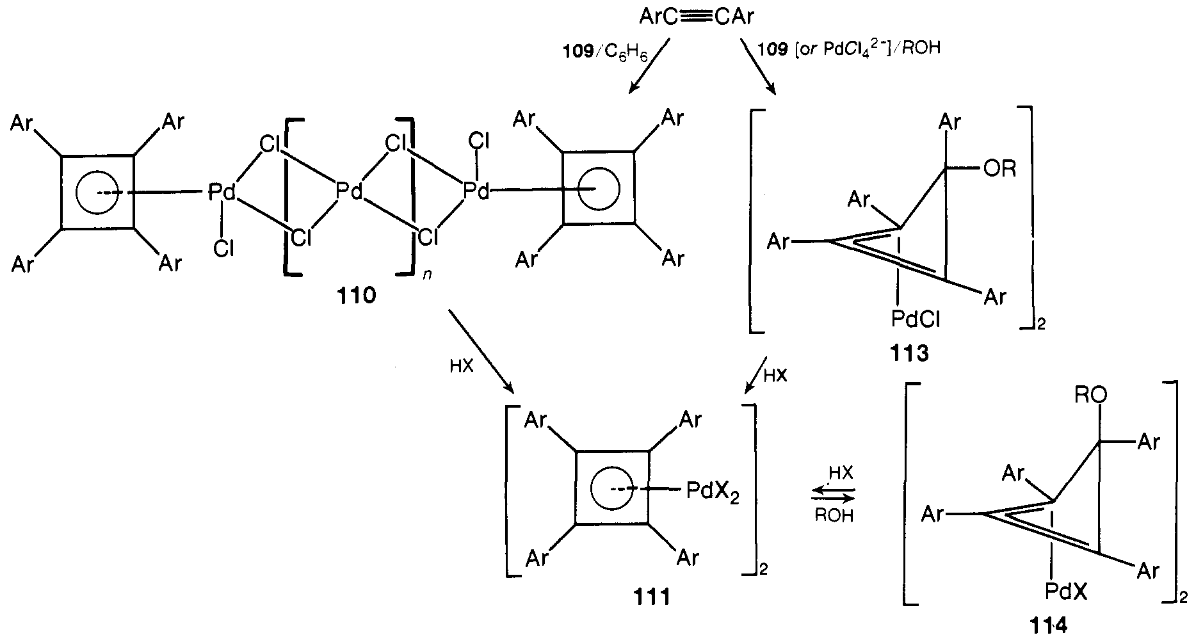
A reaction between *o*-di(phenylethynyl)benzene and $PdCl_2$ in anhydrous dry benzene was claimed to afford, among others, a biscyclobutadienepalladium dichloride[138] complex; however, this claim is highly questionable.

Particularly interesting is the synthesis of the tetramethylcyclobutadieneplatinum complex **115** by the reaction of *trans*-$[Pt(CF_3)(acetone)(PMe_2Ph)_2]^+ X^-$ (**116**) with 2-butyne, which has been reported by Chisholm and Clark.[139,140] The structure of **115** was ultimately confirmed by an x-ray structure determination.[141] Another novel cyclobutadiene complex, **117**,[142] was reportedly prepared by the reaction of *o*,*o*′-bis(phenylethynyl)triphenylphosphine (**118**) with $(Ph_3P)_3RhCl$. An unusual reaction between $TiCl_3$ and *i*-C_3H_7MgBr in the presence of Ph_2C_2 and cyclooctatetraene has been reported by Van Oven[143] to afford the first and only known cyclobutadienetitanium complex **119** (Scheme XXI).

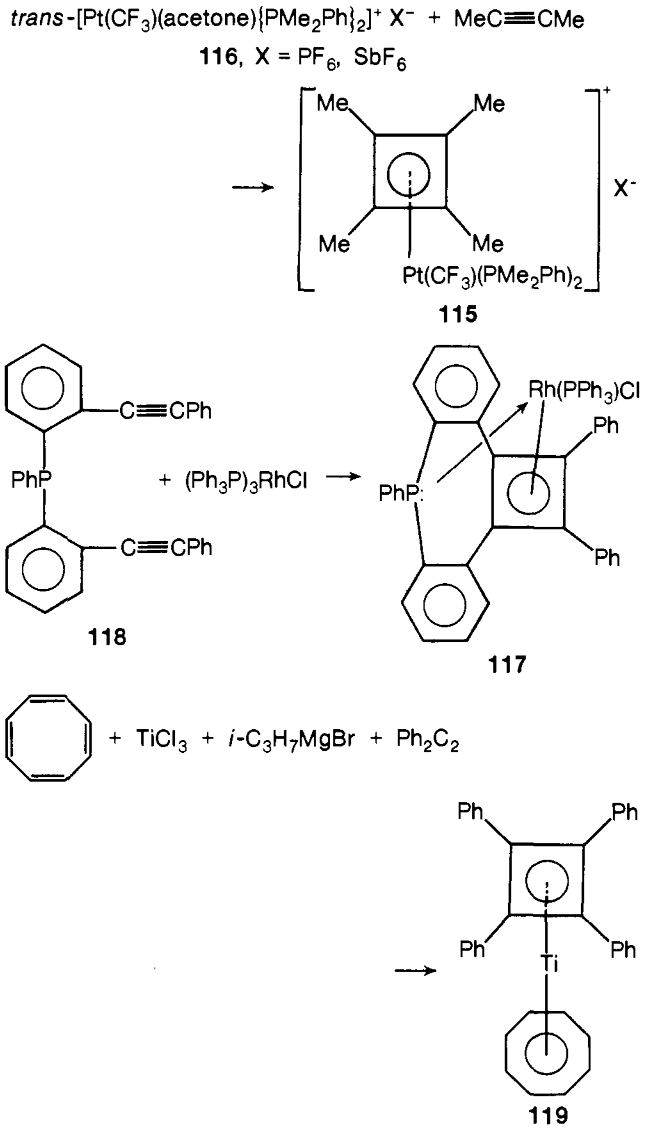
4. Syntheses via Precursors Derived Directly or Indirectly from Alkynes

The reaction of Ph_2C_2 with lithium was shown to afford 1,4-

SCHEME XX



SCHEME XXI



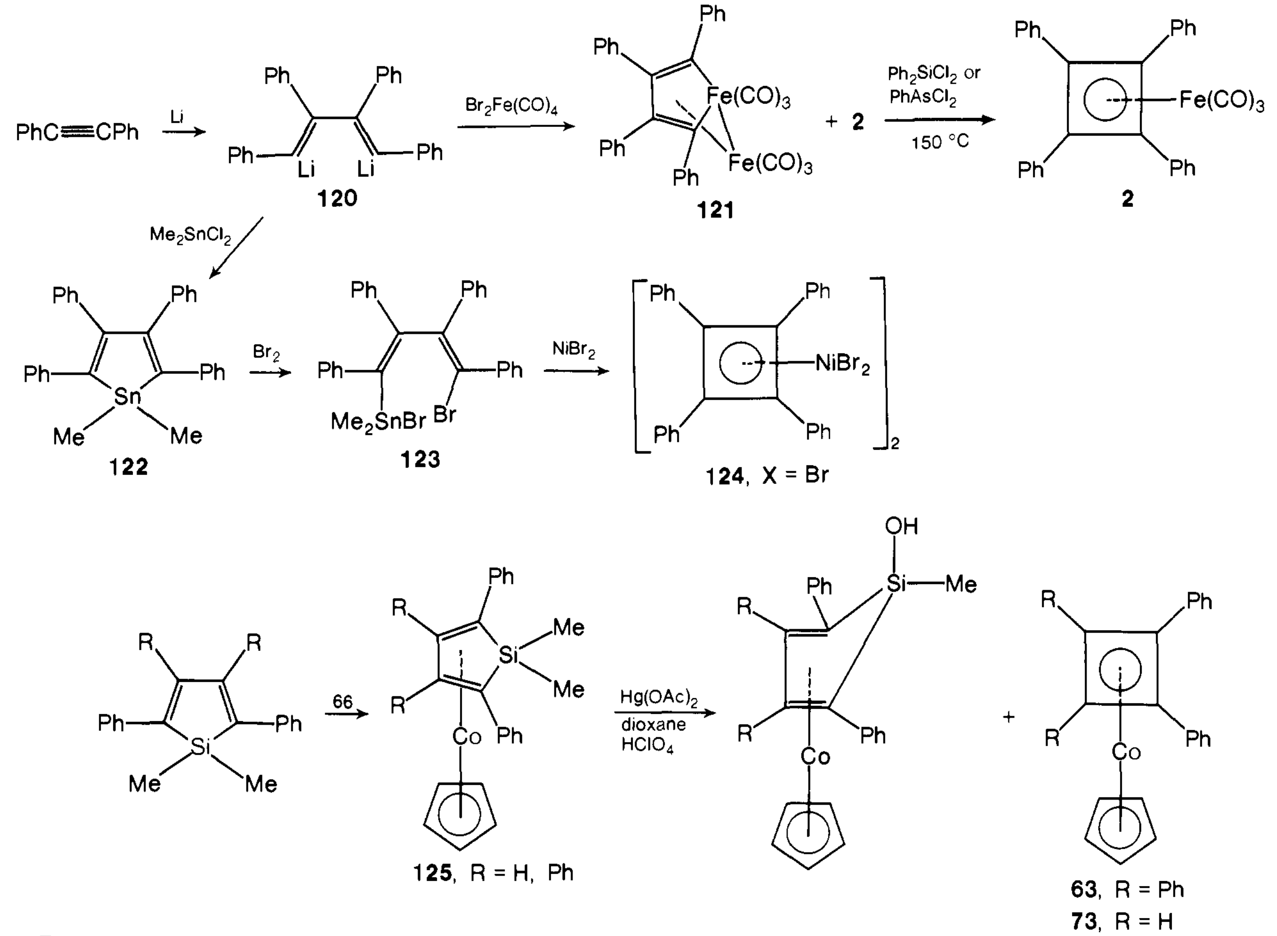
dilithio-1,2,3,4-tetraphenylbutadiene (**120**),[144] a precursor which has been utilized either directly or indirectly in the syntheses of certain tetraphenylcyclobutadienemetal complexes. A direct reaction between **120** and $Br_2Fe(CO)_4$ gave a mixture of **2** and the tetraphenylferrole complex **121**[126,145] (Scheme XXII). In the reaction under consideration, the ferrole complex **121** is not the precursor of **2**; this observation is similar to those already discussed elsewhere (section II.B.2). However, it was reported,[145] briefly, that the reaction of **121** with either Ph_2SiCl_2 or $PhAsCl_2$ at 150 °C gave **2** (~25%). The stannole derivative **122**, prepared[146] from **120** and Me_2SnCl_2, was shown by Freedman[147] to undergo ring opening to give **123** on treatment with bromine, and the latter upon reaction with $NiBr_2$ in refluxing triglyme gave a high yield of tetraphenylcyclobutadienenickel bromide dimer (**124**). Another reaction, which remotely belongs to this section and is described here as a matter of convenience, between the silacyclopentadienecobalt complex **125**[148] and mercuric acetate, gave the cyclobutadiene cobalt complexes **63** and **73** by a ring-contraction process involving the elimination of the heteroatom from the coordinated silacyclopentadiene ligand.

C. Preparation of *Tetrahapto*cyclobutadienemetal Complexes by π-Ligand Transfer Reactions

The term π-ligand transfer was proposed[149] originally by Maitlis and Games to describe reactions involving the transfer of a tetraphenylcyclobutadiene ligand from one transition metal complex to another. The ultimate objectives in the development of this novel technique were aimed at one-step, high-yield, and facile transfer processes starting from readily available and inexpensive reagents. This synthetic technique has been shown to be of special importance in instances where free ligands are either extremely labile or totally unknown, as is the case with cyclobutadiene derivatives. An extensive investigation in this area during the 60's had led to the preparation of a large variety of cyclobutadienemetal complexes,[33,38] some of which cannot be synthesized by any other route. The general area of ligand transfer and ligand exchange reactions has been the subject of recent reviews.[34,150]

The first successful transfer of a π-cyclobutadiene ligand was accomplished[149] by Maitlis and Games in the reactions of tetraphenylcyclobutadienepalladium bromide (**111**, X = Br) with $Fe(CO)_5$, $Ni(CO)_4$, and Cp_2Co (Scheme XXIII). These reactions, performed in boiling aromatic solvents, led to the isolation of **2**, **124** (X = Br), and **63** in 88, 47, and 12% yield, respectively. An alternative route to **124** was realized by the high yield cyclobu-

SCHEME XXII



SCHEME XXIII

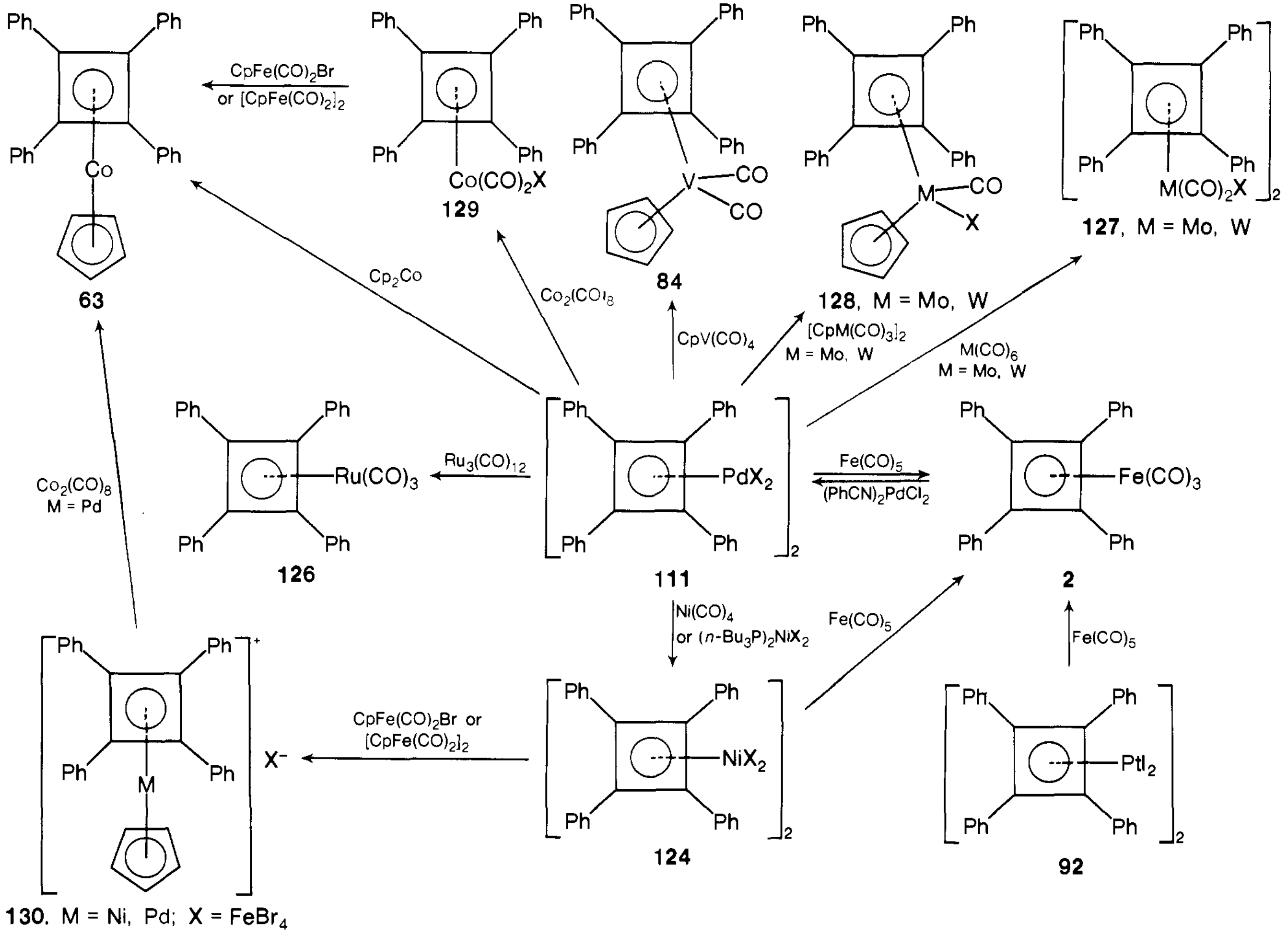


TABLE I. π-Cyclobutadiene Ligand Transfer Reactions

Reaction	Yield, %	Reaction conditions	Ref
$[Ph_4C_4PdBr_2]_2 + Fe(CO)_5 \rightarrow Ph_4C_4Fe(CO)_3$	88	Xylene, reflux, 20 min	149
$[Ph_4C_4PdBr_2]_2 + Ni(CO)_4 \rightarrow [Ph_4C_4NiBr_2]_2$	47	Benzene, reflux, 2.5 h	149
$[Ph_4C_4PdBr_2]_2 + Cp_2Co \rightarrow Ph_4C_4CoCp$	12	Xylene, reflux, 2.5 h	149
$[Ar_4C_4PdX_2]_2 + Fe(CO)_5 \rightarrow Ar_4C_4Fe(CO)_3$			
Ar = Ph; X = Br	78	Benzene, reflux, 2 h	128
Ar = p-MeC_6H_4; X = Br	47	Benzene, reflux, 2 h	128
Ar = p-$MeOC_6H_4$; X = Br	17	Benzene, reflux, 2 h	128
Ar = p-ClC_6H_4; X = Br	46	Benzene, reflux, 10 min	127
$[Ph_2(t\text{-}Bu)_2C_4]PdCl_2]_2 + Fe(CO)_5 \rightarrow [Ph_2(t\text{-}Bu)_2C_4]Fe(CO)_3$	65	Benzene, reflux, 4 h	130
$[Ph_4C_4NiX_2]_2 + Fe(CO)_5 \rightarrow Ph_4C_4Fe(CO)_3$	90	Benzene, reflux, 2 h	128
$[Ph_4C_4PtI_2]_2 + Fe(CO)_5 \rightarrow Ph_4C_4Fe(CO)_3$		Benzene, reflux, 10 min	111
$[(p\text{-}ClC_6H_4)_4C_4(PdCl_2)_4]_2 + Fe(CO)_5 \rightarrow (p\text{-}ClC_6H_4)_4C_4Fe(CO)_3$	44	Benzene, reflux, 10 min	127
$Ph_4C_4Fe(CO)_3 + (PhCN)_2PdCl_2 \rightarrow [Ph_4C_4(PdCl_2)_3]_2$		Benzene, reflux, 12 h	128
$[Me_4C_4NiCl_2]_2 + Fe_3(CO)_{12} \rightarrow Me_4C_4Fe(CO)_3$	35	THF, reflux, 20 min	162
$[Me_4C_4NiCl_2]_2 + Fe_2(CO)_9 \rightarrow Me_4C_4Fe(CO)_3$	6.3	THF, reflux, 17 h	162
$[Me_4C_4NiCl_2]_2 + Fe(CO)_5 \rightarrow Me_4C_4Fe(CO)_3$	21	Dry benzene, reflux, 25 h	162
$Me_4C_4PtCl_2 + Fe(CO)_5 \rightarrow Me_4C_4Fe(CO)_3$		Benzene, reflux	112
$[Ph_4C_4PdBr_2]_2 + Ru_3(CO)_{12} \rightarrow Ph_4C_4Ru(CO)_3$	42	Chlorobenzene, reflux, 12 h	128,152
$[(p\text{-}MeOC_6H_4)_4C_4PdBr_2]_2 + Ni(CO)_4 \rightarrow [(p\text{-}MeOC_6H_4)_4C_4NiBr_2]_2$	77	Various solvents, 40 °C	128
$[Ar_4C_4PdX_2]_2 + (n\text{-}Bu_3P)_2NiX_2 \rightarrow [Ar_4C_4NiX_2]_2 + (n\text{-}Bu_3P)_2PdX_2$			
Ar = Ph; X = Br	90	Chlorobenzene, reflux, 2 h	151
Ar = Ph; X = Cl	82	Chlorobenzene, reflux, 2 h	151
Ar = p-ClC_6H_4; X = Br	72	Chlorobenzene, reflux, 2 h	151
Ar = p-$MeOC_6H_4$; X = Br	77	Chlorobenzene, reflux, 2 h	151
Ar = p-MeC_6H_4; X = Br	73	Chlorobenzene, reflux, 2 h	151
$[(RR'R''R'''C_4)PdBr_2]_2 + (n\text{-}Bu_3P)_2NiBr_2 \rightarrow [(RR'R''R'''C_4)NiBr_2]_2 + (n\text{-}Bu_3P)_2PdBr_2$[a]	75	Chlorobenzene, reflux, 2 h	151
$[Ar_4C_4PdX_2]_2 + Co_2(CO)_8 \rightarrow Ar_4C_4Co(CO)_2X$			
Ar = Ph; X = Cl	65	CH_2Cl_2, amb., 45 h	158
Ar = Ph; X = Br	59	CH_2Cl_2, amb., 45 h	158
Ar = Ph; X = I	17	CH_2Cl_2, amb., 45 h	158
Ar = p-$CH_3C_6H_4$; X = Br	35	CH_2Cl_2, amb., 45 h	158
$[Me_4C_4NiI_2]_2 + Co_2(CO)_8 \rightarrow Me_4C_4Co(CO)_2I$	100	THF, 25 °C, 14 h	164
$[Me_4C_4NiCl_2]_2 + Co_2(CO)_8 \rightarrow Me_4C_4Co(CO)_2Co(CO)_4$	55	THF, 25 °C, 3 h	164
$[Ar_4C_4PdX_2]_2 + M(CO)_6 \rightarrow [Ar_4C_4M(CO)_2X]_2$			
Ar = Ph; X = Br; M = Mo	7	Benzene, reflux, 67 h	153
Ar = Ph; X = Br; M = Mo	18	Xylene, reflux, 10 min	165
Ar = Ph; X = I; M = Mo	9	Benzene, reflux, 67 h	153
Ar = Ph; X = I; M = W	Traces	Benzene, reflux, 5 min	153
Ar = p-MeC_6H_4; X = Br; M = Mo	18	Xylene, reflux, 5 min	154
$[Ph_4C_4PdBr_2]_2 + (\pi\text{-}C_6H_6)Mo(CO)_3 \rightarrow [Ph_4C_4Mo(CO)_2Br]_2$	14	Benzene, reflux, 15 h	165
$[Ar_4C_4PdX_2]_2 + [CpM(CO)_3]_2 \rightarrow (Ar_4C_4)(C_5H_5)M(CO)X$			
Ar = Ph; X = Cl; M = Mo	55	Benzene, reflux, 50 h	157
Ar = Ph; X = Cl; M = Mo	18	Xylene, reflux, 10 min	157
Ar = Ph; X = Br; M = Mo	7	Xylene, reflux, 10 min	157
Ar = Ph; X = Br; M = Mo	4.5	Benzene, reflux, 5 hr	157
Ar = p-MeC_6H_4; X = Br; M = Mo	6	Xylene, reflux, 5 min	154
Ar = Ph; X = Br; M = W	0.7	Benzene, reflux, 50 h	157
$[Ph_4C_4PdBr_2]_2 + CpV(CO)_4 \rightarrow (Ph_4C_4)(C_5H_5)V(CO)_2$	15	Toluene, reflux, 10 min	105

[a] A mixture of R = R' = o-anisyl, R'' = R''' = phenyl and R = R'' = o-anisyl, R' = R''' = phenyl isomers.

tadiene transfer between **111** and $(n\text{-}Bu_3P)_2NiX_2$.[151] The iron tricarbonyl complex **2** was also prepared by the reactions of the nickel complex **124** with $Fe(CO)_5$,[128] as well as by ligand transfer from the cyclobutadieneplatinum complex **92** on reaction with $Fe(CO)_5$.[111] Cyclobutadiene transfer from iron to palladium was encountered in the reaction of **2** with $(PhCN)_2PdCl_2$ (**109**);[128] the first step in this process involves the formation of the catenated cyclobutadienepalladium complex **110** (Ar = Ph), which upon reaction with anhydrous HX gave the normal dimer **111**. The extension of the cyclobutadiene transfer to ruthenium was accomplished by the reaction of **111** (X = Br) with $Ru_3(CO)_{12}$ from which tetraphenylcyclobutadieneruthenium tricarbonyl (**126**)[128,152] was isolated in 42% yield.[128] Noteworthy are the reactions involving cyclobutadiene transfer from palladium to molybdenum and tungsten. Belonging to this category are the reactions of **111** (X = Br, I) with the hexacarbonyls $M(CO)_6$ (M = Mo and W) which gave small to trace amounts of dimeric complexes whose structures were originally formulated as $[Ph_4C_4M(CO)_3X]_2$ (M = Mo, W; X = Br, I).[153] A subsequent study of these molybdenum complexes,[154] followed by a crystal structure analysis of the product obtained from the reaction of **111** (X = Br) and $Mo(CO)_6$, resulted in the reformulation of these complexes as tetraphenylcyclobutadienemetal dicarbonyl halide dimers (**127**).[155,156] Other cyclobutadiene complexes of molybdenum and tungsten whose preparation can be accomplished by ligand transfer only include the (cyclopentadienyl)(tetraphenylcyclobutadiene)metal carbonyl halide derivatives **128**, synthesized by the reaction of **111** with $[CpM(CO)_3]_2$ (M = W, Mo).[154,157] A similar reaction between **111** and $CpV(CO)_4$ has been reported to afford **84**;[105] however, this complex was also synthesized by an alternative procedure not involving ligand transfer as already cited earlier.[105] While the above-mentioned cyclobutadiene transfer processes require the use of boiling aromatic solvents, transfer under mild conditions, in methylene chloride at ambient temperature, had been encountered in the reaction of **111** with $Co_2(CO)_8$ by which the tetraphenylcyclobutadienecobalt dicarbonyl halide derivatives **129** were synthesized.[158,159] Interestingly, the yield of the transfer product **129** has been shown to depend on the nature of the halide and decreased in the order $Cl > Br \gg I$.

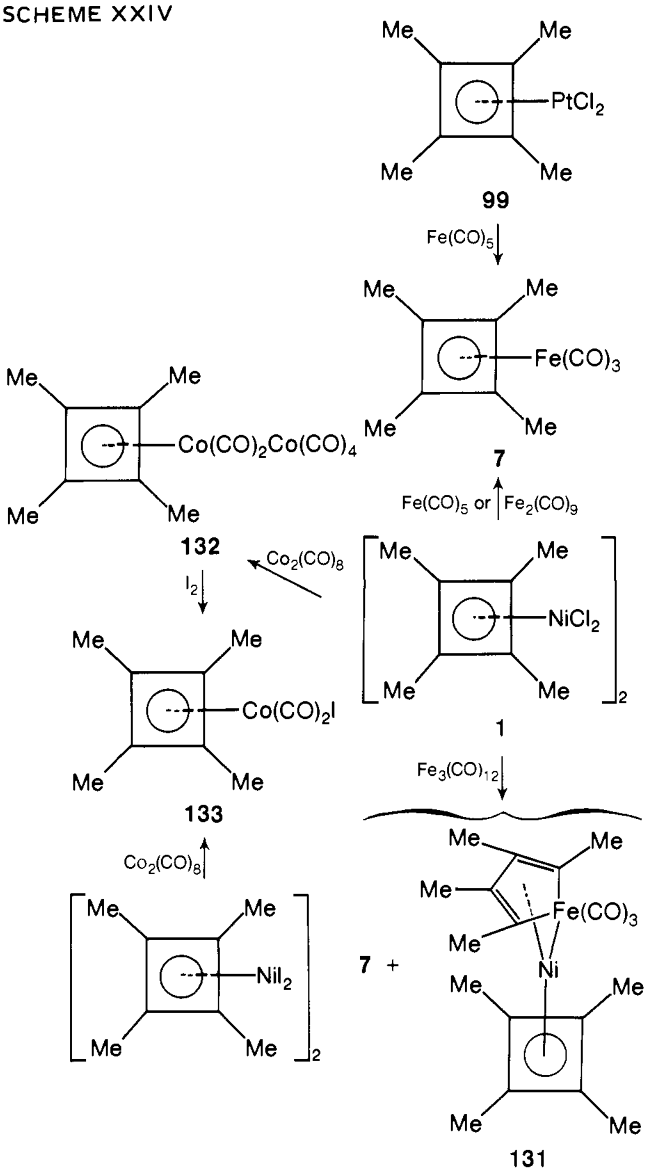
Numerous examples involving the transfer of a cyclobutadiene ligand to a metal center already containing a cyclopentadienyl group have been cited above. However, in some instances it has been shown that the reaction of cyclobutadienemetal complexes with cyclopentadienylmetal complexes could result in a cyclopentadienyl, rather than cyclobutadiene, transfer. For example, both **111** (X = Br) and **124** X = Br) have been shown to react with either $CpFe(CO)_2Br$ or $[CpFe(CO)_2]_2$ to afford the tetrabromoferrate derivatives of **130**,[160,161] where M = Pd and Ni, respectively. A similar reaction between the above-mentioned cyclopentadienylating iron reagents and **129** gave **63**. Incidentally, the paramagnetic tetrabromoferrate derivatives of **130** were converted to the diamagnetic bromide analogues by treatment with potassium ferrocyanide.

A dramatic example involving the simultaneous transfer of the cyclopentadienyl and tetraphenylcyclobutadiene ligands has also been reported. The reaction of **130** (M = Pd) with $Co_2(CO)_8$, in boiling benzene, gave **63** in 10% yield.[161]

Analogous reactions to those described above for tetraphenylcyclobutadienemetal complexes have also been reported for various other tetraarylcyclobutadienemetal derivatives (e.g., Ar = p-RC_6H_4; R = Cl, Me, OMe) as well as for related systems; these are summarized in Table I.

A number of transfer reactions involving the tetramethylcyclobutadiene ligand have also been reported, although similar reactions involving the parent cyclobutadiene ligand have not yet been realized. The reaction of the nickel complex **1** with $Fe(CO)_5$ or $Fe_2(CO)_9$ gave, among others, tetramethylcyclobutadieneiron tricarbonyl (**7**),[162] whereas a similar reaction with $Fe_3(CO)_{12}$ afforded, in addition to **7**, small amounts of the novel bimetallic ferrole-cyclobutadienenickel complex **131** whose geometry has been resolved by a crystal structure analysis[163] (Scheme XXIV). The iron complex **7** was also obtained by the reaction of the platinum complex **99**[112] with $Fe(CO)_5$. Several tetramethylcyclobutadiene transfer processes from nickel to cobalt complexes have been reported. The reaction of **1** with $Co_2(CO)_8$ gave the bimetallic cobalt complex **132**, which upon treatment with iodine was converted to **133**.[164] Starting with the iodo analogue of **1** and $Co_2(CO)_8$ permitted the obtainment of tetramethylcyclobutadienecobalt dicarbonyl iodide (**133**), under mild conditions, in a quantitative yield.[164] The presently known tetramethylcyclobutadiene ligand transfer reactions are summarized in Table I.

SCHEME XXIV



Cyclobutadiene ligand transfer reactions usually occur under heterogeneous conditions, and, to date, no meaningful kinetic studies on them have yet been reported. Nonetheless, several mechanistic approaches have been advanced in order to explain these interesting reactions.[33,34,150] It does appear almost certain that these complex reactions proceed via multistep processes involving the formation of bi- and polynuclear intermediates, some of which are probably halogen-bridged. Furthermore, it is commonly believed that the cyclobutadiene ring never becomes completely free of the metals during the course of these processes. An interesting approach to cyclobutadiene transfer mechanism, proposed by Efraty,[34] presumes a stepwise transfer process involving a sequence of intramolecular rearrangements via intermediates in which the cyclobutadiene is bonded simultaneously to two transition elements in combinations of mono-, di-, and trihapto fashions. According to this mechanistic approach, illustrated in Figure 2 for the transfer encountered between the palladium complex **111** and $Fe(CO)_5$ or $Ni(CO)_4$, the metal accepting the cyclobutadiene ligand during the transfer process will remain electronically and coordinatively saturated throughout the intermediate stages of the reaction. In this context bridging halide bonds are envisaged to function as electron density modifiers. The plausibility of this mechanistic approach is supported by the recent discovery of *dihapto*cyclobutadienemetal complexes.[36,37]

D. Preparation of *Dihapto*cyclobutadienemetal Complexes

The reactions of dihalocyclobutenes and metal carbonyls do not necessarily result in the formation of cyclobutadienemetal complexes. For instance, the metathesis between **5** and $CpFe(CO)_2Na[NaFp]$ has been shown by several investigators[166-170] to afford the ring-opening binuclear butadienylene complex FpCH═CHCH═CHFp (**134**) whose structure consists of a trans-trans geometry. In 1972, King, Efraty, and Zipperer reported[171] the synthesis of 1,2-bis(cyclopentadienyldicarbonyliron)benzocyclobutene (**135**) by the reaction of **6** with NaFp in THF solution at −78 °C (Scheme XXV). This novel complex constituted the first known example of a compound with two transition elements σ-bonded to a pair of saturated vicinal carbon

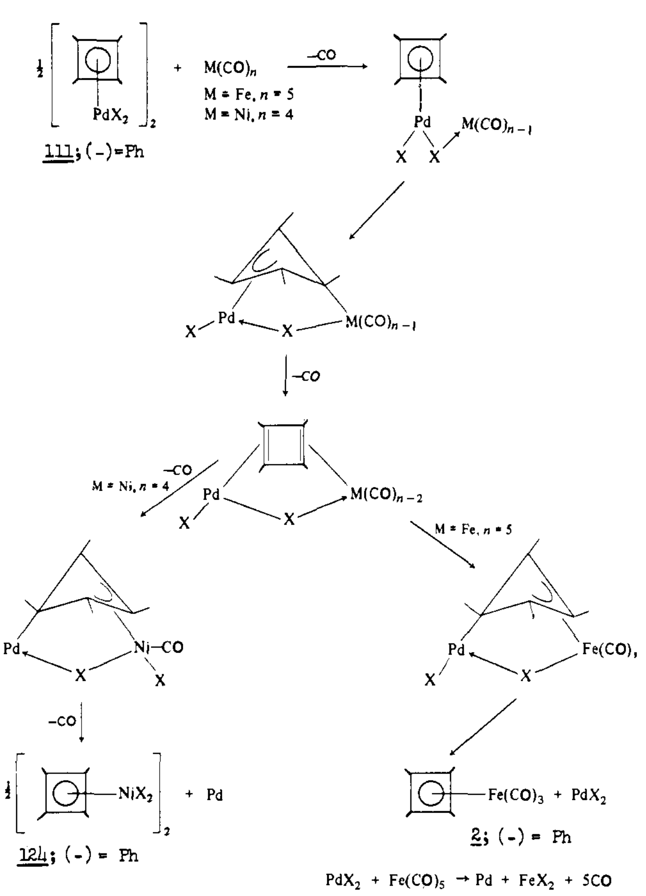
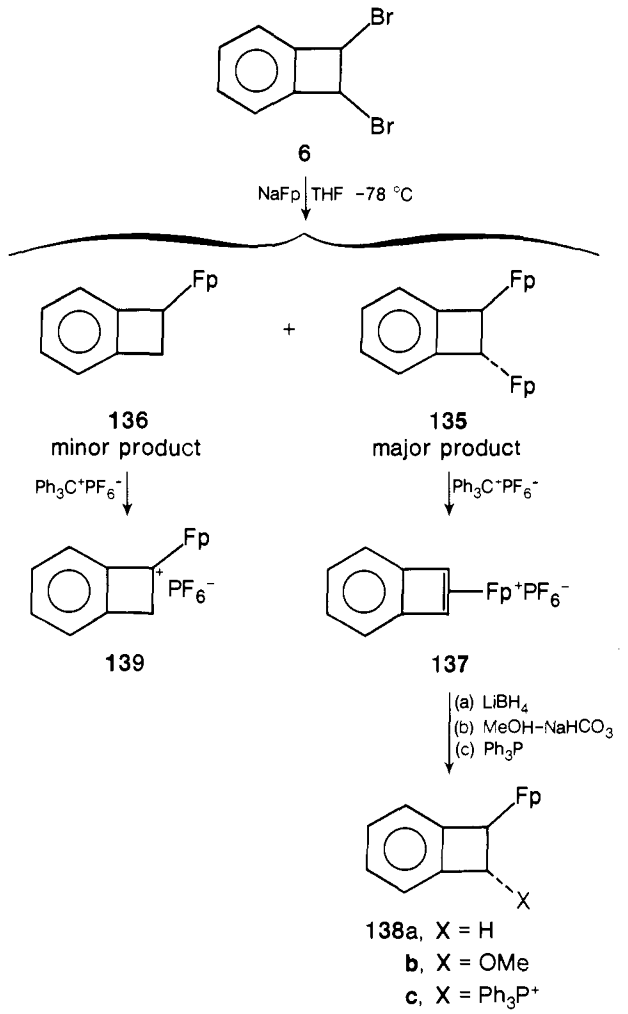


Figure 2. Mechanism proposed for π-cyclobutadiene transfer from palladium to iron and nickel.[34]

SCHEME XXV

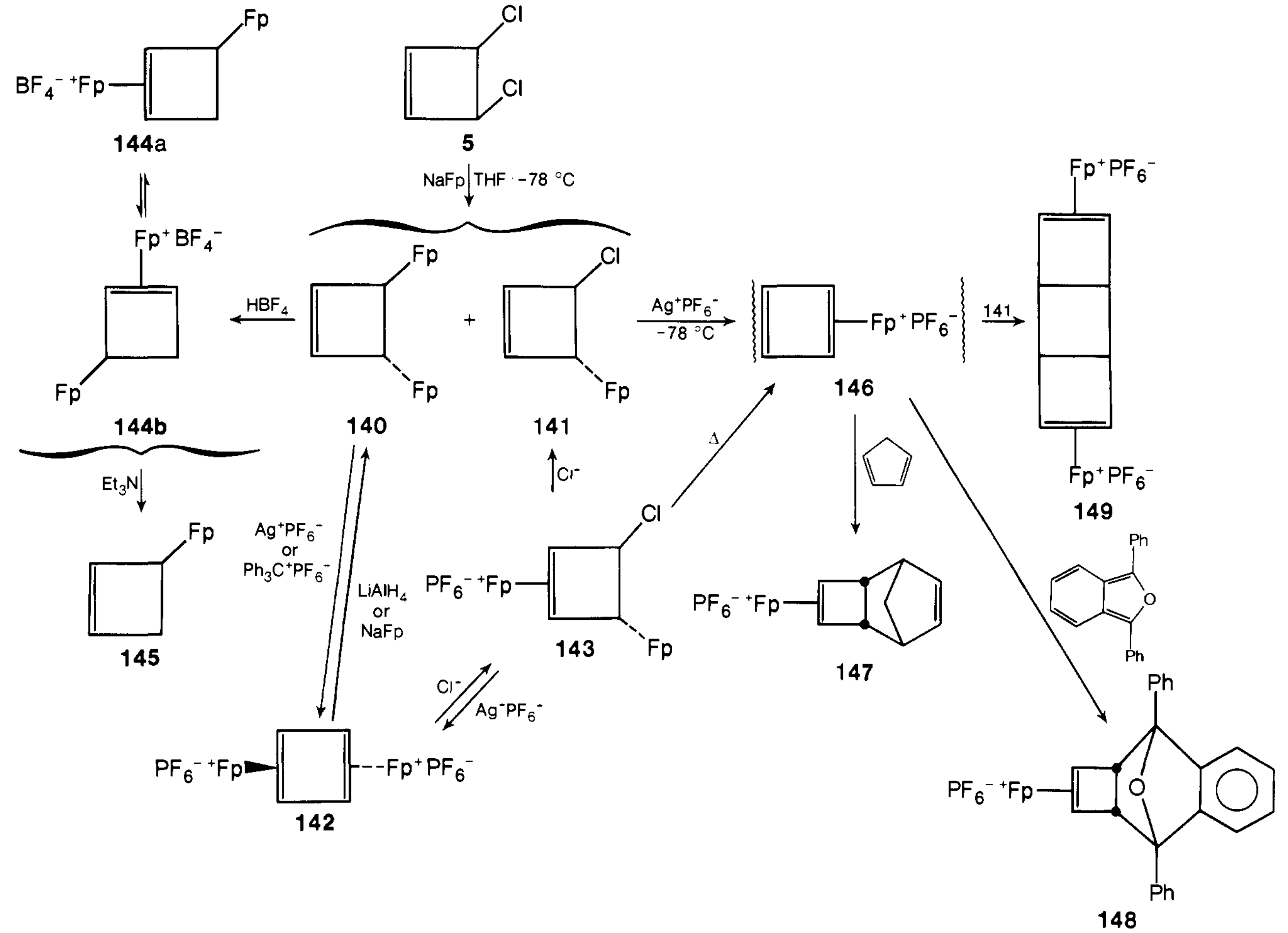


atoms of a hydrocarbon system. More importantly, this complex represented the first known example of a monohapto-bonded cyclobutene system, and the conditions utilized in its synthesis were found, ultimately, to be essential for the preparation of related derivatives, to be discussed at a later stage. A subsequent investigation[172] of the reactions of NaFp with dihalobenzocyclobutenes (e.g., *trans*-1,2-dibromo-, *cis*-1,2-diiodo-, and *trans*-1,2-diiodobenzocyclobutene) has revealed the formation of a second product, 1-(cyclopentadienyldicarbonyliron)benzocyclobutene (**136**), in 5–6% yield under the above specified conditions. The mechanism of formation of **135** and **136** was proposed[172] to involve free benzocyclobutadiene and Fp radicals. The synthesis of the first known example of a dihaptocyclobutadienoid transition metal complex, reported in 1974 by Giering and his co-workers,[36] involved the reaction of **135** with $Ph_3C^+PF_6^-$ in CH_2Cl_2 solution at −78 °C from which (η^2-1,2-benzocyclobutadiene)(η^5-cyclopentadienyl)dicarbonyliron hexafluorophosphate (**137**) was isolated in 60–70% yield. The red-orange complex **137** was characterized from its spectroscopic and chemical properties. For instance, the reactions of **137** with $LiBH_4$, MeOH-$NaHCO_3$, and Ph_3P afforded the derivatives **138**, where X = H, OMe, and Ph_3P^+, respectively. Treatment of **136** with trityl hexafluorophosphate was claimed[173] to afford the cationic carbene complex **139**.

Noteworthy is the extension of the investigation on η^2-cyclobutadienoid transition metal complexes to the parent ligand.[37,174–176] The treatment of *cis*-3,4-dichlorocyclobutene (**5**) with NaFp in THF solution at −78 °C gave a mixture consisting of *trans*-3,4-(η^5-cyclopentadienyldicarbonyliron)cyclobutene (**140**) and *trans*-3-chloro-4-(η^5-cyclopentadienyldicarbonyliron)cyclobutene (**141**), whose constituents could easily be separated owing to their different solubilities in common organic solvents (see Scheme XXVI). The oxidation of **140** with $Ph_3C^+PF_6^-$ or $Ag^+PF_6^-$ gave μ-(η_1^2-1,2-η_2^2-3,4-cyclobutadiene)-bis(η^5-cyclopentadienyldicarbonyliron)bis(hexafluorophosphate) (**142**), a novel binuclear complex with a bridging cyclobutadiene ligand.[37] This complex was obtained in 35–56% yield as a bright-yellow air-stable solid.[175] Treatment of the dicationic complex **142** with benzyltriethylammonium chloride effected chloride addition to afford μ-(η_1^1-4-η_2^2-1,2-(3-chlorocyclobutenyl))bis(η^5-cyclopentadienyldicarbonyliron)hexafluorophosphate (**143**). The oxidation of **143** with Ag^+ led to the regeneration of **142**. The reduction of the latter with either $LiAlH_4$ or NaFp gave back the neutral complex **140**. The conversion of **143** to **141** was achieved by means of chloride addition to the former complex. Protonation of **140** with HBF_4 in acetic anhydride gave a mixture of the monocationic binuclear isomers **144a** and **144b**, which according to their spectral data undergo interconversion.[176] Treatment of the isomeric mixture **144** with Et_3N afforded the neutral mononuclear complex 3-(η^5-cyclopentadienyldicarbonyliron)cyclobutene (**145**).

Specially significant is the generation of the highly reactive *dihapto*cyclobutadieneiron complex **146**[174,175] by the oxidation of **141** with $Ag^+PF_6^-$ in CH_2Cl_2 at −78 °C, or alternatively, by the thermal decomposition of **143**. Although the attempted isolation of the labile complex **146** has not been successful, its trapping by dienes to afford Diels–Alder adducts provides strong evidence in support of the intermediacy of this reactive η^2-cyclobutadieneiron complex. For instance, the generation of **146** in the presence of cyclopentadiene and 1,3-diphenylisobenzofuran gave the monocationic Diels–Alder adducts **147** and **148**, respectively. Another noteworthy reaction is that of **146** with its precursor **141** by which the dicationic complex with bridging *syn*-tricyclo[4.2.0.0^{2,5}]octa-3,7-diene was obtained. The formation of **149** was presumed to involve a sequence of metal-

SCHEME XXVI



assisted additions. The liberation of the polycyclic ligands from the Diels–Alder adducts **147**, **148**, and **149** was accomplished by the treatment of the respective complexes with NaFp in THF solution.

The contrasting behaviors of **142** and **146** are of clear interest. Except for its susceptibility toward nucleophiles (e.g., AlH_4^-, Fp^-, Cl^-, etc.), the former complex has been shown to exhibit a remarkable kinetic stability which contrasted dramatically with the transient nature of the latter. In part, the kinetic stability of **142** could be accounted for by the presence of two rather bulky Fp groups which are situated on both faces of the bridging cyclobutadiene ligand. Moreover, the reduced reactivity of the cyclobutadiene ligand in **142** is probably a direct consequence of having both olefinic bonds coordinated. Therefore, intermolecular reactions with **142** are greatly inhibited owing to a kinetic effect, whereas the decomplexation of the coordinated Fp groups appears to be energetically unfavored. Conversely, the removal, in part, of the kinetic effect from **146** and the presence of an exposed olefinic bond in the η^2-cyclobutadiene ligand should account for its enhanced reactivity. The retention of the coordinated Fp moiety during the Diels–Alder addition reactions with **146** is consistent with the presence of a strong η^2-cyclobutadiene-Fp^+ bond in this complex as well as in related complexes. The susceptibility of the cationic η^2-cyclobutadiene-Fp-containing complexes toward strong as well as mild nucleophiles is understandable in view of their ionic nature.

III. Chemistry of Cyclobutadienemetal Complexes

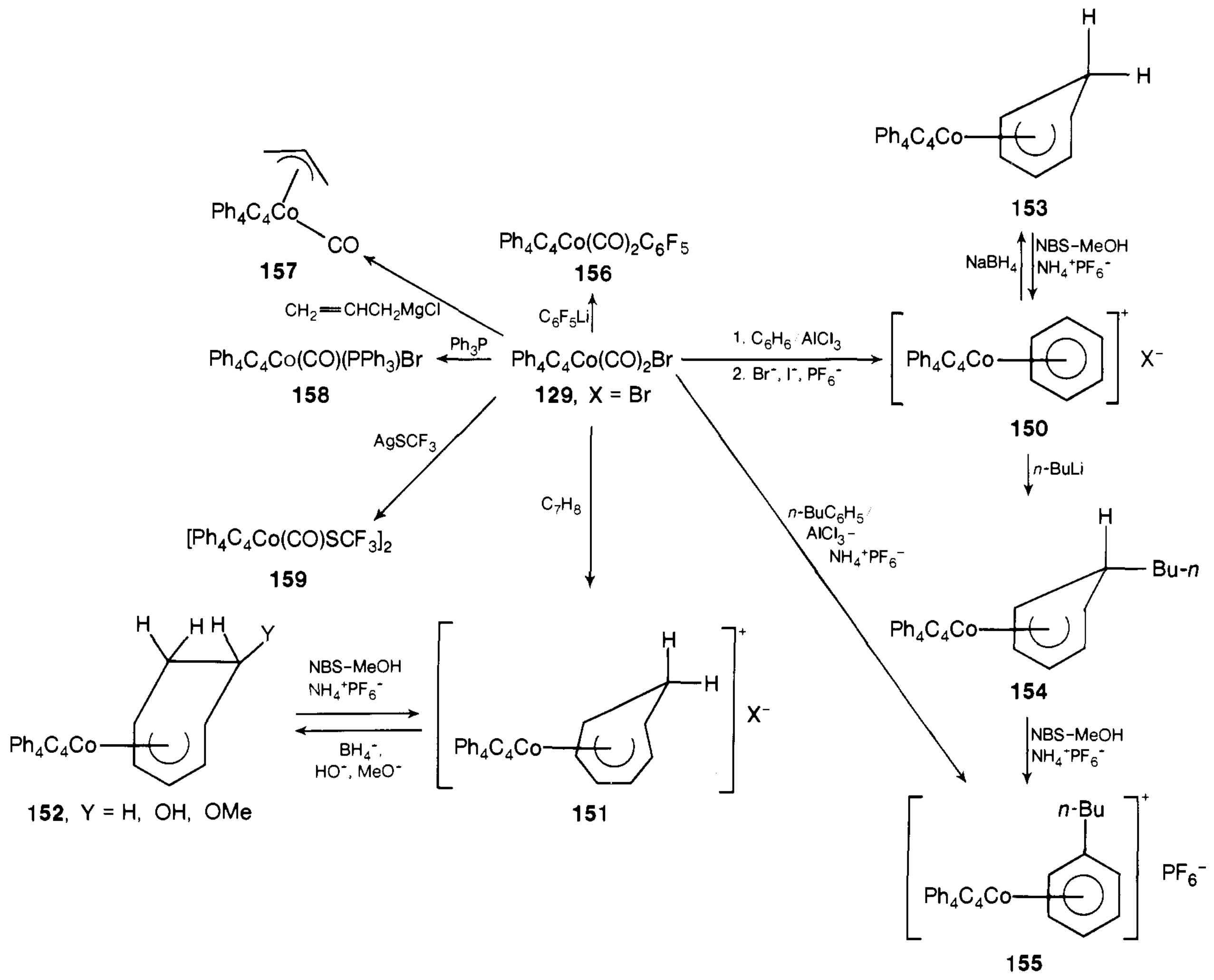
A considerable effort has been made, for over a decade, to investigate the chemical properties of cyclobutadienemetal complexes. In general, the chemistry of these complexes can conveniently be divided into four major categories: reactions not affecting the coordinated cyclobutadiene ligand, reactions involving the conversion of coordinated cyclobutadiene to other complexed ligands, organic chemistry of coordinated cyclobutadiene, and reactions causing the displacement of coordinated cyclobutadiene from its complexes. The term coordinated cyclobutadiene will, henceforth, be reserved for the tetrahapto ligand. In the instances where dihapto cyclobutadiene ligands are discussed, a special reference will be made in order to specify the nature of the ligand.

A. Reactions Not Affecting the Coordinated Cyclobutadiene Ligand

The chemistry of the complexes in this section will be reviewed according to transition elements rather than by reaction types. Reactions to be mentioned in this section include: anion exchange, carbonyl substitution by donor ligands, nucleophilic addition to ligands other than coordinated cyclobutadiene, organic reactions of ligands other than coordinated cyclobutadiene, introduction of σ- or π-ligands to a metal already containing a coordinated cyclobutadiene, photolytic processes involving the formation of binuclear complexes, and others.

The most extensive investigations in this area were carried out on a variety of cyclobutadienecobalt complexes. In this context, noteworthy is the study reported on tetraphenylcyclobutadienecobalt dicarbonyl bromide (**129**, X = Br) by Efraty and Maitlis.[158] The cobalt complex **129** (X = Br) readily underwent an aluminum chloride catalyzed reaction with benzene to afford (η^4-tetraphenylcyclobutadiene)(η^6-benzene)cobalt (**150**) (Scheme XXVII), a yellow diamagnetic cationic complex which was isolated and characterized in the forms of bromide, iodide, and hexafluorophosphate salts.[158,159] The same counterions

SCHEME XXVII



(Br^-, I^-, and PF_6^-) were also utilized in the characterization of the other cationic cobalt complexes to be discussed next. Similar reactions between **129** (X = Br) and some other arenes including toluene, *p*-xylene, mesitylene, biphenyl, and aniline gave the respective cationic π-arenecobalt complexes $[(\pi\text{-}Ph_4C_4)Co(\pi\text{-arene})]^+X^-$ (X = Br, I, PF_6).[158] By contrast with the arenes, the cobalt complex **129** (X = Br) reacted with cycloheptatriene under thermal conditions, and in the absence of a catalyst, to afford the cationic π-cycloheptatrienecobalt complex **151**. It might be of interest to mention that the counterion in **151**, as obtained from the initial reaction, consisted of X ≈ $Br\cdot CoBr_2$. This was confirmed by the treatment of the original product with potassium thiocyanate which led to the isolation of **151**, X = $0.5\text{-}[Co(NCS)_4^{2-}]$. It is therefore conceivable that $CoBr_2$, formed by the thermal decomposition of **129** (X = Br) acted as a mild Friedel–Crafts catalyst during the formation of the cycloheptatrienecobalt complex **151**.

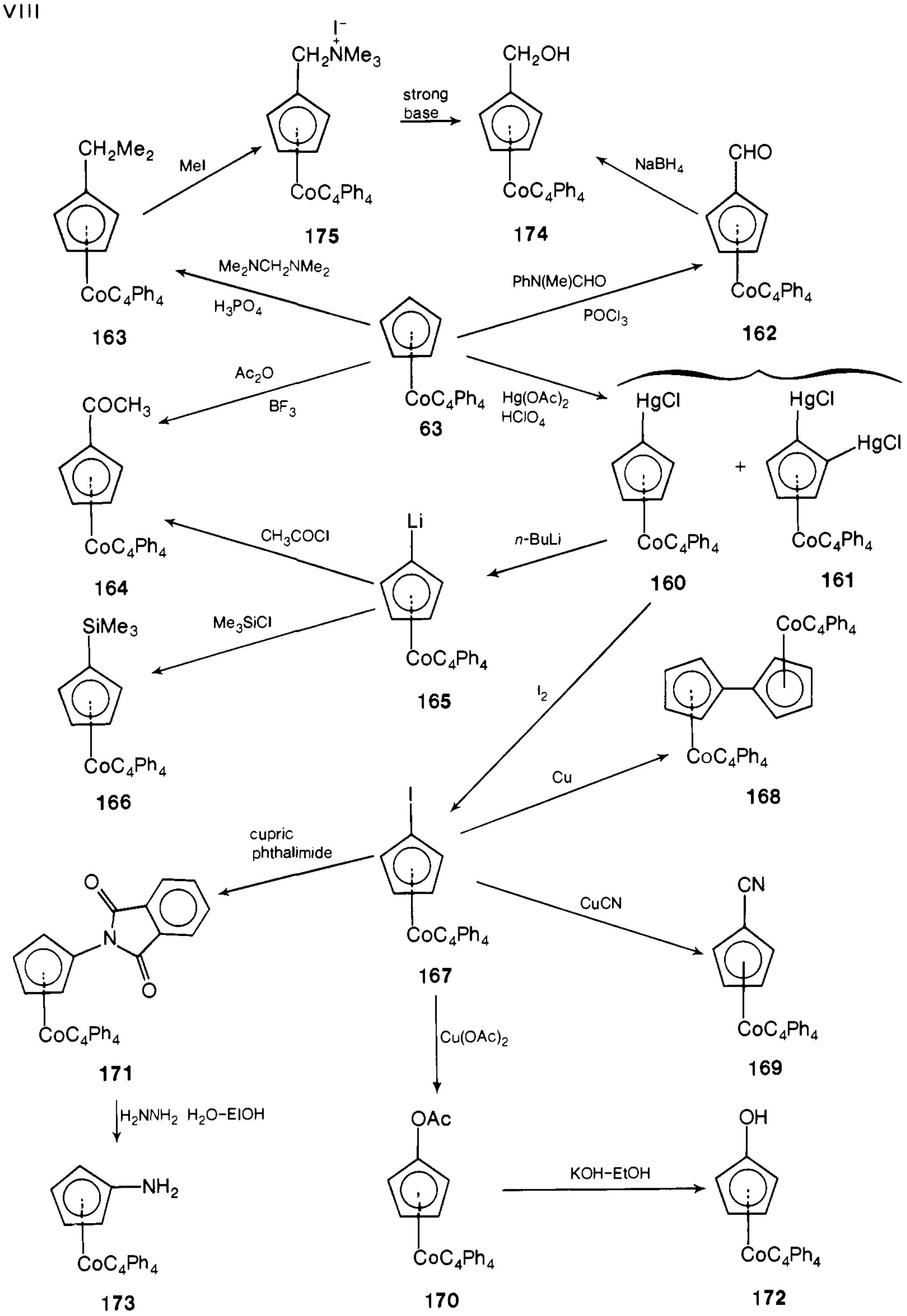
The cationic cycloheptatrienecobalt complex **151** readily underwent nucleophilic attack by water (in the presence of Et_3N), methoxide, or borohydride to afford the neutral cycloheptadienylcobalt derivatives **152**, where Y = OH, OMe, and H, respectively. The conversion of **152** (Y = H) to **151** (X = PF_6), a process involving hydride abstraction, was accomplished by using *N*-bromosuccinimide (NBS) in methanol. By contrast with the high susceptibility of the π-cycloheptatrienecobalt complex **151** toward nucleophiles, the cationic π-benzenecobalt complex **150** has been shown to be essentially inert toward nucleophiles such as potassium methoxide and methylmagnesium bromide. Nonetheless, the π-benzenecobalt complex **150** reacted with sodium borohydride in methanol and *n*-butyllithium in hexane to afford the neutral cyclohexadienylcobalt complexes **153** and **154**, respectively. Hydride abstraction from **153**, using NBS-CH_3OH, led to the regeneration of **150**, whereas a similar reaction with **154** gave the cationic π-*n*-butylbenzenecobalt complex **155**. The latter complex **155** was also synthesized independently by the reaction of **129** (X = Br) with *n*-butylbenzene in the presence of aluminum chloride. Attempts to effect hydride abstraction from **152**, **153**, and **154** by using established procedures involving reagents such as Ph_3C^+, air in the presence of acid, or H_2O_2 in acid were totally unsuccessful.[158] It should also be pointed out that the mode of addition of nucleophiles to the cationic complexes **150** and **151** does not involve an attack on the coordinated cyclobutadiene.

The reaction of **129** (X = Br) with perfluorophenyllithium gave the *monohapto*perfluorophenylcobalt derivative **156**,[158] a very stable yellow crystalline complex. A similar reaction with allylmagnesium chloride afforded the *trihapto*allylcobalt derivative **157** by a process presumably involving the decarbonylation of a *monohapto*allylcobalt intermediate.[165] Triphenylphosphine has been reported to react with **129** (X = Br) in benzene at ambient temperature to afford the monocarbonyl substitution product **158**.[158] The trifluoromethylthio-bridged binuclear cobalt complex **159** was obtained[177] by the reaction of **129** (X = Br) with $AgSCF_3$.

The analogous tetrakis(*p*-tolyl)cyclobutadienecobalt derivatives of **150**, **151**, **152**, **153**, **154**, and **156** were also prepared,[158] either directly or indirectly, starting from tetrakis(*p*-tolyl)cyclobutadienecobalt dicarbonyl bromide.

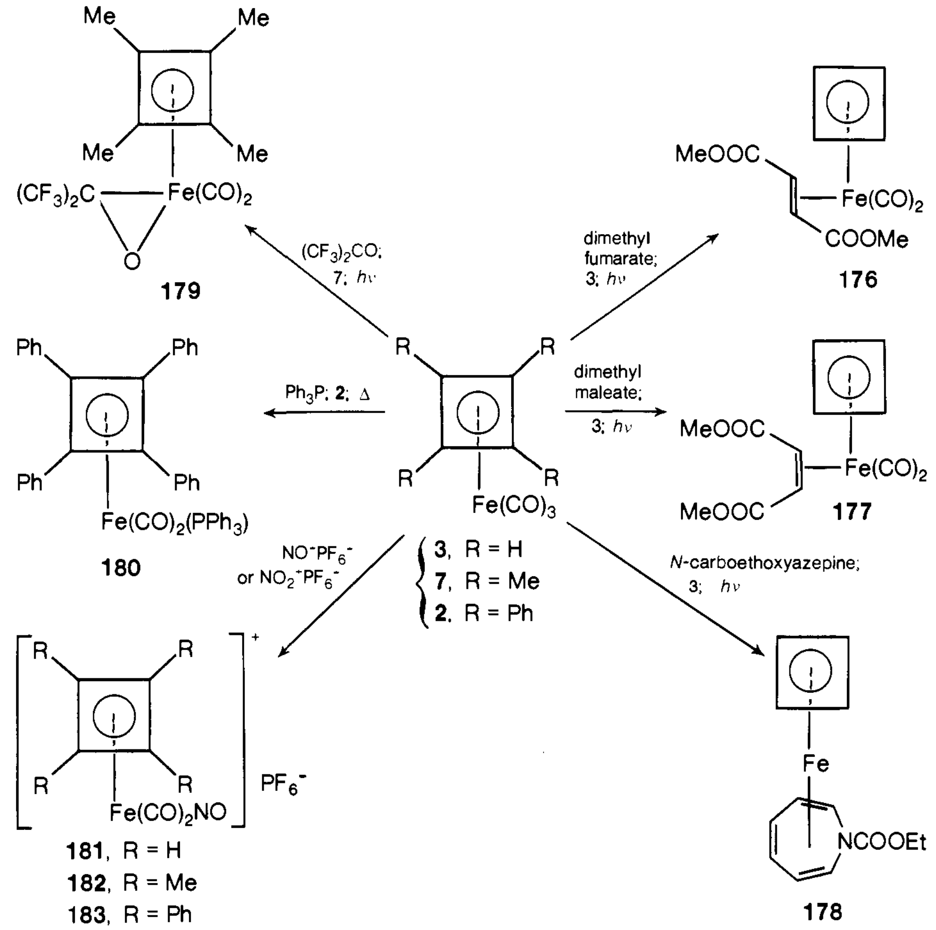
The organic chemistry of the cyclopentadienyl ligand in (cyclopentadienyl)(tetraphenylcyclobutadiene)cobalt (**63**) was investigated rather extensively by Rausch and Genetti.[93,97] Typical electrophilic substitution reactions performed on **63** included

SCHEME XXVIII



the following: acetomercuration in the presence of perchloric acid as catalyst (to afford **160** and **161**); Vilsmeier formylation with *N*-methylformanilide and phosphorus oxychloride (to afford **162**); Mannich-type aminomethylation with bis(dimethylamino)methane and phosphoric acid (to afford **163**); and Friedel-Crafts acetylation using acetic anhydride and boron trifluoride (to afford **164**, in trace amounts only) (see Scheme XXVIII). Interestingly, the Friedel-Crafts acylation of **63** with benzoyl chloride and aluminum chloride gave a product (~1% yield) in which substitution appeared to have occurred on a phenyl rather than the cyclopentadienyl ring. The chemistry of some of the abovementioned products was explored further, and in this regards the chloromercuri complex **160** has been shown to be a particularly valuable reagent for the synthesis of numerous new tetraphenylcyclobutadienecobalt derivatives. Transmetalation of **160** with *n*-BuLi led to the rapid generation of the monolithium derivative **165**, which then upon treatment with either acetyl chloride or trimethylchlorosilane gave **164** or **166**, respectively. The iodo derivative **167**, obtained in high yield by the iodination of **160**, when heated with copper-bronze gave the Ullmann coupling product **168**, while in the presence of cuprous cyanide in *N*-methyl-2-pyrrolidone it underwent the Rosenmund-von Braun reaction to afford the cyano derivative **169**. Similarly, treatment of the iodo complex **167** with cupric acetate or cupric phthalimide gave the acetoxy and phthalimido derivatives **170** and **171**, respectively. The acetoxy derivative **170** was converted to the hydroxy derivative **172** on treatment with ethanolic KOH solution, whereas the phthalimido derivative **171** when hydrolyzed with aqueous ethanolic hydrazine solution gave the amino compound **173**. Other noteworthy results described in the elegant work of

SCHEME XXIX



Rausch and Genetti[93,97] included the conversion of the aldehyde **162** to the hydroxymethyl derivative **174** by means of Cannizzaro reaction (KOH, H_2O-EtOH) or $NaBH_4$ reduction. An alternative synthetic route to **174** involved the treatment of the methiodide **175**, prepared from **163** and MeI, with a strong base (e.g., KOH in 95% EtOH).

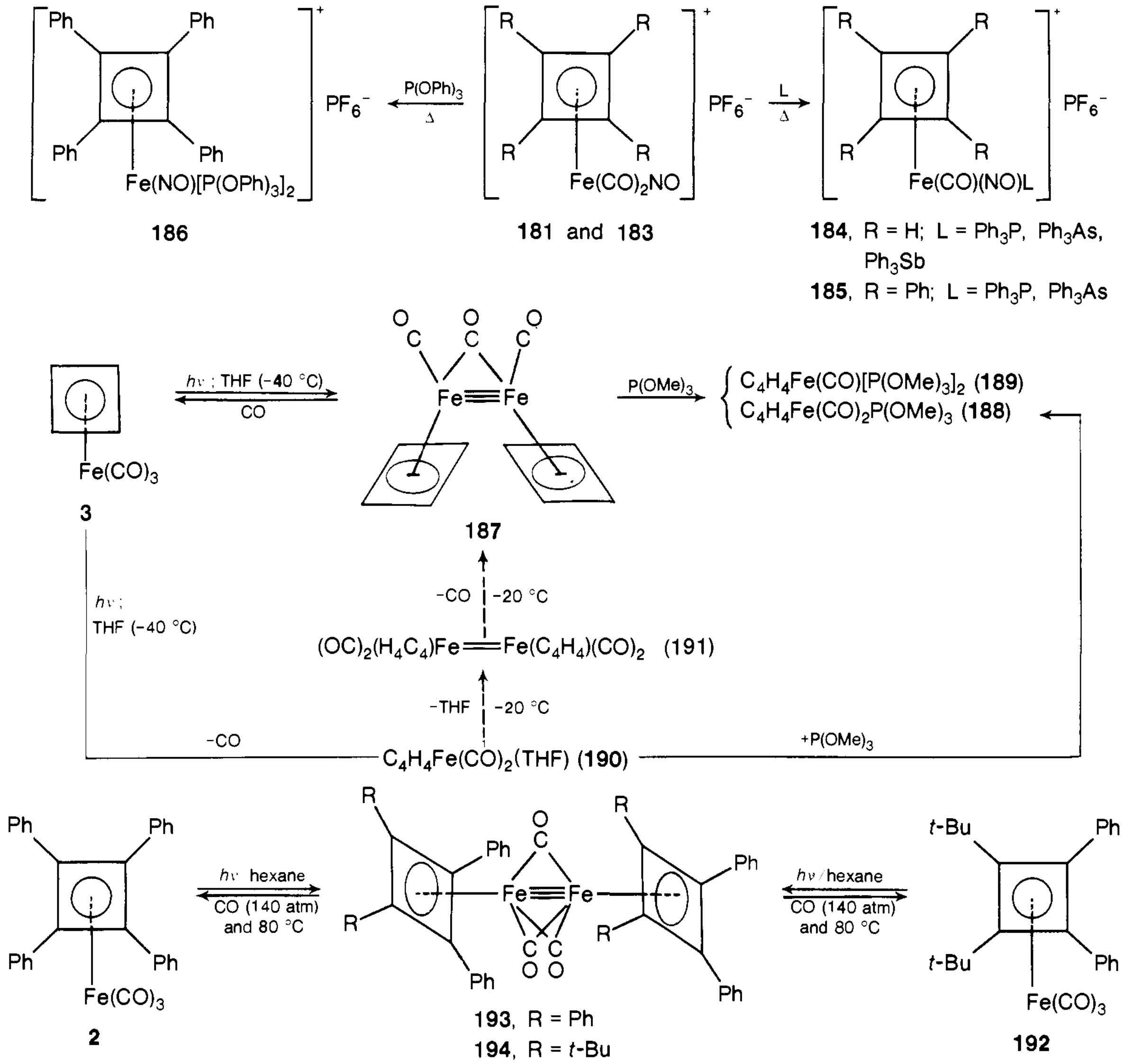
In general, the susceptibility of the cyclopentadienyl ring in **63** toward electrophilic substitutions has been shown to be significantly lower than that of ferrocene. In order to ascertain the importance of the electronic effects in this system, the appropriate p*K* values of the hydroxy **172** and amino **173** derivatives were determined in nonaqueous solvents and compared with those of related systems. By this procedure, it was found that **172** is a slightly stronger acid than phenol, while both **173** and aniline are of the same base strength. An earlier study has revealed that hydroxyferrocene is a weaker acid than phenol,[178] whereas aminoferrocene is a stronger base than aniline.[179] The foregoing appear to suggest that the cyclopentadienyl ring in **63** is electron-poor compared with that of ferrocene. Evidently, this conclusion is consistent with the lower reactivity of the former system toward electrophilic substitution reactions.

In the context of the topic under consideration, the reactions of cyclobutadieneiron complexes will be discussed next. The parent complex cyclobutadieneiron tricarbonyl (**3**) reacted under irradiation with dimethyl fumarate,[180] dimethyl maleate,[180] and *N*-carboethoxyazepine[181] to afford the cyclobutadieneiron derivatives **176, 177,** and **178,** respectively. Incidentally, the formation of **178** by the replacement of all three carbonyl groups from **3** is a highly unusual process. Moreover, similar photochemical reactions between **3** and other cyclic trienes were shown to involve an attack on the coordinated cyclobutadiene (see section III.B). Irradiation of the tetramethyl complex **7** with an excess of hexafluoroacetone[182,183] gave the monocarbonyl substituted product **179**. Carbonyl substitution with a phosphine was encountered[184] in the thermal (140 °C) reaction between **2** and Ph_3P which gave complex **180** (Scheme XXIX).

Specially significant are the nitrosylation reactions of the cyclobutadieneiron complexes **2, 3,** and **7,** reported by Efraty and his co-workers.[185,186] Previously, attempts to prepare cyclobutadienemetal nitrosyl derivatives by a direct synthesis, using nitric oxide as a reactant, were unsuccessful.[187] In contrast, the tricarbonyl iron complexes **3, 7,** and **2** underwent a facile nitrosylation on reaction with nitrosonium hexafluorophosphate to afford the cationic dicarbonylnitrosyliron derivatives **181, 182** and **183,** respectively (Scheme XXIX). The nitrosylation of **3** with nitronium hexafluorophosphate also led to the formation of **181**[188] by a process presumed to involve an intramolecular oxygen transfer followed by CO_2 elimination. It should be of interest to note that despite the oxidizing power of nitrosonium, its reaction with the cyclobutadieneiron tricarbonyl complexes led to the oxidative substitution of a carbonyl group rather than the oxidative displacement of the cyclobutadiene ligand. The latter type process was shown to occur rather readily on treatment of **3** with oxidizing agents[39] such as those containing Fe^{3+} or Ce^{4+}. The mononitrosyl cationic complexes **181** and **183** underwent facile monocarbonyl substitution reactions with various Lewis bases (L = Ph_3P, Ph_3As, and Ph_3Sb) under mild thermal conditions to afford the products[185,186] **184** (l = Ph_3P, Ph_3As, and Ph_3Sb) and **185** (L = Ph_3P and Ph_3As), respectively. Evidently, attempts to effect similar monocarbonyl substitution reactions with the tetramethylcyclobutadieneiron complex **182** were totally unsuccessful. In a single instance involving the reaction of **183** with triphenyl phosphite, the carbonyl-free product **186** was also obtained.

Very recently, von Gustorf and his co-workers[189] have reported the formation of the novel binuclear complex **187,** with a Fe≡Fe triple bond, by the irradiation ($\lambda \geqslant 280$ nm) of **3** in THF at −40 °C in the presence of nitrogen. The structure of this

SCHEME XXX



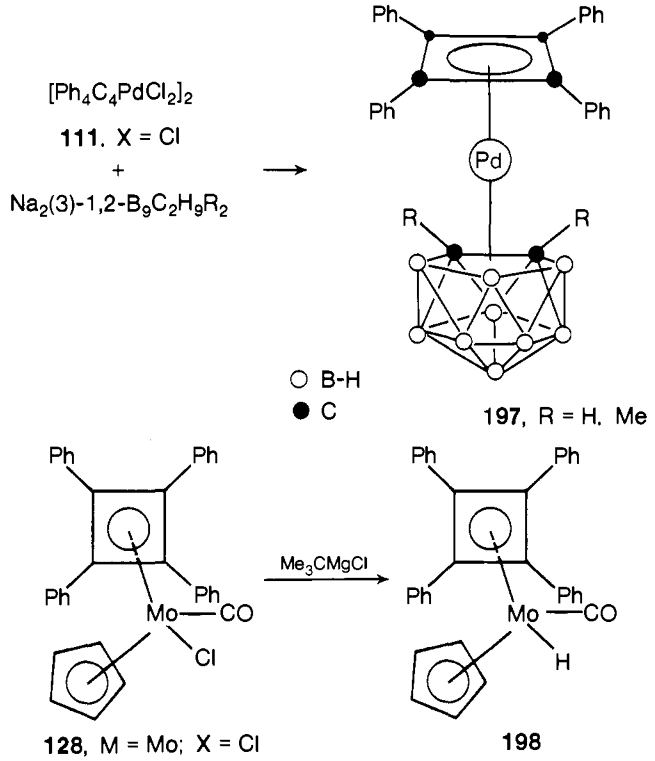
extremely sensitive, dark-red, diamagnetic complex was assigned on the basis of various spectral data. A quantitative regeneration of **3** was achieved by the treatment of **187** with carbon monoxide at −20 °C, whereas the reaction of **187** with trimethyl phosphite gave an equimolar mixture of the mono- and disubstituted cyclobutadieneiron complexes **188** and **189**, respectively (Scheme XXX). Mechanistically, the formation of **187** was presumed to involve the intermediates **190** and **191**. Confirmatory evidence for the presence of the former intermediate was obtained by following the progress of the reaction using infrared spectroscopy as well as by the exclusive formation of **188** on adding trimethyl phosphite to the initially photolyzed reaction mixture at −40 °C. The carbonyl stretching vibrations of **187** appeared only after the irradiation (at −40 °C) was stopped and the solvent (THF) removed at −20 °C. Therefore, it may appear that the transformation **190** → **191** → **187** proceeds extremely readily under mild thermal conditions, rather than photochemically.

Similar binuclear cyclobutadieneiron complexes, with an iron–iron triple bond were prepared[190] by irradiating the hexane solution of $Ph_4C_4Fe(CO)_3$ (**2**) or that of 1,2-diphenyl-3,4-di(*tert*-butyl)cyclobutadienetricarbonyliron (**192**). The latter reactant was obtained by the ligand transfer reaction[130] between the palladium derivative **112** and $Fe(CO)_5$. The photoreactions cited above gave the binuclear iron complexes **193** and **194** as products; the regeneration of the respective starting complexes (**2** and **192**) was achieved under carbon monoxide pressure (140 atm) at 80 °C. The crystal structure of the *tert*-butyl derivative **194**, determined by x-ray diffraction,[190] was shown to contain, among others, an extremely short Fe–Fe bond distance [2.117(3) Å] as well as three bridging carbonyl groups. The distinct differences between the carbonyl stretching frequencies in the infrared spectra of **187**[189] and **194**[190] are consistent with the nonequivalent, nonetheless related, molecular geometries of these complexes.

Other cyclobutadieneiron complexes were also shown to undergo similar reactions to those discussed above. For example, benzocyclobutadieneiron tricarbonyl (**9**) reacted with typical Lewis bases (L) under thermal conditions to afford the complexes (benzocyclobutadiene)$Fe(CO)_2L$ (**195**) where L = Ph_3P,[7] Ph_3As,[191] and Ph_3Sb.[191] Nitrosylation of **9** with either the nitronium or nitrosonium salts of hexafluorophosphate afforded the highly reactive cationic complex [(benzocyclobutadiene)-$Fe(CO)_2NO]^+PF_6^-$ (**196**),[192] whose reactions with typical Lewis bases will be discussed at a later stage (section III.B).

Beside the extensive investigations of the cyclobutadiene complexes of cobalt and iron, relatively few studies, which belong to the category of reactions under consideration, were reported on complexes of the other transition elements. The formation of the nickel and palladium complexes **130** (M = Ni, Pd) by the cyclopentadienylation of the cyclobutadienemetal derivatives **124** and **111** with $CpFe(CO)_2Br$ or $[CpFe(CO)_2]_2$ have already been mentioned in section II.C. The nickel, palladium, and platinum complexes of the type $[R_4C_4MCl_2]_2$ readily undergo

SCHEME XXXI



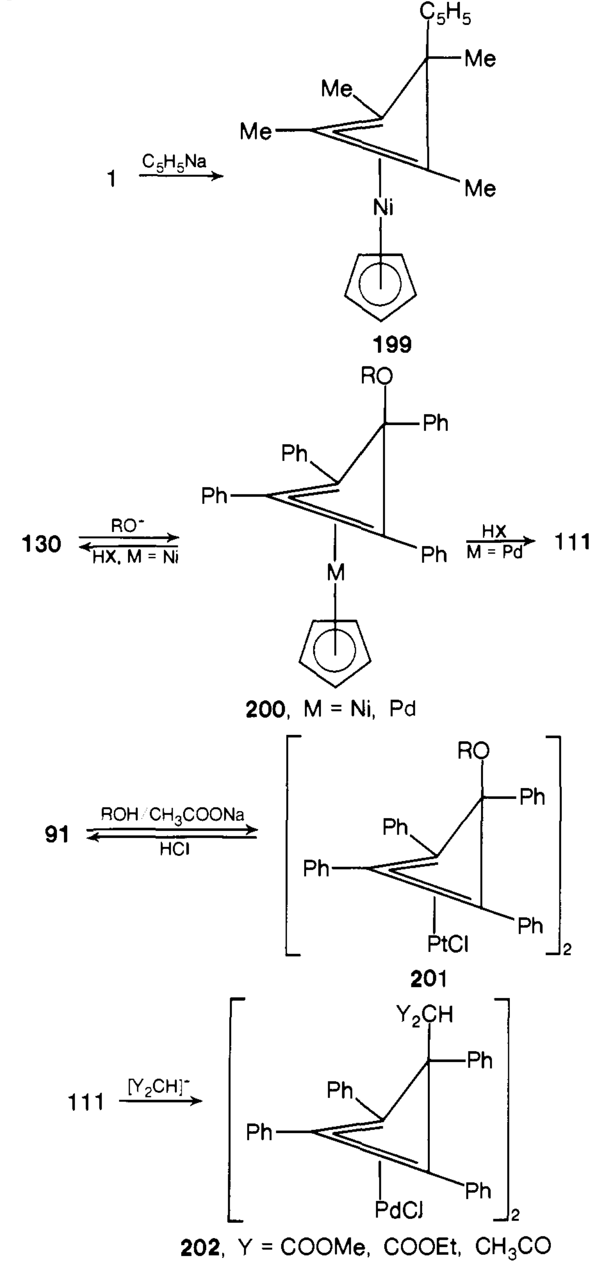
a variety of anion exchange reactions. For example, $[Me_4C_4NiCl_2]_2$ (**1**) has been shown[41] to react with aqueous solutions of iodide, azide, and tetraphenylborate to afford the complexes $Me_4C_4NiI_2$, $Me_4C_4Ni(N_3)_2$, and $Me_4C_4NiCl \cdot BPh_4$, respectively. Similarly, the tetraphenylcyclobutadienemetal chloride complexes **111**,[133] **91**,[111] and **99**[112] were reported to react with LiX (X = Br, I) in polar solvents (e.g., acetone, methanol, etc.) to afford the appropriate bromo and iodo derivatives. Tetramethylcyclobutadienenickel derivatives with nitrate, sulfate, oxalate, and acetate were obtained on treatment of **1** with the appropriate silver salt.[41] The use of a silver salt has also been demonstrated in the reaction of **111** (X = Br) with $AgSCF_3$ by which a monomeric $Ph_4C_4Pd(SCF_3)_2$ complex is formed.[177] Other examples of anion exchange with cyclobutadienemetal derivatives include the reactions of *cis*-1,2-dicyanoethylene-1,2-dithiolate dianion with **111** (X = Cl) and the bromo analogue of **1** by which the through-sulfur chelation of the ligand to the metal in the complexes was claimed[193] to have taken place. Particularly interesting are the reactions of **111** (X = Cl) with the dicarbollides $[(3)\text{-}1,2\text{-}B_9C_2H_{11}]^{2-}$ and $[(3)\text{-}1,2\text{-}B_9C_2H_9Me_2]^{2-}$, reported by Hawthorne and his co-workers.[194,195] The products of these reactions were characterized as the sandwich tetraphenylcyclobutadienepalladium derivatives $(\pi\text{-}Ph_4C_4)Pd[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_9R_2]$ (**197**), where R = H and Me (see Scheme XXXI).

The chemistry of cyclobutadiene complexes of group 6B elements has been examined in few instances only. The cyclobutadienemetal tetracarbonyl complexes **12**[49] and **19**[51] have been shown to undergo monocarbonyl substitution with Ph_3P under photolytic conditions. Lastly, the tetraphenylcyclobutadienemolybdenum complex **128** (M = Mo, X = Cl) has been shown to react with *tert*-butylmagnesium chloride to afford the metal carbonyl hydride **198**.[196] Presently, this complex is the only known cyclobutadienemetal hydride complex.

B. Conversion of Coordinated Cyclobutadiene into Other Complexed Ligands

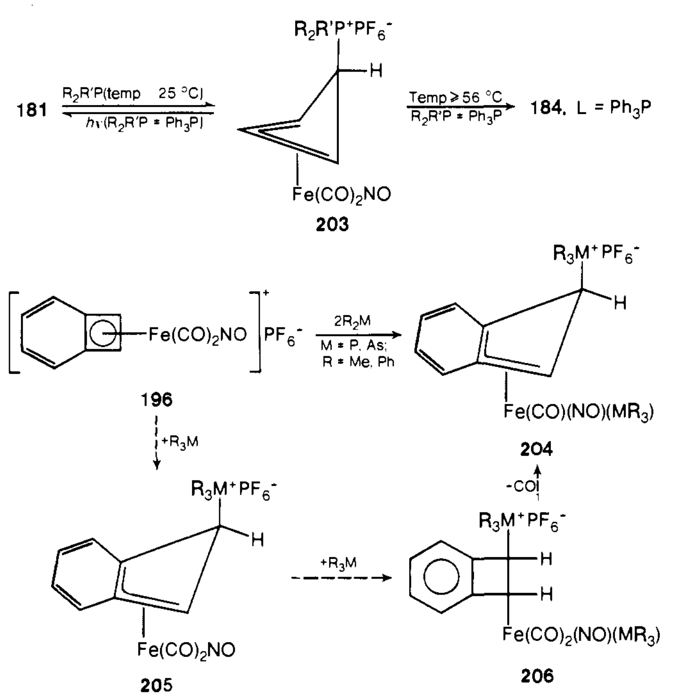
Reactions between nucleophiles and either halo-containing or cationic cyclobutadienemetal complexes have been shown in many instances to afford cyclobutenylmetal complexes.

SCHEME XXXII



Criegee and his co-workers had investigated the reaction between **1** and sodium cyclopentadienide[197,198] (see Scheme XXXII). The product of this reaction $[\eta^3\text{-}(4\text{-}exo\text{-}cyclopentadiene\text{-}1,2,3,4\text{-}tetramethylcyclobutenyl)](\eta^5\text{-}cyclopentadienyl)$nickel (**199**), whose structure was determined by an x-ray crystal analysis,[199] consisted according to its PMR spectrum of isomers which differ from each other by the arrangement of the double bonds in the cyclopentadiene moiety of the complex.[200] Similar products (**200**) were also obtained from the reactions of the cationic nickel and palladium complexes **130** (M = Ni, Pd) with nucleophiles such as RO^- (R = H, Me, Et).[161] The nucleophilic addition of ROH to **111** to afford the cyclobutenylpalladium halide complex **112** has already been cited earlier (section II.B.3), and an analogous reaction between the cyclobutadieneplatinum chloride complex **91** and ROH in the presence of sodium acetate was reported to afford the *exo*-alkoxy-η^3-cyclobutenylplatinum chloride dimer **201**.[111] In all of the above-mentioned reactions, the nucleophilic addition to the cyclobutadiene ligand occurs in an exo rather than endo fashion. The foregoings suggest against metal-assisted addition processes and in favor of a direct attack by the nucleophile at the least sterically hindered site of the cyclobutadiene ligand. The reactions of **111** (X = Cl) with methyl

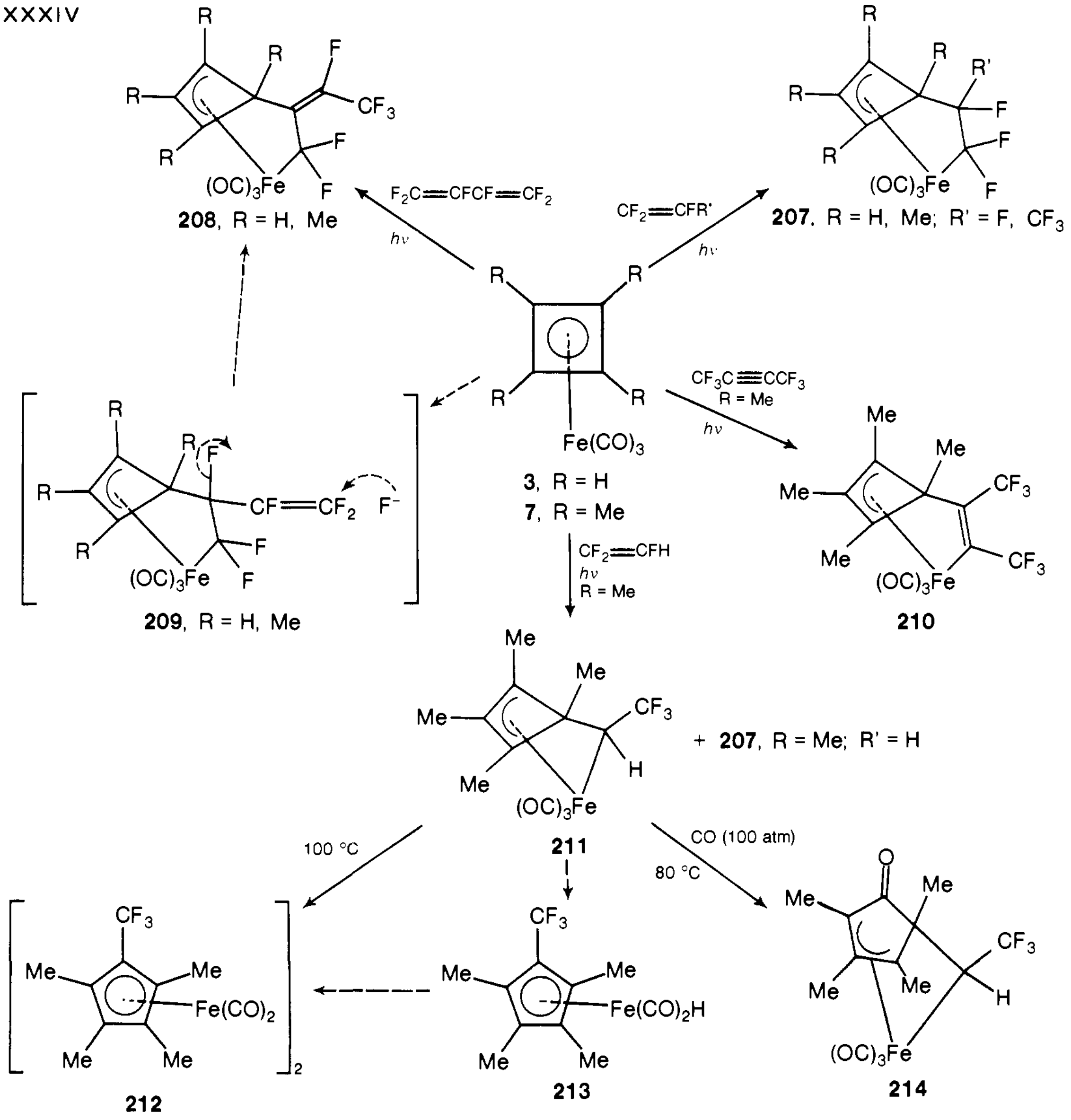
SCHEME XXXIII



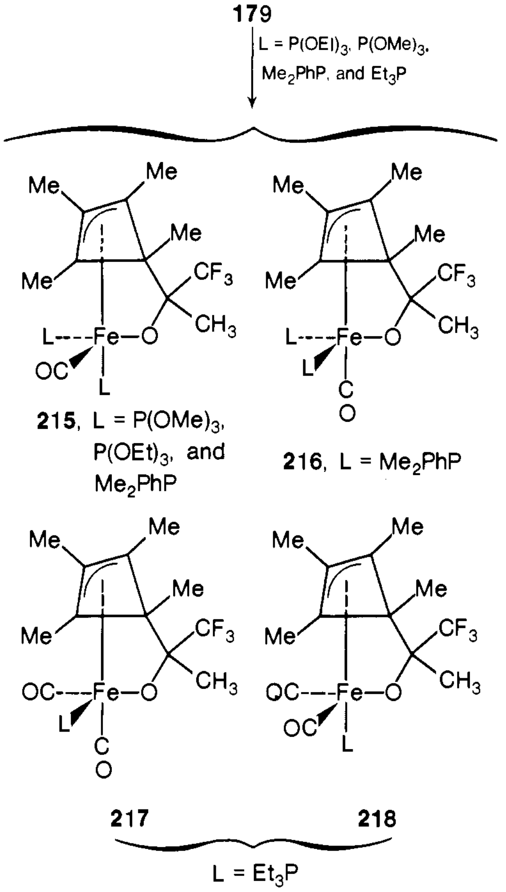
and ethyl malonate as well as acetylacetonate were reported to result in C–C bond formation and ring opening;[201] the structural assignments of complexes prepared in this study are highly doubtful and the reformulation of the products as **202** is perhaps warranted. It should be pointed out that the alkoxycyclobutenylmetal derivatives, cited above, are in general susceptible toward strong acids (HX) which effect their reconversion to cyclobutadienemetal halide complexes.

The substitution of coordinated carbonyl by phosphines and related Lewis bases of group 5A elements is a rather common reaction. By contrast, nucleophilic addition of such bases to acyclic or cyclic π-ligand is an extremely rare reaction of which only few isolated examples are known.[202,203] The parent cyclobutadieneiron dicarbonyl nitrosyl cationic complex **181** underwent a facile reaction at ambient temperature with tertiary phosphines ($R_2R'P$), such as Ph_3P, Ph_2PMe, Me_2PPh, Me_3P, Et_3P, n-Pr_3P, and n-Bu_3P, to afford the respective (*exo*-phosphonium-η^3-cyclobutenyl)dicarbonylnitrosyliron hexafluorophosphate complexes **203**[204] in high yields (Scheme XXXIII). The structure of the trimethylphosphonium derivative **203** (R = R′ = Me) was determined by single-crystal x-ray diffraction analysis.[204] Under irradiation, the regeneration of **181** from **203** (R = R′ = Ph) was achieved, whereas the conversion of the latter to the coordinated phosphine derivative **184** (L = Ph_3P) took place under thermal conditions (temperature ≥ 56 °C). Attempts to affect similar nucleophilic addition reactions with the fully

SCHEME XXXIV



SCHEME XXXV



215, L = $P(OMe)_3$, $P(OEt)_3$, and Me_2PhP

216, L = Me_2PhP

217 **218**

L = Et_3P

substituted cyclobutadieneiron complexes **182** and **183**, or with nucleophiles other than phosphines such as Ph_3As and Ph_3Sb, were totally unsuccessful. Interestingly, the reaction of **181** with Et_3N at 0 °C gave an unstable yellow complex[188] whose infrared spectrum in the carbonyl and hexafluorophosphate regions was nearly identical with those of the **203** derivatives. In view of the spectral data analogy, the product from this reaction has tentatively been assigned the structure of (*exo*-triethylammonium η^3-cyclobutenyl)dicarbonylnitrosyliron hexafluorophosphate; however, further investigation of this complex was made difficult[188] since it underwent rapid release of Et_3N to regenerate **181**.

Reactions similar to those described above for **181** were also studied with the cationic benzocyclobutadieneiron complex **196**.[192] This complex has been observed to undergo vigorous exothermic decomposition in the presence of certain coordinating organic solvent such as acetonitrile and acetone. However, the reaction of **196** with R_3M (M = P, As; R = Me, Ph), carried out in CH_2Cl_2 at ambient temperature, resulted in the formation of **204** by a simultaneous nucleophilic addition–substitution process.[192] This novel reaction was presumed to proceed via intermediates of types **205** and **206** with half-life shorter than ~2 s. Noteworthy in particular is the nucleophilic addition of Ph_3As to **196**, since it is the first reported example of an arsine addition to a π ligand. Comparison between the nucleophilic addition reactions with **181** and **196** has suggested that the carbon atoms of the coordinated cyclobutadiene ligand in the latter complex exhibit a somewhat higher electrophilic character.[192]

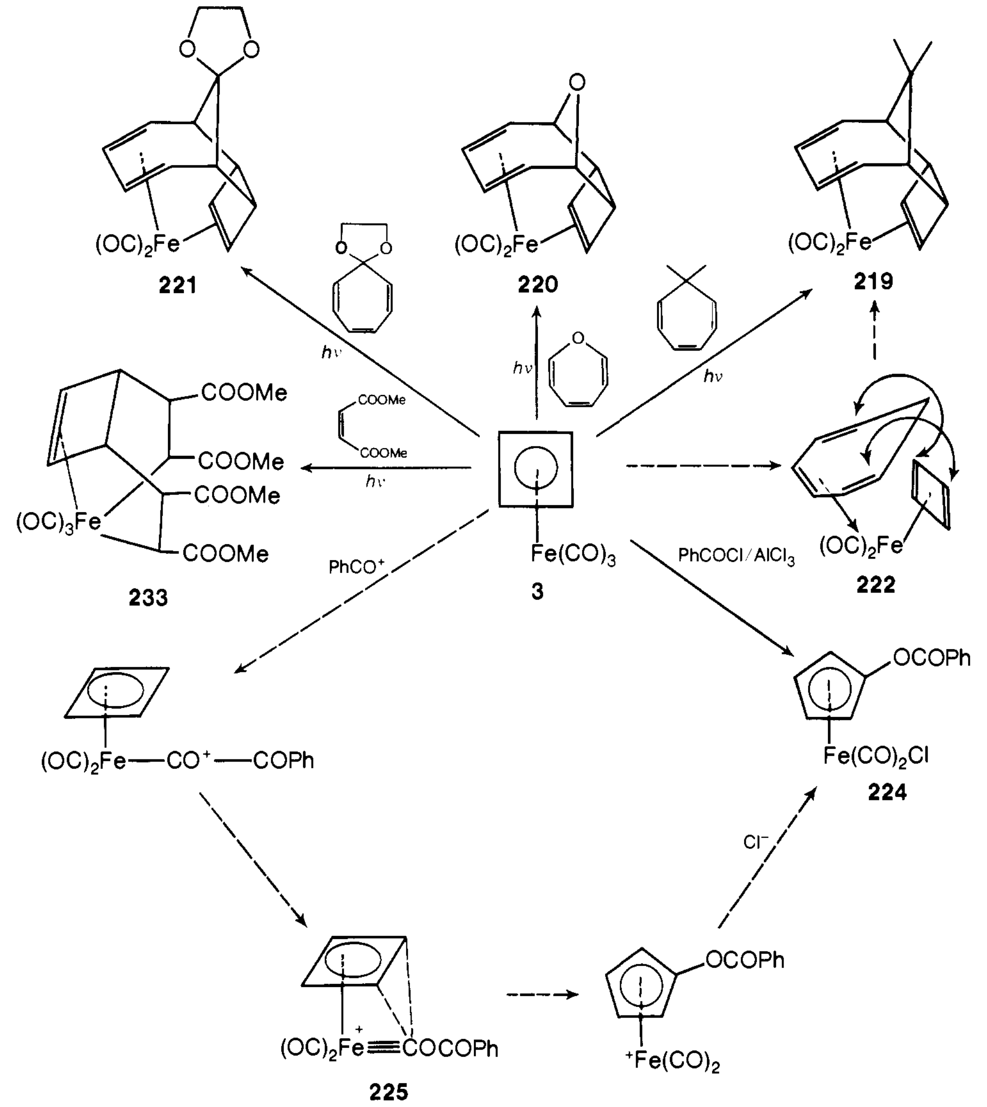
Some unusual photochemical additions of unsaturated organic molecules bearing electron-withdrawing substituents to the cyclobutadiene ligand in **3** and **7** have been reported by Green and his co-workers.[182,183,205] Tetrafluoroethylene and hexafluoropropene reacted on irradiation with **3** and **7** to afford the cyclobutenyliron derivatives **207** where R = H, CH_3 and R′ = F, CF_3 (Scheme XXXIV). A similar photoreaction between $F_2C{=}CFCF{=}CF_2$ and either **3** or **7** gave products whose structures were assigned as **208** (R = H, CH_3), based on their spectroscopic properties. It might be of interest to note that the formation of **208** was explained in terms of an initial 1,2-insertion to give intermediate **209**, followed by a fluoride anion catalyzed 1,3-fluorine shift $[S_N2]$[206,207] by which the latter was presumed to convert to **208**. A related photochemical reaction between **7** and hexafluoro-2-butyne gave the 1,2-insertion product **210**.[182,183] Irradiation of **7** with trifluoroethylene afforded the expected product **207** (R = Me, R′ = H) by a stereospecific 1,2-insertion, as well as a second product **211**[205] whose formation can be envisaged to involve an unusual insertion of 1,1,1-trifluoroethylidene. Specially interesting is the thermal conversion of **211** to the cyclopentadienyliron derivative **212**,[205] a process involving four- to five-membered ring enlargement which was presumed to proceed via the hydrido intermediate **213**. The thermal carbonylation of **211** resulted in carbonyl insertion into the four-membered ring to afford **214**.[205] It was demonstrated that on heating, **214** was neither decarbonylated nor transformed into **212**.

Transformation of coordinated cyclobutadiene into *trihapto*-cyclobutenyl has also been encountered in the reactions of the coordinated hexafluoroacetone complex **179** with various phosphines and phosphites.[183] Treatment of **179** with trimethyl phosphite, triethyl phosphite, and dimethylphenylphosphine gave the respective disubstituted complexes **215** (L = $(MeO)_3P$), **215** (L = $(EtO)_3P$), and the isomeric mixture consisting of **215** (L = Me_2PhP) and **216** (L = Me_2PhP) (Scheme XXXV). By contrast, triethylphosphine reacted with **179** to afford a monosubstituted complex whose structure was assigned as either **217** or **218**. Evidently, addition of Lewis bases to **179** activates the coordinated hexafluoroacetone ligand and induces an intramolecular insertion into the four-membered ring, a process involving carbon–carbon bond formation.

Novel intramolecular cycloadditions of cyclic trienes to the coordinated cyclobutadiene in **3** have been reported by Pettit and his co-workers. Irradiation of **3** with cycloheptatriene, oxepin, and the ethylene ketal of tropone gave the iron dicarbonyl complexes **219, 220,** and **221**, respectively[181] (Scheme XXXVI). Mechanistically, it has been suggested that these reactions proceed via an initial photolytic substitution of a carbonyl by an olefin to give cyclobutadieneiron dicarbonyl olefin intermediates (ca. **222** in the instance of cycloheptatriene), which then undergo an intramolecular cycloaddition process to afford the final products. An exception to this mode of reaction has been encounter in the photolysis of **3** with *N*-carboethoxyazepin by which the carbonyl-free cyclobutadieneiron complex **178** was reported to be formed (section III.A).[181] A different mode of addition has been encountered during the irradiation of **3** with dimethyl maleate in pentane solution. The major product from this reaction was shown to consist of **223**,[208] whose structure has been confirmed by x-ray analysis. The production of **223**, by an apparent double insertion process, was presumed to be initiated from an electronically and coordinatively unsaturated *dihapto*-cyclobutadieneiron tricarbonyl intermediate.[39] By contrast, the monocarbonyl substitution product **177**[180] has been found to be the major product when a similar photoreaction between **3**, and dimethyl maleate was conducted in ether, instead of pentane, as solvent.[39]

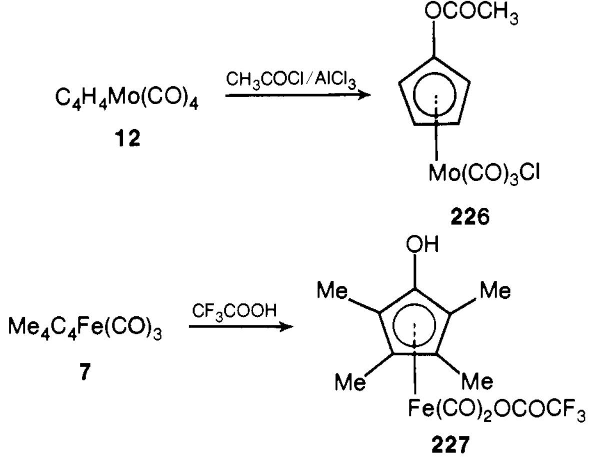
Several noteworthy cyclobutadiene ring expansion processes have also been reported by Pettit and his co-workers.[39] Acylation of **3** with benzoyl chloride in the presence of aluminum chloride gave in addition to the expected product, benzoylcyclobutadieneiron tricarbonyl, a red crystalline material whose structure according to an x-ray analysis was shown to consist of benzoyloxycyclopentadienyliron dicarbonyl chloride (**224**).[209] Mechanistically, the four-membered ring expansion encountered in this reaction was rationalized[39] in terms of an initial attack by the electrophile on a coordinated carbonyl group, followed by

SCHEME XXXVI



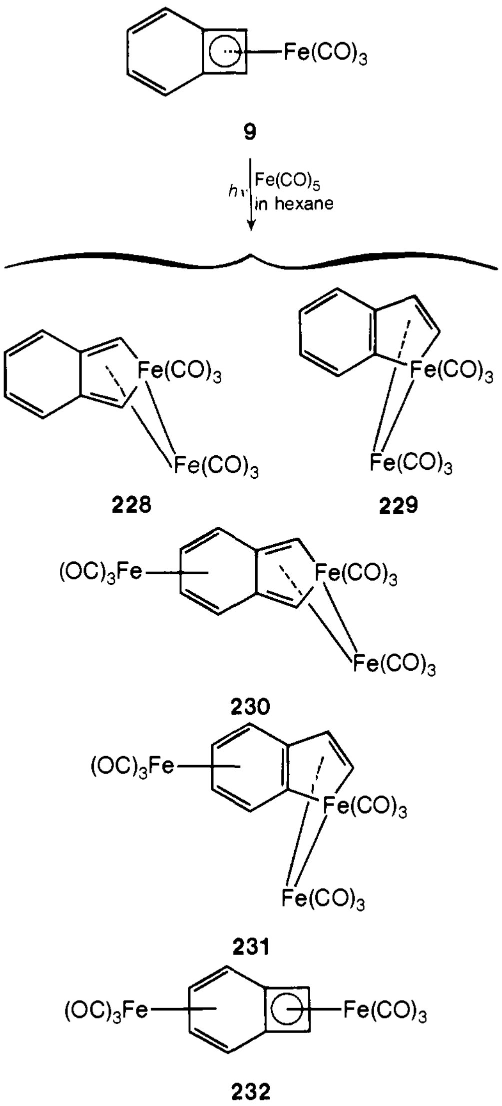
the rearrangement of the attacked species into a carbyne intermediate (**225**) which then undergoes an intramolecular insertion to effect four- to five-membered ring expansion. Similar ring expansion processes were also encountered in the Friedel-Crafts acetylation of cyclobutadienemolybdenum tetracarbonyl (**12**) as well as in the reaction of **7** with CF_3COOH by which the respective cyclopentadienylmetal derivatives **226**[210] and **227**[211] are being formed (Scheme XXXVII). At this stage, it should be appropriate to indicate that in the instance of **3** electrophilic substitution reactions are greatly favored over ring expansion processes, whereas the molybdenum complex **12** shows a greater propensity for the insertion process and lack of reactivity toward electrophilic substitutions. Evidently, the contrasting reactivity modes of these complexes are not due to any apparent fundamental changes in the nature of their cyclobutadiene ligands. In terms of bonding, the carbon atoms of the four-membered ring in the molybdenum tetracarbonyl complex **12** should be somewhat more electrophilic than those of the iron tricarbonyl complex **3**, since a weaker metal-to-cyclobutadiene, $d\pi \rightarrow p\pi$, back-bonding interaction would be expected in the former system. This assessment is consistent with the experimentally observed highly susceptibility of the cyclobutadiene ligand in **3** toward electrophilic substitutions as compared with that in **12**.

SCHEME XXXVII

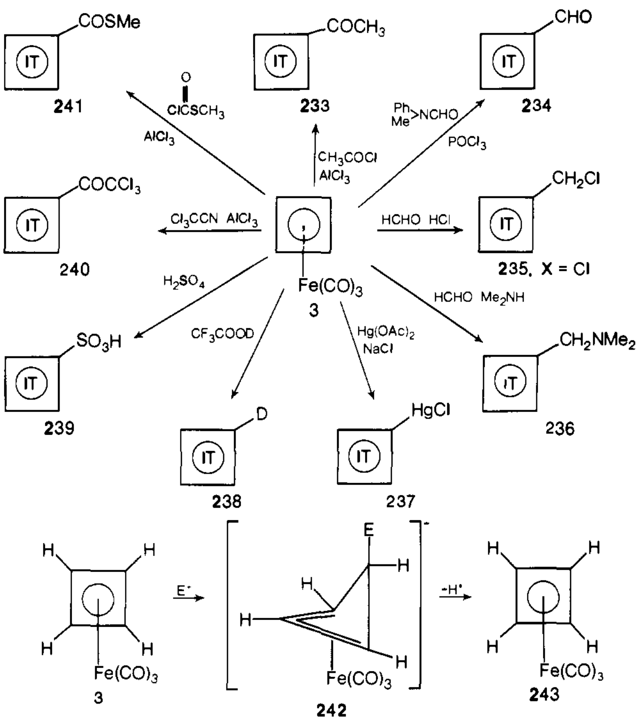


The interrelationship between coordinated cyclobutadienes and metallocycles has already been discussed in some length elsewhere in this review (section II.B.2). Recently, the results of two independent investigations on the thermal and photoreactions between benzocyclobutadieneiron tricarbonyl (**9**) and iron carbonyls have been reported.[122,123] In both instances, the insertion of an iron carbonyl moiety into the coordinated cyclobutadiene has been shown to take place to afford a variety of ferrole derivatives. Noteworthy in particular is the photoreaction of **9** with $Fe(CO)_5$ from which five different complexes (**228, 229, 230, 231,** and **232**)[123] have been isolated and characterized (Scheme XXXVIII), and this in addition to another two unidentified complexes which were obtained in trace amounts only. The

SCHEME XXXVIII



SCHEME XXXIX



thermal reaction between **9** and $Fe_3(CO)_{12}$, conducted in hydrocarbon solvents at 120 °C, gave an equimolar mixture of **228** and **229**, each formed in 38% yield.[124]

C. Organic Chemistry of Coordinated Cyclobutadiene

Reactions to be discussed in this section are those which take place on the coordinated cyclobutadiene without disrupting its bonding with the metal atom. Most studies in this area have so far been performed on the cyclobutadieneiron tricarbonyl systems. In general, the organic chemistry of the system under consideration can conveniently be divided into two broad categories: electrophilic substitution reactions and chemical transformations by which existing substitutents are being converted into new functionalities. The combination of electrophilic substitution reactions and chemical transformations gave an extensive series of cyclobutadieneiron tricarbonyl derivatives. It should be noted that many of the chemical transformations, performed on the system under consideration by utilizing standard reagents and techniques commonly used in organic synthesis, might appear on the outset to be of little or no particular interest. In fact, the reader should bear in mind that simply substituted "free" cyclobutadienes are extremely labile molecules; nevertheless, such molecules can presently be generated in situ, rather readily by the oxidation of their iron tricarbonyl complexes. The generation of "free" cyclobutadienes and their use as reagents in organic synthesis represents a novel synthetic approach in organic chemistry. In this context, cyclobutadieneiron tricarbonyl derivatives can be regarded as valuable reagents. The utilization of such derivatives as reagents in organic synthesis will be examined in further detail elsewhere in this review (section IV).

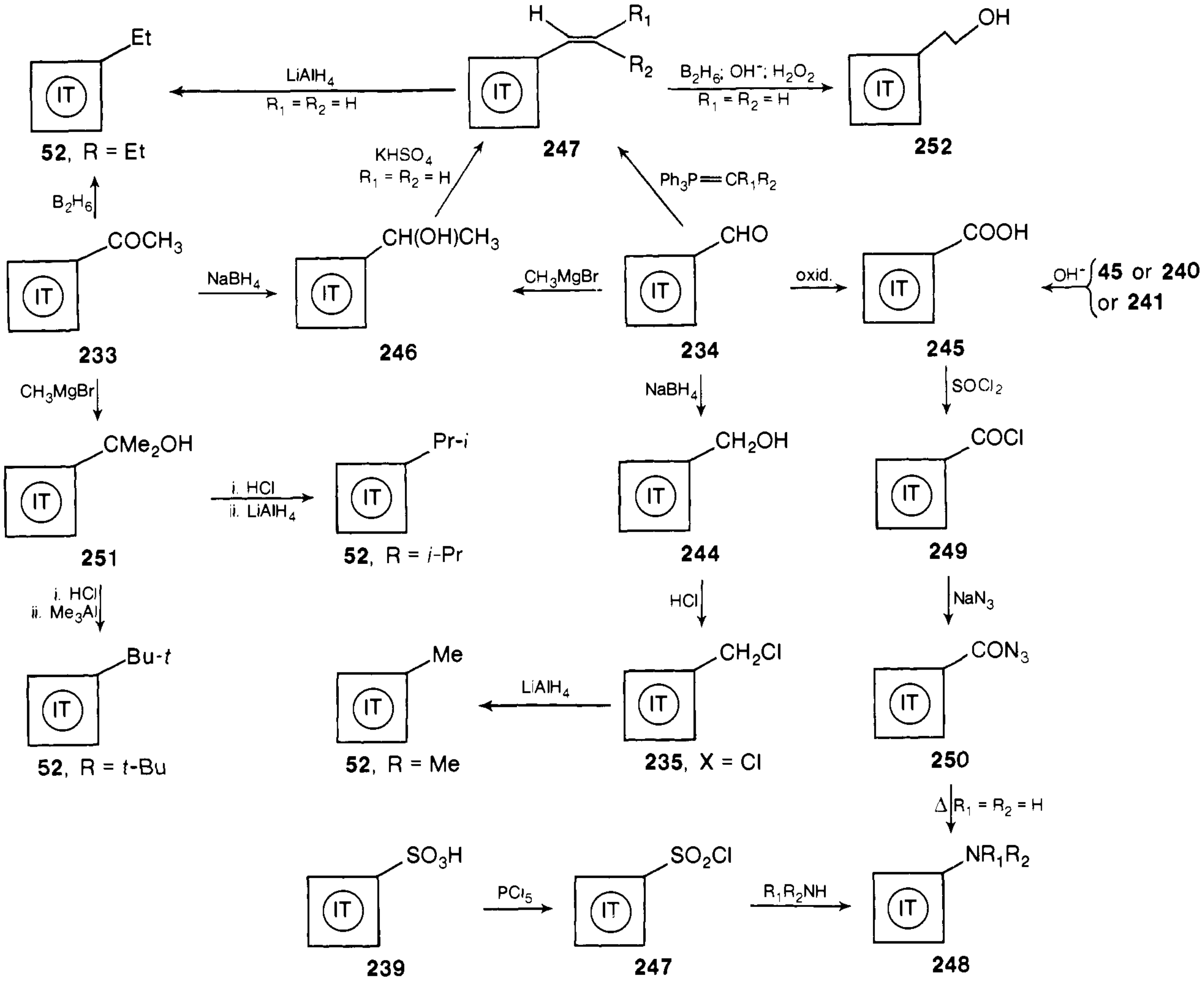
The discussion on the organic chemistry of coordinated cyclobutadiene will conveniently be divided into three parts according to the type of complexes: (1) monosubstituted cyclobutadieneiron tricarbonyl derivatives, (2) di- and polysubstituted cyclobutadieneiron tricarbonyl derivatives, and (3) cyclobutadiene complexes of metals other than iron.

1. Monosubstituted Cyclobutadieneiron Tricarbonyl Derivatives

In 1965, Pettit and his co-workers were the first to demonstrate[35] that the parent cyclobutadiene ligand in **3** readily undergoes a variety of electrophilic substitution reactions similar to those of ferrocene[212] and related metallocenes. The electrophilic substitutions performed on **3** which were reported in the original paper[35] included Friedel-Crafts acetylation (to afford **233**), Vilsmeier formylation (to afford **234**), chloromethylation (to afford **235**), aminomethylation (to afford **236**), acetoxy mercuration (to afford **237**), and deuteration (to afford **238**) (Scheme XXXIX). Other noteworthy substitution reactions of **3** included sulfonation with H_2SO_4 to give the sulfonic acid derivative **239**,[213] a Hoesch-type addition of trichloroacetonitrile in the presence of aluminum chloride to afford the trichloroacetyl derivative **240**,[214] and methylthioformylation using methylchlorothioformate and $AlCl_3$ to afford **241**.[211]

The significance of the above reactions stems from the characterization of coordinated cyclobutadiene as a typical aromatic system. Mechanistically, the electrophilic substitution of **3** was rationalized in terms of an electrophilic addition of E^+ to give a cationic η^3-cyclobutenyliron tricarbonyl (**242**) intermediate, followed by proton abstraction to afford the final product **243**. Although intermediates of type **242** have not yet been isolated, a closely related complex, η^3-allyliron tricarbonyl cation, was synthesized and characterized.[215,216] The existence of such a complex appears to support the plausibility of **242** as an intermediate in the electrophilic substitution of **3**.

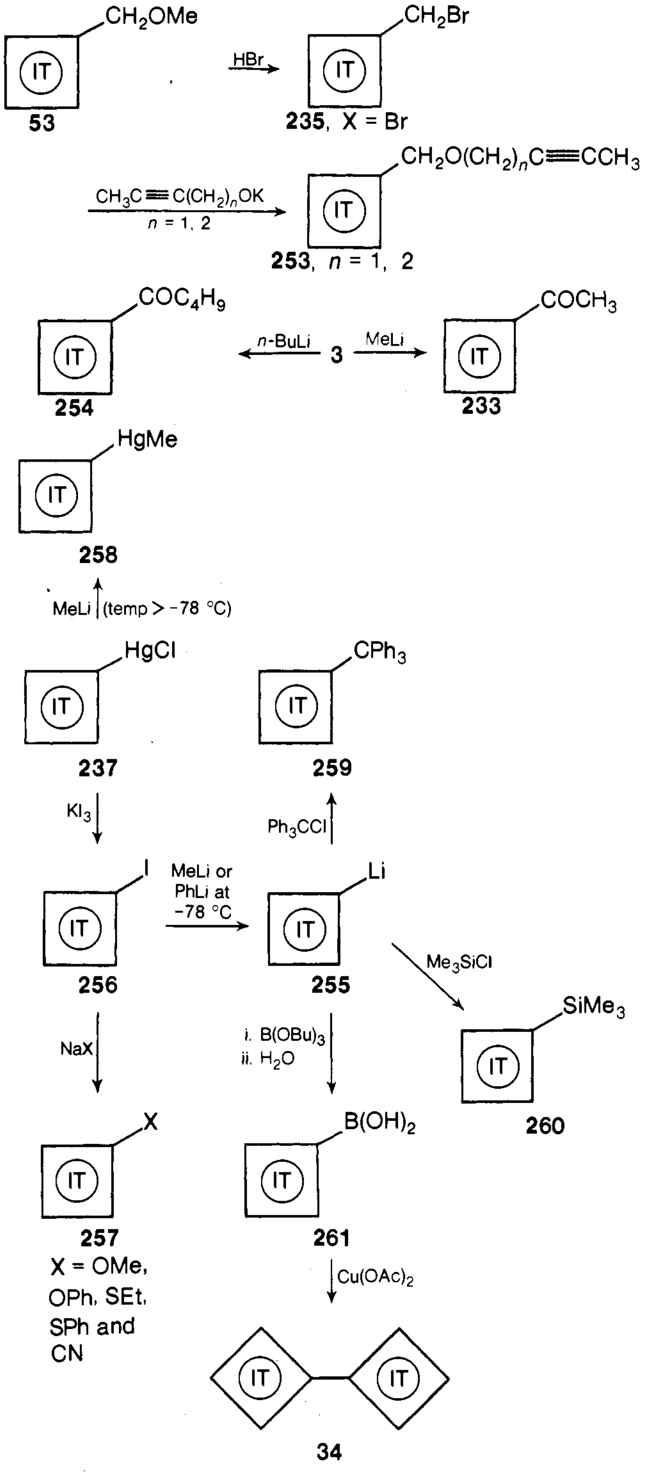
SCHEME XL



Fairly extensive chemical transformations have been performed on the monosubstituted cyclobutadieneiron tricarbonyl system. Reduction of the aldehyde **234** with $NaBH_4$ gave the primary alcohol **244**, which on treatment with HCl was converted to **235** (X = Cl)[35] (Scheme XL). Oxidation of **234** with silver oxide was reported to afford a low yield of the carboxylic acid **245**. A more convenient synthetic route to the carboxylic acid **245** involves the alkaline hydrolysis of either **45**,[75] **240**,[214] or **241**.[211] Other noteworthy reactions of the aldehyde **234** are those with methylmagnesium bromide and phosphoranes. The former reaction gave the secondary alcohol **246**,[35] whereas the latter reaction (Wittig reaction) gave the vinylcyclobutadieneiron derivatives **247**:[217] $R_1 = R_2 = H$; $R_1 = H$, $R_2 = Ph$ (cis isomer); $R_1 = Ph$, $R_2 = H$ (trans isomer); $R_1 = R_2 = Me$; $R_1 = R_2 = Et$; $R_1 = H$, $R_2 = Me$ (cis isomer); $R_1 = Me$, $R_2 = H$ (trans isomer); and $R_1 = COOEt$, $R_2 = H$. The stereospecific formation of the *trans*-styrylcyclobutadieneiron complex **247** ($R_1 = Ph$, $R_2 = H$) has been reported by the $Pd(OAc)_2$-catalyzed reaction between styrene and **3**,[218,219] and the parent vinylcyclobutadieneiron complex **247** ($R_1 = R_2 = H$) was also synthesized by the dehydration of **246**.[220] A general route to aminocyclobutadieneiron tricarbonyl derivatives (**248**) involves the treatment of the sulfonyl chloride **247** (prepared by the reaction of **239** with PCl_5) with amines.[221] This synthetic procedure permitted the obtainment of **248** with $R_1 = R_2 = H$; $R_1 = H$, $R_2 = PhCH_2$; $R_1 = H$, $R_2 =$ *n*-Bu; $R_1 = H$, $R_2 =$ allyl; $R_1 = R_2 = Me$; $R_1 = R_2 = Et$; $R_1R_2 =$ *N*-piperidino and $R_1R_2 =$ *N*-morpholino. The synthesis of the parent aminocyclobutadieneiron complex **248** ($R_1 = R_2 = H$) by route from the acid chloride **249** and via the Curtius rearrangement of the azide **250** has also been reported.[39] The acetyl derivative **233** reacted with methylmagnesium bromide to afford the tertiary alcohol **251**.[220] Incidentally, simple monosubstituted alkyl derivatives of coordinated cyclobutadiene cannot be obtained by the direct alkylation of the parent system; nevertheless, many such derivatives are accessible by chemical transformations. For example, the monoalkyl derivatives **52** ($R = CH_3$) and **52** (R = Et) were obtained by the $LiAlH_4$ reduction of **235** (X = Cl) and **247** ($R_1 = R_2 = H$), respectively. The monoethyl derivative of **52** was also reported to be formed by the reaction of the acetyl **233** with diborane.[222] A somewhat similar reaction between the parent vinyl **247** ($R_1 = R_2 = H$) and diborane, followed by alkaline hydrolysis in the presence of H_2O_2 yielded the primary alcohol **252**.[223] The monoalkyl derivatives **52** (R = *i*-Pr) and **52** (R = *t*-Bu) were prepared by the treatment of **251** with HCl followed by further reaction with $LiAlH_4$ or Me_3Al, respectively.[220]

Numerous additional noteworthy transformations of monosubstituted derivatives have also been reported. Cleavage of the methoxymethyl derivative **53** with HBr gave a quantitative yield of the bromide **235** (X = Br), which on further reaction with $CH_3C{\equiv}C(CH_2)_nOK$ ($n = 1$ and 2) was converted to the alkyne ether derivatives **253** ($n = 1, 2$)[79] (Scheme XLI). Attempts to prepare the monolithium salt of coordinated cyclobutadiene by the reaction of **3** with either methyl- or butyllithium resulted in the formation of the acetyl and valeryl derivatives **233** and **254**, respectively.[224] The formation of these unusual products could perhaps be explained by an initial nucleophilic attack on the coordinated carbonyl to give an acyl-type intermediate which then undergoes an intermolecular acyl transfer process to afford the observed products. The monolithium salt **255** was produced by the reaction of either the chloromercury derivative **237** or the monoiodo derivative **256** with MeLi or PhLi at −78 °C. The

SCHEME XLI



monoiodo derivative **256,** obtained by the treatment of **237** with KI_3,[225] was shown to undergo facile nucleophilic substitutions with NaOMe, NaOPh, NaSEt, NaSPh, and KCN to afford the respective derivatives **257**.[226] At a temperature higher than −78 °C, the reaction of **237** with MeLi resulted in the formation of the methylmercury derivative **258,** rather than **255.** Reactions of **255** with the halo derivatives Ph_3CCl and Me_3SiCl gave the expected products **259** and **260,** respectively. Another reaction between **255** and butyl borate gave, after hydrolysis, the boronic acid derivative **261**.

So far, the discussion has been centered on the chemistry of monosubstituted mononuclear cyclobutadieneiron tricarbonyl derivatives. Certain such derivatives can react further to afford some interesting monosubstituted binuclear complexes. For instance, treatment of the boronic acid derivative **261** with $Cu(OAc)_2$ yielded the coupling product **34**. The acetyl derivative **233** has been reported[222] to undergo a bimolecular reduction to the glycol **262** (Scheme XLII). A pinacol-type rearrangement of the latter via the preferential migration of the $C_4H_3Fe(CO)_3$ moiety gave **263**. Dehydration of **262** also afforded **264**. Under alkaline conditions, the acetyl derivative **233** was reported to undergo an aldol-type condensation followed by dehydration to afford the binuclear complex **265**.

In recent years, some attention has been given to the study of α-carbonium stabilized cyclobutadieneiron tricarbonyl systems. Hexachloroantimonate and hexafluorophosphate salts of the parent α-carbonium cyclobutadieneiron tricarbonyl **266** were obtained by the treatment of **235** (X = Cl) with $SbCl_5$ and $Ag^+PF_6^-$, respectively (Scheme XLIII). These salts readily decompose in presence of air, although it should be pointed out that stable solutions of the parent α-carbonium and some of its simple derivatives were obtained upon the dissolution of the previously mentioned alcohols **244, 246,** and **251** in sulfuric acid.[227] A manifestation of the high stability of the α-carbonium ion in this system is the extremely rapid rate of hydrolysis of the chloromethyl derivative **235** (X = Cl) which is approximately 10^8 times faster than that of benzyl chloride.[228] Additional support to the same comes from the rapid cycloaddition of tetracyanoethylene to the parent vinylcyclobutadieneiron complex **247** ($R_1 = R_2 = H$) in polar solvents at ambient temperature. The cycloaddition product of this reaction, **267,**[220] was presumed to be formed via a dipolar mechanism involving intermediate **268.** Particularly interesting α-carbonium derivatives have been reported with the biscyclobutadieneiron tricarbonyl system.[228] The binuclear α-carbonium derivatives **269** were synthesized by the Friedel-Crafts acylation of **3** with **249** as well as by the reaction of the lithium derivative **255** with the ketones **233** and **270** (see Scheme XLIII). The α-carbonium ions of the binuclear derivatives **269** (R = H, Me, and Ph) appeared to be highly stabilized, and their prolonged exposure to air did not result in any noticeable decomposition. Noteworthy are some of the structural features of the α-carbonium derivative **269** (R = Ph).[228] In this complex the cyclobutadiene rings were found close to being coplanar with the plane formed by the three carbon-carbon bonds associated with the exocyclic carbon atom, whereas the phenyl ring was observed to be twisted (~43°) from this plane. The iron-carbon (cyclobutadiene) bonds in this complex were found to be nearly equidistant and similar to those reported for $C_4H_4Fe(CO)_3$.[229] Based on the crystallographic data, it has been concluded that the stabilization of the α-carbonium ion in the system under consideration originates from a pπ–pπ transmission of electron density from the coordinated cyclobutadiene rings into the electron-deficient exocyclic carbon atom. An alternative mechanism of stabilization involving an ancillary iron–exocyclic carbon interaction, of the type invoked in the case of the α-carbonium derivatives of ferrocene,[230] has been ruled out entirely in the current instance for lack of sufficient structural evidence. It should perhaps be pertinent to speculate that the stabilizing effect exerted by the $C_4H_3Fe(CO)_3$ moiety might, in part, be due to a strong iron–cyclobutadiene back-bonding interaction by which enhancement of the electron density on the coordinated cyclobutadiene is expected to be achieved. The rather high electrophilic susceptibility of the ring carbon atoms in **3** appears to be consistent with the above expressed view.

2. Di- and Polysubstituted Cyclobutadieneiron Tricarbonyl Derivatives.

In recent years, a considerable effort has been made at investigating the syntheses and chemical properties of di- and polysubstituted cyclobutadienemetal complexes. The syntheses of some complexes which fall into this category have already been explored elsewhere in this review (section II). In the current

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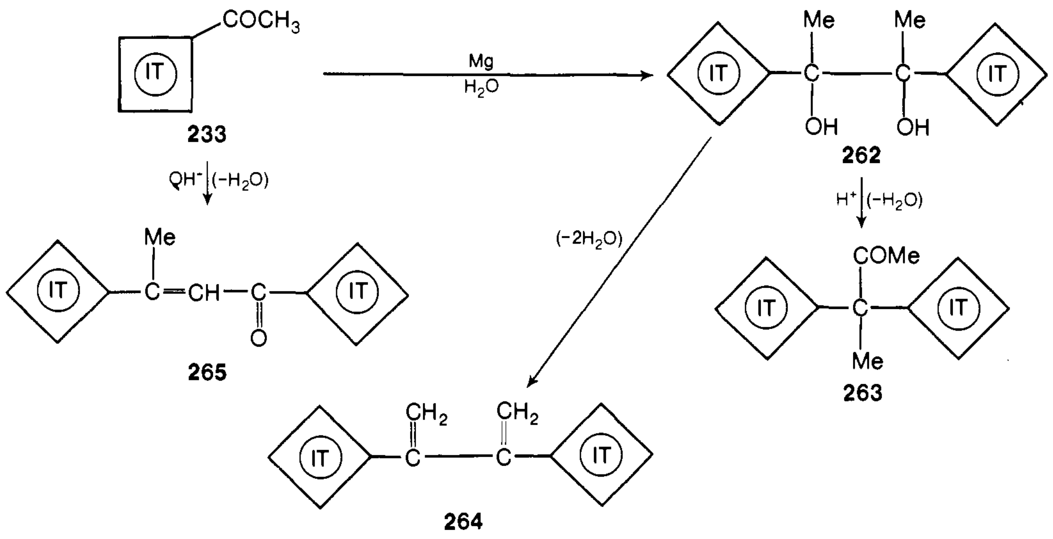
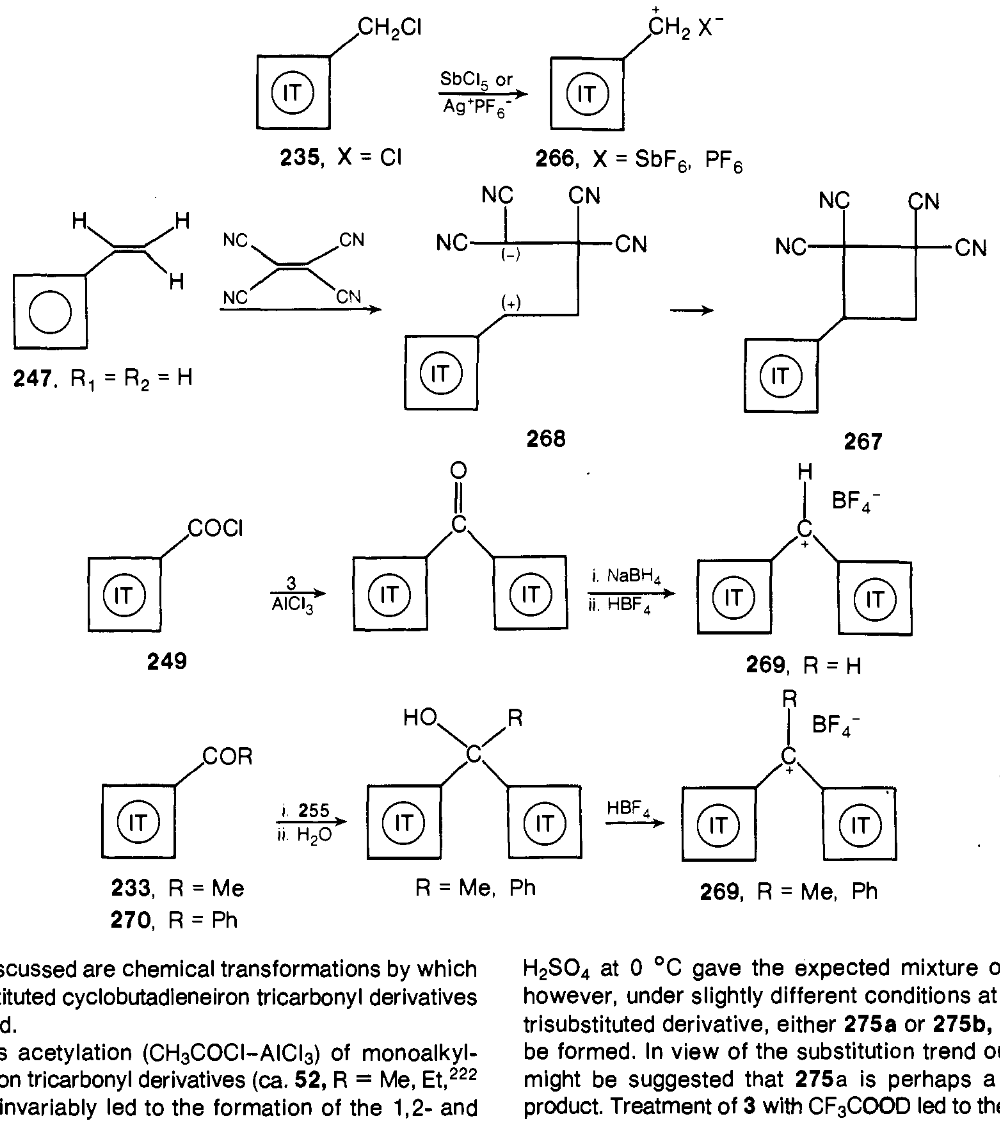


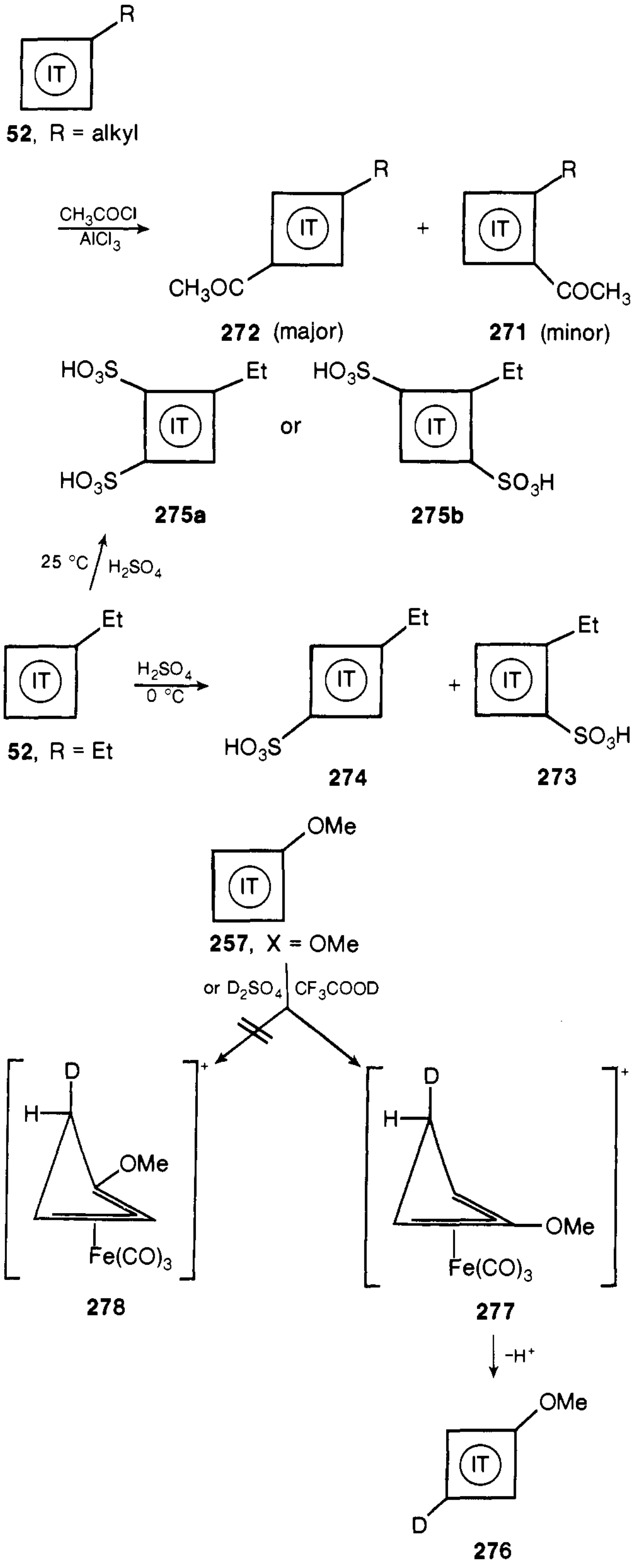
SCHEME XLIII



section, to be discussed are chemical transformations by which di- and polysubstituted cyclobutadieneiron tricarbonyl derivatives are being formed.

Friedel-Crafts acetylation ($CH_3COCl-AlCl_3$) of monoalkylcyclobutadieneiron tricarbonyl derivatives (ca. **52**, R = Me, Et,[222] *i*-Pr, *t*-Bu, etc.) invariably led to the formation of the 1,2- and 1,3-disubstituted derivatives **271** and **272**, respectively (Scheme XLIV). Accounting for statistical factors, the 1,3-disubstituted derivatives **272** are formed in a ratio of fourfold excess, or better, compared with **271**. These results reveal that weakly electron-releasing substituents exert a pronounced activation of the 3 position, as compared to the statistically favored 2 position, toward electrophilic substitutions. Sulfonation of **52** (R = Et) with H_2SO_4 at 0 °C gave the expected mixture of **273** and **274**; however, under slightly different conditions at 25 °C, only the trisubstituted derivative, either **275a** or **275b**, was reported to be formed. In view of the substitution trend outlined above, it might be suggested that **275**a is perhaps a more plausible product. Treatment of **3** with CF_3COOD led to the rapid formation of a mixture consisting of the mono- and polydeuterated derivatives,[35] whereas successive treatment of the parent system with CF_3COOD gave perdeuteriocyclobutadieneiron tricarbonyl. Deuteration of methoxycyclobutadieneiron tricarbonyl (**257**, X = OMe) by its dissolution in CF_3COOD or D_2SO_4 afforded the 3-deuterated product **276**, exclusively. Accordingly, the methoxy group, a moderately strong electron-releasing substituent,

SCHEME XLIV



52, R = alkyl

272 (major)

271 (minor)

275a

275b

52, R = Et

274

273

257, X = OMe

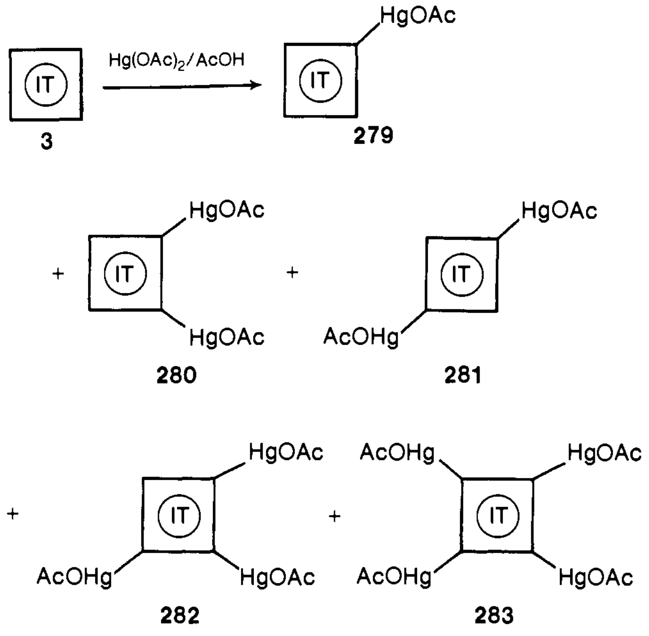
278

277

276

produced an extraordinarily strong activation of the 3 position as compared to the 2 position. A plausible explanation of this directing effect in terms of the intermediate **277** being energetically favored over **278**, was proposed by Pettit.[39]

The formation of the monochloromercury derivative by the acetoxymercuration of **3** has already been cited[35] earlier. This interesting reaction also afforded a mixture of all the possible acetoxymercury derivatives.[225] For instance, treatment of equimolar quantities of $Hg(OAc)_2$ and **3** in acetic acid for 30 min at ambient temperature gave an equilibrium mixture consisting of **279–283** . The reversibility of the mercuration process in this system was demonstrated by the formation of all possible derivatives from either the pure monoacetoxymercury **279** or the peracetoxymercury **283** on standing in acetic acid for about 30 min. The conversion of the monoacetoxymercury **279** to the chloromercury derivative **237** and iodo derivative **256** on treatment with NaCl and KI_3, respectively, has already been cited earlier. Similar procedures gave the respective di-, tri-, and tetrasubstituted chloromercury and iodo derivatives from the acetoxymercury complexes **280–283**. Adjustment of the initial molar ratio of **3** and $Hg(OAc)_2$ during the acetoxymercuration afforded a convenient route to the mono- and tetrasubstituted derivatives.



3

279

280

281

282

283

The most extensive chemical transformations performed on the disubstituted cyclobutadieneiron tricarbonyl system were those reported by Roberts and his co-workers[70,71] on **38**. Saponification of **38** gave the 1,2-dicarboxylic acid **284**, which then, on treatment with $SOCl_2$ was converted into the bis(acid chloride) form **285** (Scheme XLV). Reactions of **285** with benzene (in the presence of $AlCl_3$), $PhCH_2OH$, NH_3, CH_2N_2, and $NaBH_4$ afforded the disubstituted derivatives **286, 287, 288, 289** (X = Cl), and **290,** respectively. Dehydration of the diamide **288** with P_4O_{10} gave the 1,2-dinitrile derivative **291**. Conversion of the bis(chloromethyl ketone) **289** (X = Cl) to the iodo form **289** (X = I) was achieved on treatment with NaI, whereas the reductive cleavage of the former, using NaI–AcOH and then $Na_2S_2O_3$, gave the bis(methyl ketone) derivative **292**. A more convenient synthetic route to **292** was shown to involve the treating of the bis(diazo ketone) intermediate, resulting from the reaction of **285** and diazomethane, with hydriodic acid. The diol **290,** also obtained by one-step reduction of **38** with di(isobutyl)aluminum hydride, was converted to the known 1,2-dimethyl derivative **23**[54] via the reduction of the bis(chloromethyl) derivative **293** with $LiAlH_4$. Incidentally, a more direct synthesis of **23** involved the reduction of the diacid **284** with diborane in the presence of BF_3. In another sequence, the diester **38** was converted to (1,2-di-*tert*-butyl)cyclobutadieneiron tricarbonyl by the steps: (a) MeLi then NH_4Cl, (b) HCl, and (c) Me_3Al–MeCl (−50 °C). Attempts to prepare a bis(phosphorane) derivative by the reaction of the bis(chloromethyl) **293** with two equivalents of Ph_3P were totally unsuccessful. Since the ultimate objective of this particular study was the synthesis of polyenic cyclobutadienoid systems, an alternative approach involving the Wittig olefination of the di-

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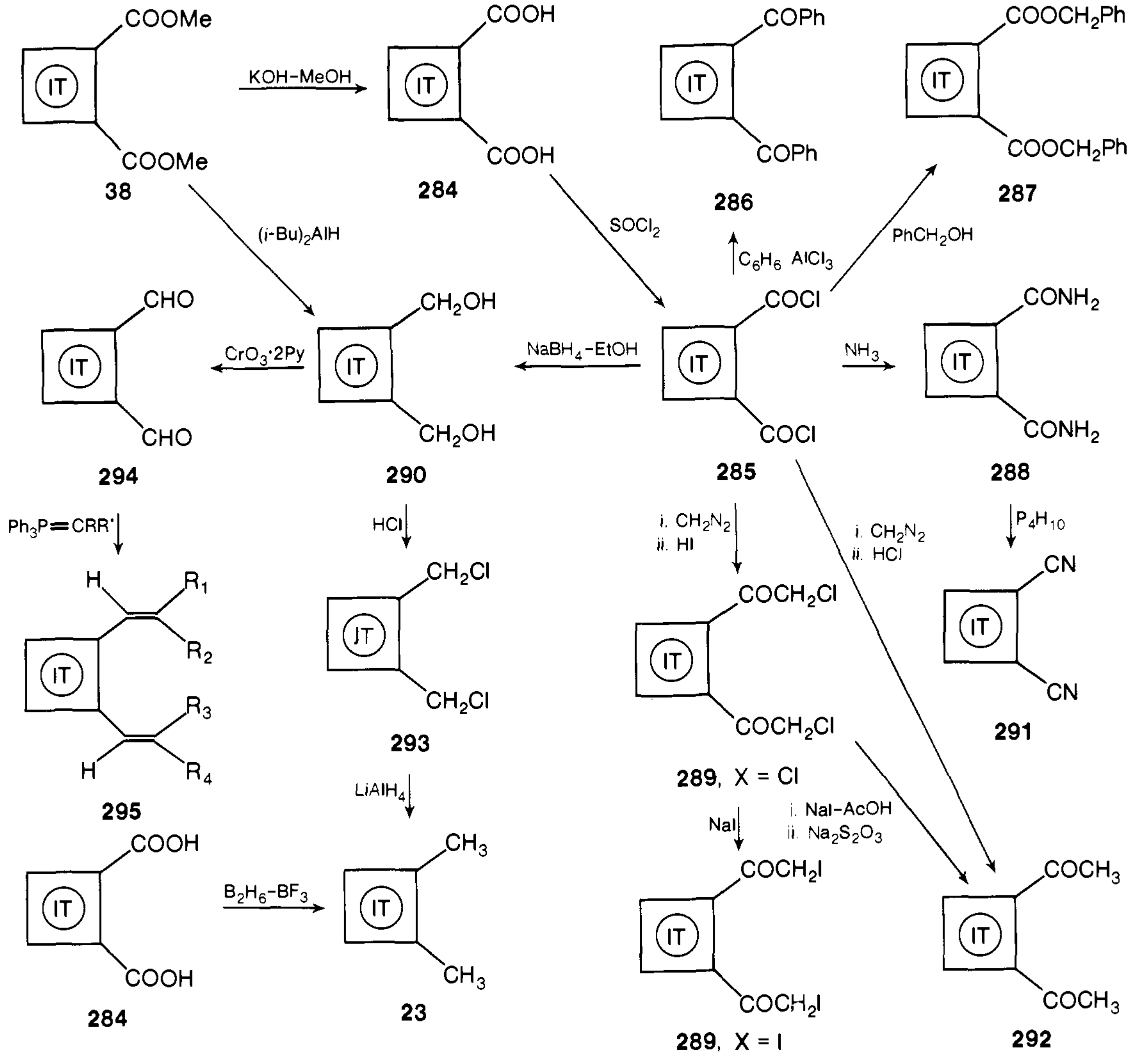

aldehyde **294**, synthesized in 60–65% yield by the oxidation of the diol **290** with Collin's reagent ($CrO_3 \cdot 2Py$), was tried and shown to be successful. This procedure gave the divinyl derivatives **295** ($R_1 = R_2 = R_3 = R_4 = H$; $R_1 = R_2 = R_3 = R_4 = Ph$; $R_1 = R_4 = Ph$, $R_2 = R_3 = H$; $R_1 = R_3 = Ph$, $R_2 = R_4 = H$; and $R_1 = R_4 = H$, $R_2 = R_3 = Ph$) from **294** and the appropriate triphenylphosphorane. The above cited 1,2-distyryl derivatives were obtained as a mixture having nearly the expected statistical distribution (3:5:2) from the reaction of **294** with benzylidenetriphenylphosphorane.

The chemical transformations described above are those in which both substituents simultaneously undergo the same reaction. Several chemical transformations involving the reaction of only one of the two substituents have also been reported. Roberts and his co-workers[71] have reported the transformation of the diester **38** to the [1-nitrile-2-(*N*,*N*-dimethyl)amino]cyclobutadieneiron derivative **305** by a ten-step sequence involving the derivatives **296–304** (Scheme XLVI). The first step in the sequence involved the partial saponification of **38** to **296**, whereas the remaining steps were accomplished by use of common synthetic organic procedures. Another chemical transformation involving the sequence **296** → **297** → **306** → **307** → **308** → **309** has been reported by Schmidt.[231] This sequence is noteworthy in particular since it was utilized to generate chiral cyclobutadieneiron tricarbonyl complexes. The above sequence afforded the racemic mixture of **309**. Resolution of the racemic acid by quinine gave the optically active acid (−)-**308**. Esterification of (−)-**308** with diazomethane afforded (−)-**307** whose optical activity (>99%) was determined by a PMR technique. Reduction of (−)-**308** with B_2H_6-BF_3 gave (−)-**309**. The issue of chirality of nonidentical 1,2-disubstituted cyclobutadieneiron tricarbonyl derivatives has also been examined by Grubbs and Grey.[80] Diastereomeric esters **310** were obtained by the treatment of the bromide derivative **311**, prepared from the reaction between **54** and HBr, with sodium (+)-trifluoromethylmethoxyphenylacetate (Scheme XLVII), and characterized from the PMR spectrum. In another sequence, the racemic amine **312**, prepared from **311** and excess Me_2NH, was partially resolved by using (+)-camphor-10-sulfonic acid followed by fractional crystallization. After two fractional crystallizations, the salt was decomposed and the resulting amine **312** was converted into **54** via **313**. The diastereoisomeric esters **310**, prepared from the partially resolved **54**, were shown by the integration of their PMR spectra to have optical purities of 30–40%. Interestingly, the resolved complex showed less than 5% racemization on being heated at 120 °C for 48 h, whereas a related complex (+)-(methyl 5-formylpenta-2,4-dienoate)iron tricarbonyl was shown to racemize with $t_{1/2} = 46.5$ h at 119.4 °C.[232] The slow racemization rate of the cyclobutadieneiron complex was attributed to the unfavored decomplexation of the coordinated cyclobutadiene by which such a process was presumed to take place.

In concluding the discussion on disubstituted cyclobutadieneiron tricarbonyl derivatives, it should be of interest to comment concerning the scope and limitations of ring-forming reactions in the system under consideration which have been reported by Roberts and Wissner.[233,234] Attempts to affect an intramolecular aldol cyclization of the diketone **292**, in the pres-

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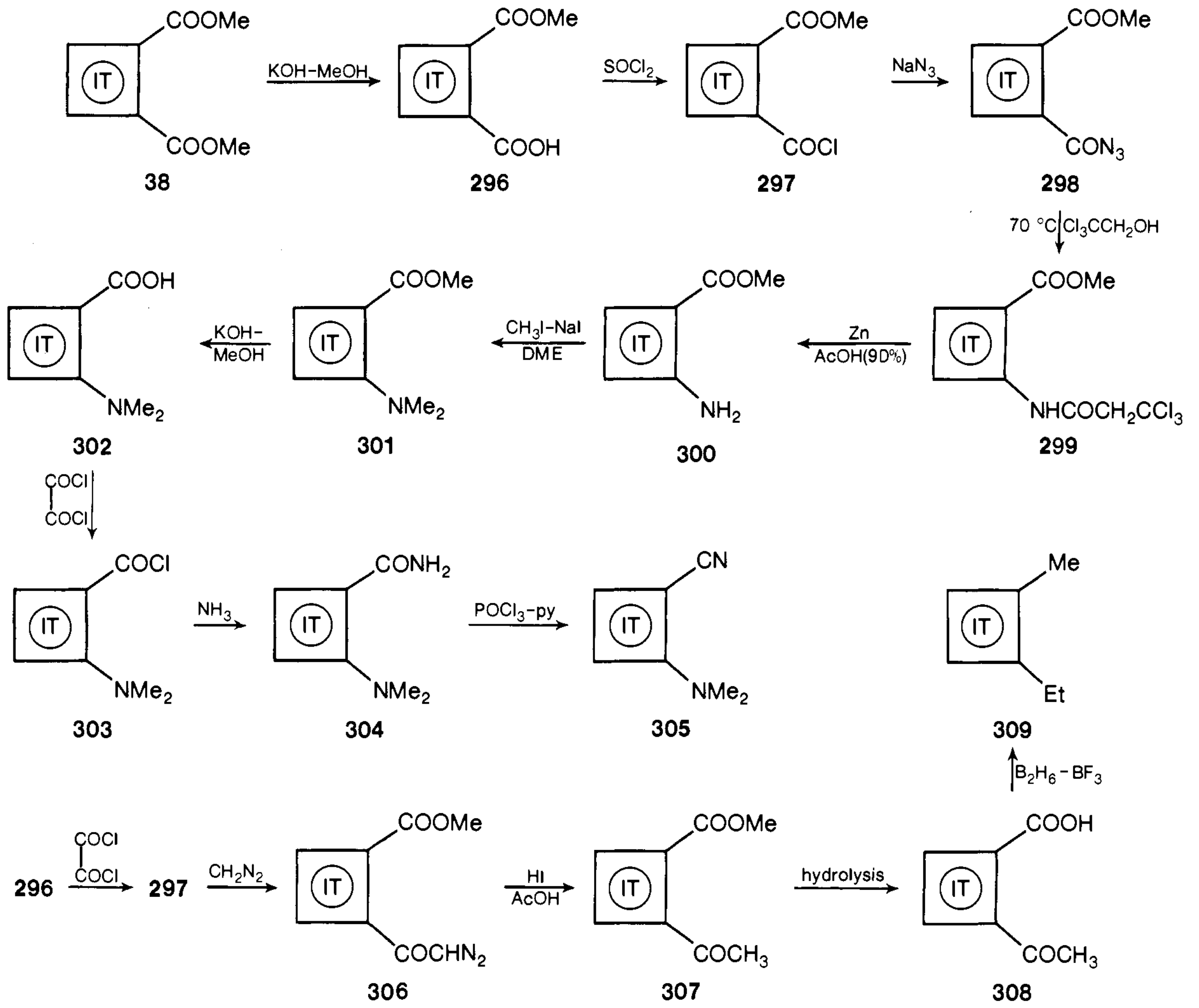
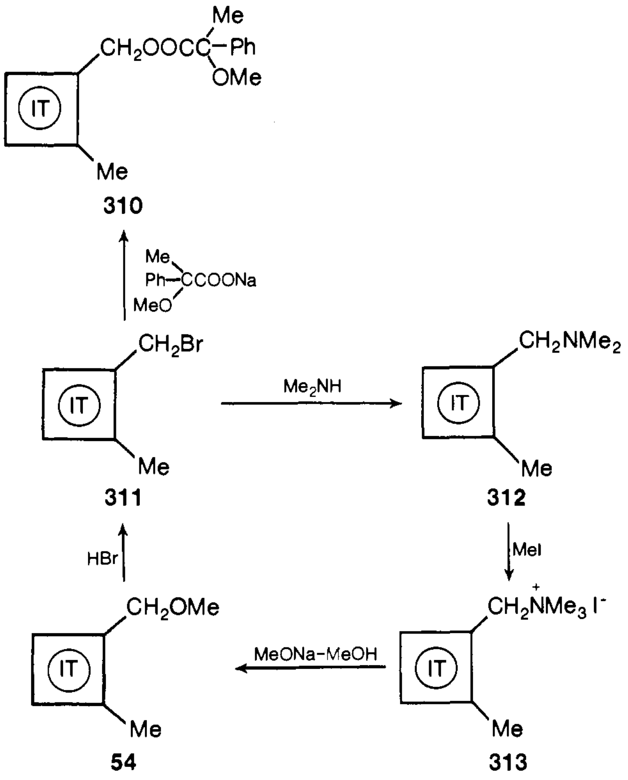


SCHEME XLVII

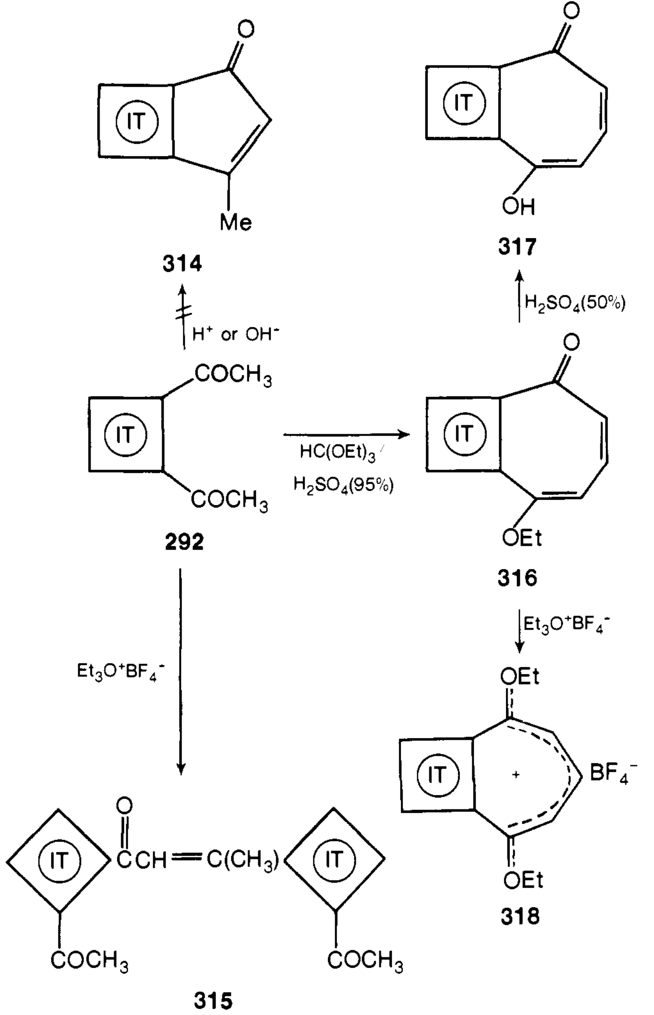


ence of acidic or basic catalysts, with the purpose of synthesizing **314** were evidently unsuccessful. However, in the presence of $BF_3 \cdot Et_2O$ or $Et_3O^+BF_4^-$ the diketone underwent a bimolecular condensation to afford a mixture of two isomers with the gross structure **315**[233] (Scheme XLVIII). Treatment of the diketone **292** with ethyl orthoformate in 95% H_2SO_4 gave the tropone derivative **316**, which on further hydrolysis was converted into **317**. The presumed diethoxytropylium derivative **318** was obtained by the treatment of **316** with $Et_3O^+BF_4^-$; it should however be pointed out that certain alternative structures for the product of this reaction are also plausible. In another procedure, the bis(acid chloride) **285** on reaction with naphthalene or acenaphthene, under Friedel-Crafts conditions (CS_2–$AlCl_3$), gave the fused-ring derivatives **319** and **320**, respectively[233] (Scheme XLIX). Reductions of **319** to the diol **321** and **321'** were achieved by using diborane. A similar procedure was utilized in reducing **286** to the diol $[1,2\text{-}(PhCHOH)_2H_2C_4]Fe(CO)_3$.[234]

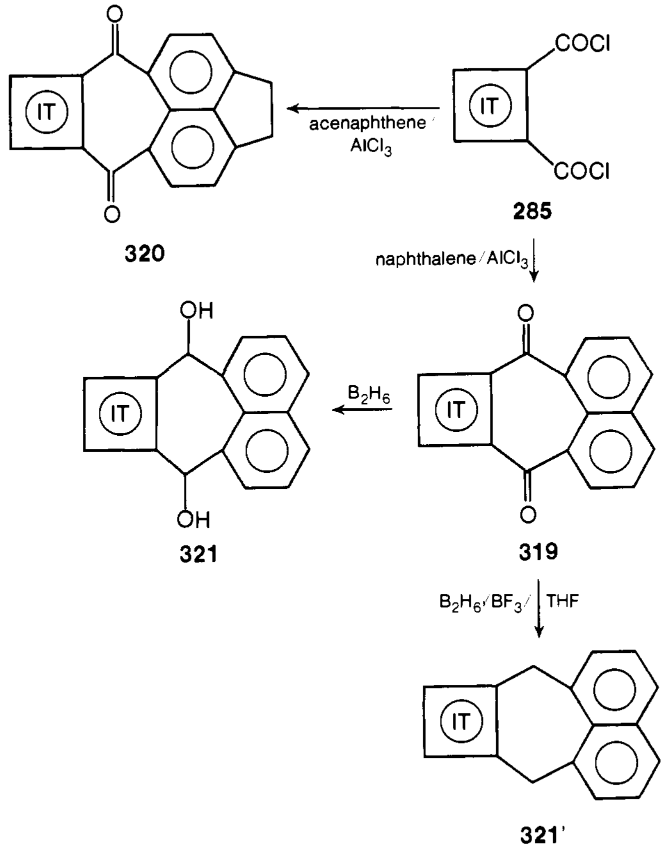
3. *Cyclobutadiene Complexes of Metals Other Than Iron*

Relatively little has been reported on the organic chemistry of coordinated cyclobutadiene in complexes other than those of iron. The sandwich complex (η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt (**46**), prepared originally[50] by the reaction of the iodide **17** with cyclopentadiene in the presence of Et_3N, was shown to undergo Friedel-Crafts acetylation[50,76] and acetoxymercuration[50] at the four-membered ring to afford **322** and **323**, respectively (Scheme L). Acetoxymercuration of **46** conducted in CH_3COOD followed by decomposition in D_2O gave a mixture

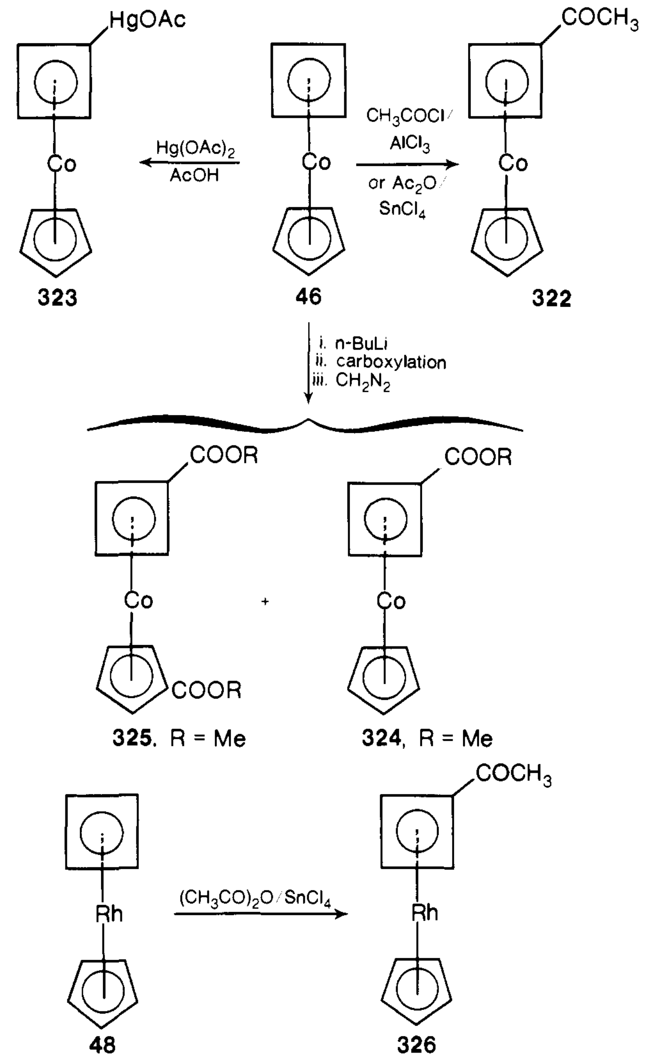
SCHEME XLVIII



SCHEME XLIX



SCHEME L



of the mono-, di-, tri-, and tetradeuteriocyclobutadienecobalt derivatives. Metalation of **46** with *n*-BuLi, followed by carboxylation and esterification using diazomethane, gave the monoester **324** (R = Me; 30% yield) and diester **325** (R = Me; 18% yield).[76] The above reaction did not afford the monoester **47**, although this complex was prepared by a different route (section II.A.3).[76] Noteworthy is the comparison between the K_a' ($=K_a \times 10^7$) values of benzoic acid (6.5), **324**, R = H (2.8), **47**, R = COOH (1.9), and ferrocene monocarboxylic acid (1.6). The similar K_a' values of the ferrocene monocarboxylic acid and **47** (R = COOH) indicate that the π-electron densities of the coordinated C_5H_4-COOH rings in these complexes differ by only little, and are higher than that of the coordinated C_4H_3-COOH ring in **324** (R = H). Furthermore, the higher acidity of the benzoic acid suggests that in the carboxylic acids of the complexes the π-electron densities of the coordinated ligands are higher than that of the benzene ring. Comparison between **324** (R = H) and **47** (R = COOH) suggests that η^4-C_4H_4 is a better electron-withdrawing ligand than is η^5-C_5H_5. This interpretation is evidently consistent with the experimentally determined greater susceptibility of the former ligand toward electrophilic substitution. In a similar system to that discussed above, the sandwich rhodium complex **48** was shown to undergo Friedel-Crafts acetylation with acetic anhydride, in the presence of stannic chloride, to afford the monoacetyl cyclobutadienerhodium complex **326**.[77] By contrast, cyclobutadienemolybdenum tetracarbonyl (**12**) reacted with CH_3COCl in the presence of $AlCl_3$ to afford the ring expansion product **226**,[210] rather than an electrophilic substitution product.

IV. Displacement of Coordinated Cyclobutadiene from Its Complexes

Extensive investigations on the thermal and/or chemical decompositions of cyclobutadienemetal complexes have been reported. The acyclic and/or cyclic organic products formed by the various degradation processes were initially studied in order to gain structural information concerning the complexes themselves. The generation of free cyclobutadiene by its oxidative displacement from **3**, first reported by Pettit[39] and his coworkers, has triggered extensive research work to do with the utilization of cyclobutadienemetal complexes in organic synthesis. Moreover, this dramatic discovery has had important ramifications on certain theoretical aspects connected with the "cyclobutadiene problem". Accordingly, the discussion in this section will conveniently be divided into two parts depending on whether or not the integrity of the cyclobutadiene ligand is retained upon displacement.

A. Displacement Involving the Destruction of the Cyclobutadiene Ligand

Studies falling into this category are in general of mild interest, and, therefore, they will be mentioned briefly. The thermal decompositions of $[Me_4C_4NiCl_2]_2$ (**1**) and $Me_4C_4NiCl_2 \cdot phen \cdot 2H_2O$ were reported by Criegee[42] and his co-workers,[27,235] and similar studies were also performed on $[Ph_4C_4NiBr_2]_2$ (**124,** X = Br)[147,236–238] and $[Ph_4C_4PdCl_2]_2$ (**111,** X = Cl).[132,134,239,240] The organic products obtained from the pyrolyses of the complexes were characterized by chemical and/or spectrometric methods. In most instances, the composition of the pyrolyzates depended rather markedly on the conditions under which the pyrolyses were carried out.

Chemical degradations of cyclobutadienemetal complexes were examined by various investigators. The water-soluble nickel complex **1** on heating to 100 °C decomposed to the permethylated *anti*-tricyclooctadiene isomer,[27] whereas the di- and trimethylcyclobutadienenickel chloride complexes **24** ($R_1 = R_2$ = H; R_1 = H, R_2 = Me) were shown to rapidly decompose in water already at ambient temperature.[241] Degradations with reducing agents [in brackets] of the cyclobutadienemetal complexes have been reported: $[Me_4C_4NiCl_2]_2$ (**1**) [Zn–HCl],[42] $[Ph_4C_4NiBr_2]_2$ (**124,** X = Br) [$LiAlH_4$,[236,242] catalytic hydrogenation[134,147]], $[Ph_4C_4PdCl_2]_2$ (**111,** X = Cl) [$NaBH_4$,[129,133] $LiAlH_4$[133,134]], $Ph_4C_4Fe(CO)_3$ (**2**) [$LiAlH_4$,[28,242] Na–NH_3 (liquid)[28]], and $Ph_4C_4CoC_5H_5$ (**63**) [Na–NH_3 (liquid)[90]]. Reactions of cyclobutadienemetal derivatives with oxidizing agents [in brackets] were reported with the following complexes: $[Me_4C_4NiCl_2]$ (**1**) [$NaNO_2$–H_2O[27]], $[Ph_4C_4NiBr_2]_2$ (**124,** X = Br) [$NaNO_2$–H_2O[147]], and $[Ph_4C_4PdCl_2]_2$ (**111,** X = Cl) [HNO_3[129,133]]. The oxidation of the parent iron complex **3** and related derivatives with Fe(III) and Ce(IV) will be discussed in the following section (IV.B). Halogenation of cyclobutadienemetal complexes leads, in most instances, to extensive decomposition. Treatment of the nickel complex **124** (X = Br) with bromine has been reported[243,244] to result in extensive decomposition, whereas this complex on reaction with $pyHBr_3$ gave a high yield of *trans*-3,4-dibromotetraphenylcyclobutene. Bromination of the parent cyclobutadieneiron complex **3** afforded[245] a mixture of trans-cis-cis-trans, cis-trans-cis-trans, and trans-trans-trans-trans isomers of tetrabromocyclobutene. Bromination of certain tetraphenylcyclobutadienemolybdenum complexes have also been reported.[87]

Finally in this category are the reactions of the tetraphenylcyclobutadienepalladium halides **111** with tertiary phosphines and phosphites. The deep green paramagnetic solutions[134,246,247] produced in these reactions were presumed to consist of the chloro- or bromotetraphenylcyclobutenyl radicals.[240] The green color of the above-mentioned solutions persists for a long time at ambient temperature; however, in refluxing benzene rapid decoloration was observed to be followed by the formation of octaphenylcyclooctatetraene.[246]

B. Generation of Free Cyclobutadiene and Its Use in Organic Synthesis

By analogy with other diene-iron tricarbonyl complexes, cyclobutadieneiron tricarbonyl (**3**) has been shown, by Pettit[39] and his co-workers, to undergo facile oxidative decomposition when treated with Ce(IV) or Fe(III). A considerable amount of evidence, which is mostly circumstantial, has accumulated to indicate that transient free cyclobutadiene is being generated during the oxidative decomposition of **3**. This issue will be discussed in further detail later on in this section. At this stage it would perhaps be pertinent to examine the nature of products obtained by the oxidative decomposition of the parent cyclobutadieneiron complex **3** in the presence of dienophiles as well as other substrates. In the absence of a trapping agent the decomposition of **3** with Ce(IV) yielded a mixture of *syn*- and *anti*-tricyclooctadienes in a 5 (**327**): 1 (**328**) ratio.[248] The oxidative decompositions of **3** carried out in the presence of the dienophiles methyl propiolate,[6] phenylacetylene,[249] dicarbomethoxyacetylene,[6,250,251] dibenzoylacetylene,[251] dimethyl maleate,[248] dimethyl fumarate,[248] acrylophenone,[252] *p*-benzoquinone,[253,254] 2,4-dibromobenzoquinone,[253] 1,2-naphthoquinone,[255] cyclopentadiene,[248] cyclopentadienone diethyl ketal,[256] *trans*-7,8-diacetoxybicyclo[4.2.0]octa-2,4-diene,[257] and a mixture consisting of cis and trans isomers of 7,8-dichlorobicyclo[4.2.0]octadiene[258] were reported to afford the Diels–Alder adducts **329,**[6] **330,**[249] **331**[6] (and/or **332**[250,251] depending on the stoichiometry of the reactants), **333**[251] (and/or **334**[251] depending on the stoichiometry of the reactants), **335,**[248] **336,**[248] **337,**[252] **338,**[253,254] **339,**[253] **340,**[255] **341,**[248] **342,**[256] **343,**[257] and **344** (cis and trans mixture),[258] respectively (see Table II).

Similar reactions involving the oxidative decomposition of **3** in the presence of the azo derivatives **345,**[259] **346,**[260] **347,**[261] and **348**[262] were reported to afford the products **349,**[259] **350,**[260] **351,**[261] and **352,**[262] respectively. The oxidative decomposition of **3** with $FeCl_3$–EtOH, or with Ce(IV) in the presence of LiCl using acetone as a solvent, gave *trans*-3,4-dichlorocyclobutene (**353,** X = Cl).[7] The latter procedure using LiX (X = Br, I) was utilized for the preparation[263] of **353** (X = Br, I). Compounds **353** (X = Br, I, and ONO_2), were also obtained[264] by the reaction of **3** with bromine, iodine, and ceric(IV) ammonium nitrate, respectively. The results described above, and others[265] of types related to the parent complex **3,** have been summarized in Table II.

Besides the parent cyclobutadieneiron tricarbonyl (**3**), the oxidative decomposition of other related derivatives was also investigated. The oxidative decomposition of benzocyclobutadieneiron tricarbonyl (**9**) with either Ce(IV) or Fe(III) in the absence of a trapping dienophile yielded mainly polymeric material[7] which has not been fully characterized. In contrast, the polycyclic organic compound **354**[7] was claimed to be formed by the oxidative decomposition of **9** with $AgNO_3$, whereas its oxidative decomposition with $Pb(OAc)_4$ gave **355.**[266] Noteworthy in particular is the simultaneous oxidative decomposition of **3** and **9** with $Pb(OAc)_4$ by which the tetracyclic compound **356**[266] was reported to be formed in 75% yield. In the presence of cyclopentadiene and the tetrazines **347,** the oxidative decomposition of **9** led to the formation of **357**[266] and **358,**[261] respectively.

The oxidative decompositions of several mono- and disubstituted cyclobutadieneiron tricarbonyl complexes were also investigated. Phenylcyclobutadieneiron tricarbonyl (**28**) has been shown to react with tetracyanoethylene in the presence of an oxidizing agent (not specified) to produce predominantly, if not exclusively, the adduct **359.**[25] Similar stereochemical results were also obtained by utilizing other monosubstituted methyl-, ethyl-, isopropyl-, and iodocyclobutadieneiron tricarbonyl derivatives.[25] In the context of the monosubstituted derivatives, noteworthy are the results obtained with the alkyne–ether derivatives **253** (n = 1, 2).[78] Direct oxidative decomposition of **253** (n = 2) with Ce(IV) gave a mixture of unspecified organic products. However, initial photolysis of **253** (n = 2) gave the dicarbonyl derivative **360** which was then decomposed with Ce(IV) to **361** presumably via the intermediate **362**.[79] The direct oxidative decomposition of **253** (n = 1) with Ce(IV) afforded **363**[79] via **364.** In order to explain the difference in behavior between **253** (n = 2 and 3), the shorter methylene chain was suggested to increase the rate of intramolecular addition and to decrease the probability of intermolecular side reactions.

Some interesting results have been reported on the trapping of a variety of disubstituted cyclobutadienes. The oxidative decomposition of 1,2-diphenylcyclobutadieneiron tricarbonyl (**8**) in the presence of benzoquinone or *N*-phenylmaleimide, both moderately active dienophiles,[267] yielded[25] **365** and **366,** respectively. Under similar conditions, the reaction of **8** with the extremely active dienophiles tetracyanoethylene[267] and dicyanomaleimide[268] produced two isomeric adducts in each instance [(**367** and **368**) and (**369** and **370**), respectively].[25] In both instances, the ratio of the first to the second listed products was found to be approximately 5:1.

Specially interesting studies have been reported on the oxidative decomposition of optically active nonidentical 1,2-disubstituted cyclobutadieneiron tricarbonyl complexes, such as the methyl–methoxymethyl derivative **54** and the methyl–ethyl derivative **309**. The oxidative decomposition of the optically active **54** with Ce(IV) carried out in the presence of dienophiles such as tetracyanoethylene, benzoquinone, and *N*-phenylmaleimide produced,[269] in each instance, a mixture of four isomers **371** (predominant isomer), **372, 373,** and **374.** More importantly, the products obtained in these experiments were shown to consist of racemic mixtures, indicating that the optical activity of the starting iron complex is being lost during the course of formation of the adducts. Similar results were also encountered during the oxidative decomposition of the optically active disubstituted derivative **309** with Ce(IV) in the presence of dimethyl maleate[231,270] and maleic anhydride[231] which yielded the racemic mixtures of the adducts **375** and **376,** respectively. The decomposition of the optically active complex **309** in the presence of tetracyanoethylene gave the racemic mixture[231] of **377, 378,** and **379.** By contrast, bromination and iodination of the optically active disubstituted derivative **309** yielded the respective cyclobutenes **380** (X = Br and I) with retention of activity.[264]

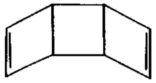
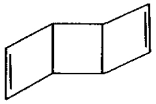
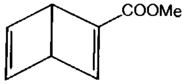
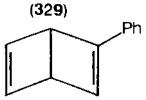
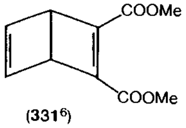
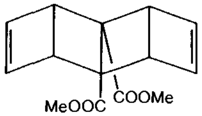
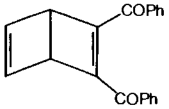
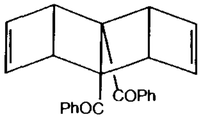
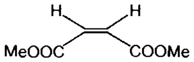
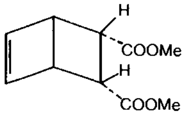
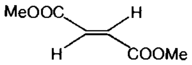
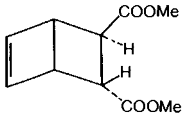
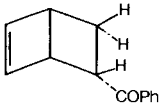
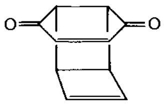
Finally, a mention will be made of several miscellaneous oxidative decompositions of cyclobutadieneiron derivatives. The decompositions of tetraiodocyclobutadieneiron tricarbonyl (**381**) and 1,3-di-*tert*-butylcyclobutadieneiron tricarbonyl (**382**) in the presence of tetracyanoethylene were reported to afford **383**[225] and **384,**[180] respectively. The formation of the benzvalene derivative **384** can readily be explained in terms of a concerted cis,trans,trans [2 + 2 + 2] cycloaddition involving a singlet ground-state cyclobutadiene derivative, a process which is allowed according to the Woodward–Hoffmann rules. Particularly interesting is the oxidative decomposition of tri-*tert*-butylcyclobutadieneiron tricarbonyl (**385**),[271] with either ceric ammonium nitrate or ferric nitrate, which was reported to afford the known cyclopropenyl ketone **386**[272] exclusively, rather than the expected dimer of tri-*tert*-cyclobutadiene. The mechanistic details of this novel transformation remain obscure at the present time. Lastly, the degradation of the diols **321** and **387** with HCl in THF was reported to give cyclobutadienopleiadiene (**388**) and α,α'-diphenyldimethylenecyclobutene (**389**), respectively.[234]

The oxidative decomposition reactions which have been described so far are summarized in Table II.

The oxidative decomposition reactions described above demonstrate the usefulness of cyclobutadieneiron tricarbonyl derivatives as reagents in organic synthesis. This novel area of research, which was initially discovered and developed by Pettit[24,39] and his co-workers, is of a considerable synthetic value for the preparation of various simple as well as complex polycycles. For instance, this procedure permitted, among others, the syntheses of a large variety of Dewar benzenes and bicyclo[2.2.0]hexene derivatives.[24,39] The adduct *endo*-tricyclo[4.4.0.$0^{2,5}$]deca-3,8-diene-7,10-dione (**338**),[253,254] prepared by the oxidative decomposition of **3** with Ce(IV) in the presence of *p*-quinone, has been shown to be a useful starting material for the syntheses of organic compounds such as tetracyclo[5.3.0.$0^{2,6}$.$0^{3,10}$]deca-4,8-diene,[273] tricyclo[4.4.0.$0^{2,5}$]-deca-3,7,9-triene,[274] *cis,syn,cis*-tricyclo[5.3.0.$0^{2,6}$]deca-4,8-diene-3,10-dione,[275] and 4-oxahexacyclo[5.4.0.$0^{2,6}$.-$0^{3,10}$.$0^{5,9}$.$0^{8,11}$]undecane.[254] A noteworthy synthesis of cubane starting with the oxidative decomposition of **3** in the presence of 2,5-dibromobenzoquinone has also been reported.[253]

The chemical transformations of the adducts obtained by the oxidative decomposition of cyclobutadieneiron tricarbonyl derivatives in the presence of dienophiles are beyond the scope of this review. However, the mechanism of the oxidative decomposition process is of considerable importance, and thus it will be dealt with in light of known experimental results. It is imperative first to examine whether free cyclobutadiene is implicated in the Diels–Alder addition step leading to the formation of the adducts. Already in 1965, Pettit and his co-workers[6] had reported that trace amounts of free cyclobutadiene, obtained by the oxidative decomposition of **3,** were transferred in the gas phase from the reaction vessel into a cold trap. Very recently, Rebek and Gavina[276,277] synthesized a polymer (cross-linked polystyrene)-bound o-phenanthroline derivative of η^4-$C_4H_4Fe(CO)_n$ (n = 2 or 1) and demonstrated that in the presence of a trapping polymer (cross-linked polystyrene N-bonded to maleimide functionality), the oxidative decomposition of the former with ceric ammonium nitrate in the usual medium resulted in the transfer of free cyclobutadiene between the two polymers. This three-phase test for the detection of free cyclobutadiene was reported to involve a 96% transfer. The formation of racemic adducts by the oxidative decomposition of the optically active cyclobutadieneiron tricarbonyl derivatives **54**[269] and **309**[231,270] with Ce(IV) in the presence of symmetrical dienophiles (e.g., tetracyanoethylene, benzoquinone, *N*-phenylmaleimide, etc.) has provided rather strong evidence in support of free cyclobutadiene involvement in these processes. Evidently, in order for a racemic mixture to be formed in such a process, the cyclobutadiene has to acquire a plane of symmetry. Therefore, the above results would indicate that the Diels–Alder addition step occurs after the cyclobutadiene is no longer subjected to the influence of the metal sphere. It should also be pertinent to point out that the oxidative decomposition of **3** in the presence of cyclic dienophiles occurs to invariably afford the endo product (e.g., **338, 339, 340, 341,** etc.); this would be expected if the free cyclobutadiene were to act as a normal, but very reactive diene. Moreover, the observed endo stereochemistry of the Diels–Alder addition step is inconsistent with such a process taking place with a coordinated cyclobutadiene ligand. Evidently, the endo position of a coordinated cyclobutadiene is rather excessively hindered by the metal atom and some of the ligands bonded to it. These observations provide either circumstantial or conclusive evidence to the implication of free cyclobutadiene during the oxidative decomposition of cyclobutadieneiron tricarbonyl derivatives in the presence of dienophiles. It should, however, be recognized that in some instances the degradation of such complexes occurs without the initial liberation of the cyclobutadiene ligand. For instance, halogenation of the optically active complex **309** was shown to give the dihalocyclobutenes **380** (X = Br, I) with retention of activi-

TABLE II. Oxidative Decomposition of Cyclobutadieneiron Tricarbonyl Derivatives in the Presence of Dienophiles or Other Substrates

Reactants				
Cyclobutadieneiron complex	Dienophile or other substrate	Oxidizing agent	Product(s)^b	Ref
		Reactions of the Parent Cyclobutadieneiron Complex 3		
 (3)		Ce^{4+a}	 (327, *syn* isomer)† +  (328, *anti* isomer)	248
3	CH≡CCOOMe	Ce^{4+}	 (329)	6
3	PhC≡CH	Ce^{4+}	 (330)	249
3	MeOOCC≡CCOOMe	Ce^{4+}	 (331^6) and/or  (332^{250,251})	6, 250, 251
3	PhCOC≡CCOPh	Ce^{4+}	 (333) and/or  (334)	251
3		Ce^{4+}	 (335)	248
3		Ce^{4+}	 (336)	248
3	$CH_2 = CHCOPh$	Ce^{4+}	 (337)	252
3		Ce^{4+}	 (338)	253, 254

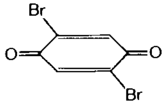
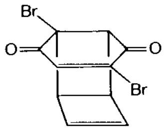
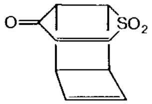
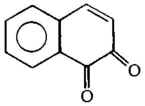
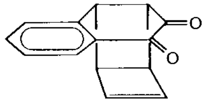
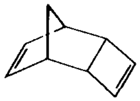
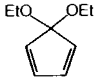
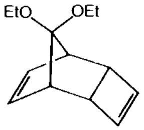
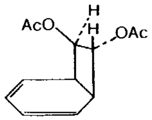
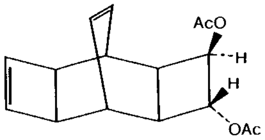
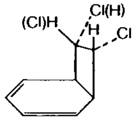
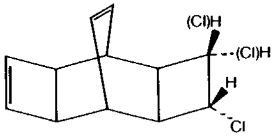
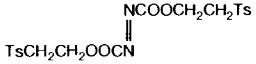
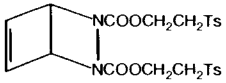
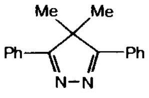
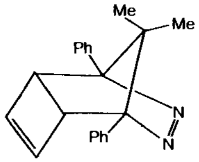
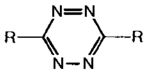
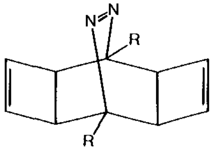
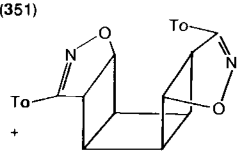
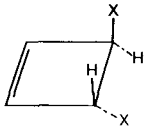
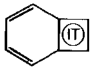
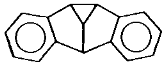
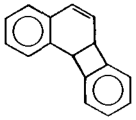
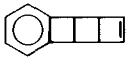
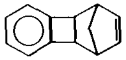
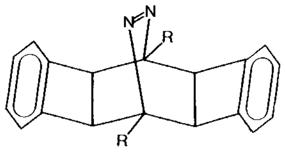
3		Ce^{4+}	 (339)	253
3		Ce^{4+}		265
3		Ce^{4+}	 (340)	255
3		Ce^{4+}	 (341)	248
3		$Pb(OAc)_4$	 (342)	256
3		Ce^{4+}	 (343)	257
3	 cis and trans mixture	Ce^{4+}	 (344)	258
3	 $TsCH_2CH_2OOCN{=}NCOOCH_2CH_2Ts$ (345)	Ce^{4+}	 (349)	259
3	 (346)	Ce^{4+}	 (350)	260

TABLE II (Continued)

Reactants				
Cyclobutadieneiron complex	Dienophile or other substrate	Oxidizing agent	Product(s)^b	Ref
3	 (347, R = Me, Ph)	Ce^{4+}	 (351)	261
3	p-$CH_3C_6H_4CNO$ (348)	Ce^{4+}	327 + 328 +  (352)	262
3	—	$FeCl_3$	 (353, X = Cl)	7
3	LiX (X = Cl, Br, I)	Ce^{4+}	353, X = Cl, Br, I	7, 263
3		X_2 (X = Br, I)	353, X = Br, I	264
3		$Ce(NH_4)_2(NO_3)_6$	353, X = ONO_2	264
		Reactions of the Benzocyclobutadieneiron Complex 9		
 (9)		Ce^{4+} or Fe^{3+}	Unidentified polymeric product(s)	7
9		$AgNO_3$	 (354)	7
9		$Pb(OAc)_4$	 (355)	266
9	3	$Pb(OAc)_4$	 (356)	266
9		$Pb(OAc)_4$	 (357)	266

9	347	Ce^{4+}	 (358, R = Me, Ph)	261

Reactions of Mono-, Di-, Tri-, and Tetrasubstituted Cyclobutadieneiron Tricarbonyl Derivatives

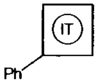
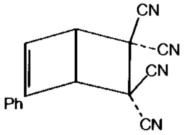
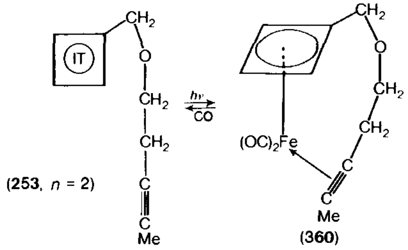
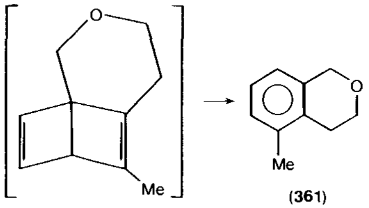
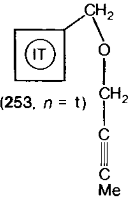
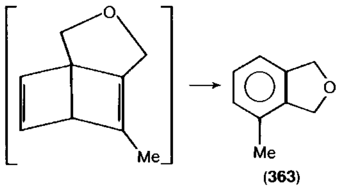
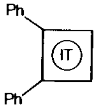
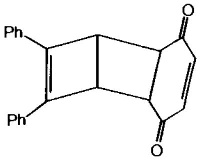
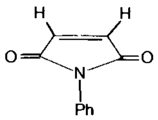
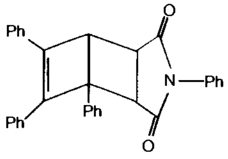
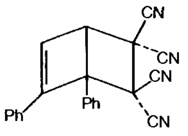
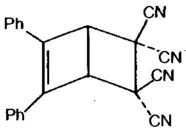
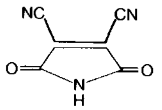
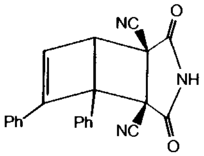
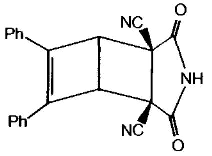
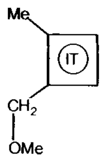
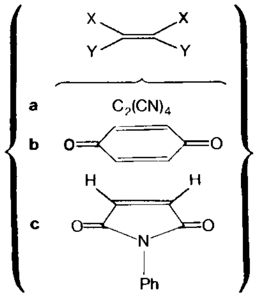
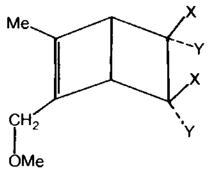
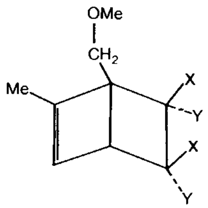
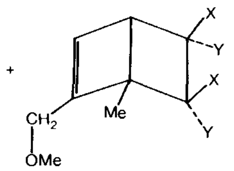
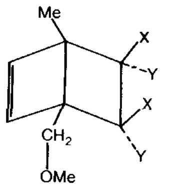
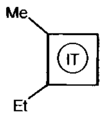
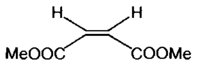
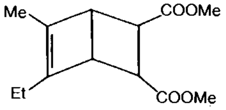
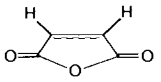
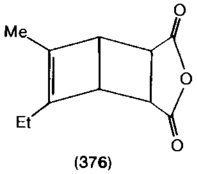
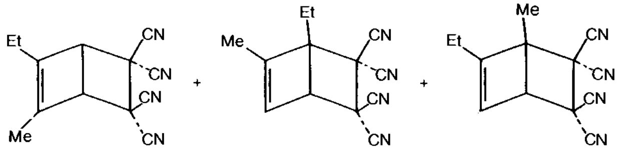
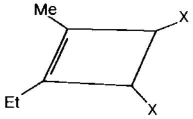
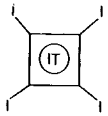
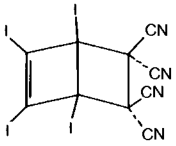
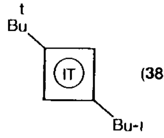
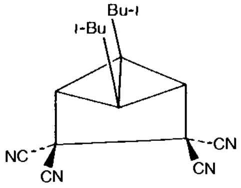
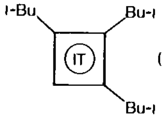
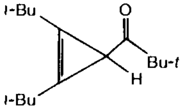
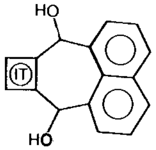
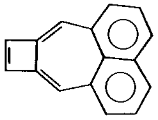
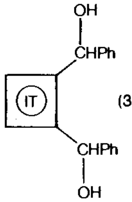
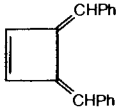
 (28)	$C_2(CN)_4$	NS^c	 (359)	25
 (253, *n* = 2) (360)		Ce^{4+}	 (362) (361)	79
 (253, *n* = 1)		Ce^{4+}	 (364) (363)	79
 (8)		Ce^{4+}	 (365)	25
8		Ce^{4+}	 (366)	25

TABLE II. (Continued)

Reactants Cyclobutadieneiron complex	 Dienophile or other substrate	Oxidizing agent	Product(s)^b	Ref
8	$C_2(CN)_4$	Ce^{4+}	 **(367†)** +  **(368)**	25
8		Ce^{4+}	 **(369†)** +  **(370)**	25
 (54)		Ce^{4+}	 **(371a–c)‡** +  **(372a–c)** +  **(373a–c)** +  **(374a–c)**	269
 (309)		Ce^{4+}	 **(375)**	231, 270
309		Ce^{4+}	 **(376)**	231

309	$C_2(CN)_4$	Ce^{4+}	 (377)† (378) (379)	231
309		X_2 (X = Br, I)	 (380)	264
 (381)	$C_2(CN)_4$	Ce^{4+}	 (383)	225
 (382)	$C_2(CN)_4$	Ce^{4+}	 (384)	180
 (385)		Ce^{4+} or Fe^{3+}	 (386)	271
 (321)		HCl/THF	 (388)	234
 (387)	—	HCl/THF	 (389)	234

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[a] Ce^{4+}: in general, this ion was obtained from the ceric ammonium nitrate salt $Ce(NH_4)_2(NO_3)_6$. [b] The symbol† signifies the major product in instances where mixture of isomers were obtained. [c] NS: not specified; probably Ce^{4+} was used to effect this oxidative displacement.

ty.[264] This implies that the reaction proceeded via a coordinated, rather than free, cyclobutadiene ligand. In another case, the degradation of the diols **321** and **387** with HCl/THF was presumed to involve metal-containing intermediates.

The ground state of cyclobutadiene has been the focus of considerable attention (see Introduction). It should therefore be instructive to examine this issue in light of the nature of the Diels–Alder adducts obtained during the oxidative decomposition of the cyclobutadieneiron derivatives in the presence of dienophiles. In the absence of dienophiles, free cyclobutadiene, generated by the decomposition of **3**, dimerizes stereoselectively[248] to the syn isomer **327** in favor of the anti isomer **328**. Evidently, in this particular instance the cyclobutadiene acts as both a very reactive diene and dienophile, and this might perhaps explain why the reaction is nonstereospecific. By contrast, the parent cyclobutadiene, generated from **3**, was shown to react with dienophiles in a stereospecific manner. The stereochemical nature of the adducts provides very strong evidence that the reactions leading to their formation proceed in a concerted manner and involve a normal diene having a singlet ground-state electronic configuration. The oxidative decomposition of **3** with Ce(IV) in the presence of equimolar quantities of dimethyl maleate and 1,1-diphenylethylene (the latter is more reactive as a radical trapping reagent, whereas the former is more reactive as a dienophile) resulted in the exclusive formation of **335**.[180] This result clearly negates the possibility of radical involvement as might have been expected from a triplet ground-state configuration.

Except for the spin multiplicity issue, there exists the question of ground-state geometry of free cyclobutadiene, namely, square or rectangle. In this context, specially significant are results of the oxidative decomposition of mono- and vicinal disubstituted cyclobutadieneiron tricarbonyl derivatives in the presence of dienophiles. Relatively few such studies were performed with monosubstituted derivatives; however, in the instances where this was attempted [e.g., **28** with $C_2(CN)_4$],[25] the reactions occurred with regiospecificity. Several studies[25,231,264,269,270] have been reported on the decomposition of vicinal disubstituted derivatives in the presence of a variety of different dienophiles (see Table II). In these cases, the adducts were shown to be formed by either regioselective or regiospecific reactions, depending on the nature of the dienophile and substituents. For example, regiospecific reactions were encountered between **8**[25] or **309**[231,270] and maleic anhydride, *N*-phenylmaleimide, *p*-benzoquinone, and dimethyl maleate, as appropriate (see Table II), whereas under similar conditions tetracyanoethylene reacted with these complexes in a regioselective manner. The experimental results of such reactions seem to suggest that regioselectivity is favored over regiospecificity as the dienophile becomes more reactive. The regiospecific and regioselective reactions, especially those encountered with complex **8**,[25] were taken to suggest a rectangular ground-state geometry for free cyclobutadiene. This interpretation, which is based on chemical evidence, is consistent with the results obtained by several recent theoretical treatments, described elsewhere (see Introduction).

The discussion on the oxidative decomposition of cyclobutadieneiron tricarbonyl derivatives was meant to demonstrate the utilization of cyclobutadienemetal complexes as reagents in organic chemistry as well as to dramatize the contributions made toward the solving of the "cyclobutadiene problem". Future scientific activities in this area of research are highly desirable since they would extend the scope of organic syntheses performed with cyclobutadienemetal derivatives as reagents. These complexes represent a viable source for a large variety of free cyclobutadienes whose facile generation and subsequent trapping are of considerable importance in organic synthesis especially in view of the stereospecific and regiospecific (or regioselective) nature of their reactions.

V. Structural Features of Cyclobutadienemetal Complexes

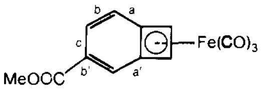
In recent years, a considerable amount of structural information has become available on cyclobutadienemetal complexes. Most of the structural data were obtained by x-ray diffraction procedures, although some were also acquired by other techniques including electron diffraction and microwave spectroscopy. The discussion in this section will focus primarily on the structural features dealing with the cyclobutadienemetal units of the complexes, although novel structural features other than those indicated will also be mentioned briefly.

Some structural information for cyclobutadienemetal complexes is furnished in Table III. In the majority of these complexes the cyclobutadiene ring has been shown to exhibit a nearly perfect square-planar geometry. Judging from individual C(CBD)–C(CBD) bond distances for complexes such as **1**·C_6H_6,[30] **56**,[86] **62**,[228] **131**,[163] and **269** (R = Ph),[228] it may appear that a small departure from the square geometry is not entirely uncommon. However, the extent to which such small deviations meaningfully reflect genuine electronic and/or steric effects is not immediately apparent. The overall averages, C(CBD)–C(CBD) [1.459 (12) Å] and C(CBD)–C(CBD)–C(CBD) [89.98 (0.12)°], computed by using all of the available relevant data on such complexes, appear to suggest that to a first approximation the bond distances and angles of the cyclobutadiene ligand are influenced little, if any, by the ring substituents and/or the nature of the complexes. In order to detect effects of the types mentioned above, it would be necessary to acquire highly accurate structural information on cyclobutadienemetal complexes.

In most instances, the metal atom in the complexes is located equidistant from all four carbon atoms of the cyclobutadiene ring. Small discrepancies in the uniformity of the M–C(CBD) distances have been reported for **56**[86] and **269** (R = Ph),[228] whereas a large deviation has been observed for the platinum complex **115** (X = SbF_6).[141] Interestingly, in the above-cited platinum complex two vicinal carbon atoms of the square-planar cyclobutadiene ring are situated significantly closer to the metal atom as evident from the following individual Pt–C(CBD) bond distances: 2.256 (14), 2.335 (14), 2.173 (14), and 2.114 (14) Å. Two alternative explanations were considered[141] in order to explain the dissymmetric bonding of the cyclobutadiene in the platinum complex: (i) weak intramolecular bonding contacts between the fluorine atoms of the trifluoromethyl group and the hydrogen atoms of two adjacent methyl substituents, or (ii) crystal packing forces. In solution, the PMR spectrum of **115** (X = PF_6)[140] has revealed equivalent methyl substituents. This undoubtedly arises because of free rotation around the Pt–C_4Me_4 bond. Genuine bonding contacts should have prevailed to some degree when the complex is dissolved in solution, and this would have been expected to restrict free rotation. This qualitative argument suggests that the second explanation (ii) is perhaps more plausible. Presently, the largest amount of structural information is available for cyclobutadieneiron complexes, and therefore it should be of interest to compare the average Fe–C(CBD) bond distances of these complexes. The appropriate data furnished in Table III indicate that the average distances under consideration are the same, to within experimental errors, and are independent of ring substituents and/or the nature of the complexes. A similar conclusion is indicated by the appropriate data for the nickel (**1**·C_6H_6[30] and **131**[163]) and molybdenum (**59**[88] and **62**[89]) complexes, although this analogy evidently breaks down for the molybdenum complex **127** (M = Mo, X = Br)[155,156] where a significantly shorter (~0.05 Å) Mo–C(CBD) distance has been reported.

Scattered structural information has been made available on several complexes which contain both cyclobutadiene and cyclopentadienyl ligands. A comparison between the average parameters of these two ligands is therefore of interest. The

TABLE III. Some Structural Parameters for Complexes Containing Coordinated Cyclobutadiene (CBD)[a]

Complex	CBD average parameters[b]			Other noteworthy structural features	Method	Ref
	M–C, Å	C–C, Å	C–C–C, deg			
$C_4H_4Fe(CO)_3$ (**3**)	2.06 (1)	1.46 (2)			ED	229
$C_4H_4Fe(CO)_3$ (**3**)	2.05 (1)	1.44 (1)			ED	282
$C_4H_4Fe(CO)_3$ (**3**)	2.05 (1)	1.44 (1)			MW	283
 (**390**)		1.47 (2)		*a* = 1.45, *a*' = 1.43, *b* = *b*' = 1.39 and *c* = 1.41 Å	XD'	281
$Ph_4C_4Fe(CO)_3$ (**2**)	2.07 (2)	1.46 (2)	90.2 (1.2)		XD	31,32
$(OC)Fe(PhC_2C_6H_4C_2Ph)_2Fe(CO)_3$ (**56**)	2.05 (4)	1.46 (3)	89.6 (1.7)	Fe–Fe; 2.494 Å	XD	86
$PhC^+[-C_4H_3Fe(CO)_3]_2\ BF_4^-$ (**269**, R = Ph)	2.05 (3)	1.44 (3)		C(exocyclic)–C(CBD), 1.40 C(exocyclic)–C(Ph), 1.47	XD	228
$[(1\text{-}Ph)(2\text{-}Ph)(3\text{-}Bu^t)(4\text{-}Bu^t)C_4]_2Fe_2(CO)_3$ (**194**)	2.06	1.47		Fe–Fe, 2.177 Å	XD	190
$[Me_4C_4NiCl_2]_2\cdot C_6H_6$ (**1**$\cdot C_6H_6$)	2.02 (2)	1.43 (3)	90.0 (2.0)		XD	30
$Me_4C_4Ni(MeC_2Me)_2Fe(CO)_3$ (**131**)	2.02 (2)	1.46 (3)	90.0 (1.0)	Fe–Ni, 2.449 Å	XD	163
$[Me_4C_4Pt(CF_3)(PMe_2Ph)_2]^+SbF_6^-$ (**115**, X = SbF_6)	2.22 (8)	1.47 (2)	90.0 (1.1)		XD	141
$(Ph_4C_4)_2Mo(CO)_2$ (**59**)	2.31 (2)	1.47 (2)	89.9 (1.1)		XD	88
$(OC)_2(Ph_4C_5O)Mo(Ph_2C_2)Mo(C_4Ph_4)(CO)$ (**62**)	2.30 (1)	1.47 (3)	90.0 (0.8)	Mo–Mo, 2.772 Å $(Ph_4C_5)O$–Mo, 2.06 Å	XD	89
$[Ph_4C_4Mo(CO)_2Br]_2$ (**127**, M = Mo, X = Br)	2.25 (1)	1.46 (2)	90.0 (0.4)	Mo–Mo, 2.954 Å	XD	155,156
$[(1\text{-}Ph)(2\text{-}Ph)(3\text{-}SiMe_3)(4\text{-}SiMe_3)C_4]CoC_5H_5$ (71, R = $SiMe_3$), cis isomer	1.97	1.46 (2)	90.0 (0.6)	Co–C(Cp), 2.05 Å C(Cp)–C(Cp), 1.40 Å	XD	278
$[(1\text{-}Ph)(2\text{-}SiMe_3)(3\text{-}Ph)(4\text{-}SiMe_3)C_4]CoC_5H_5$ (72; R = $SiMe_3$), trans isomer	1.97	1.47(1)	90.0 (1.8)	Co–C(Cp), 2.05Å C(Cp)–C(Cp), 1.40 Å	XD	278
$C_4H_4CoC_5H_5$ (**46**)	1.96 (1)	1.44 (1)	90.1 (0.3)	Co–C(Cp), 2.04 (1) Å C(Cp)–C(Cp), 1.39 (1) Å	XD	*c*
$Ph_4C_4RhC_5H_5$ (**80**)	2.10 (1)	1.47 (1)	90.0 (0.2)	Rh–C(Cp), 2.22 (1) Å C(Cp)–C(Cp), 1.40 (1) Å	XD	101
$(Ph_4C_4)(C_5H_5)V(CO)_2$ (**84**)	2.26	1.47	90.0	V–C(Cp), 2.24 Å	XD	279
$(Ph_4C_4)(C_5H_5)(Ph_2C_2)Nb(CO)$ (**89**)	2.38	1.46	90.0	Nb–C(Cp), 2.44 Å C(Cp)–C(Cp), 1.44 Å	XD	110,280

[a] Abbreviations: CBD, cyclobutadiene: ED, electron diffraction: MW, microwave spectroscopy; XD, x-ray diffraction. [b] Standard deviations (in brackets) were computed from the individual parameters and the mean values in instances where sufficient data have been reported. Since figures were rounded to 1/100th of an angstrom and 1/10th of a degree, true standard deviations are in most instances somewhat smaller than those quoted. It should also be noted that standard deviations of individual distances and angles, which are available for only part of the complexes, have not been included in the computations of the standard deviations of the average parameters in order to maintain uniformity. [c] P. E. Riley and R. E. Davis, *J. Organomet. Chem.*, **113**, 157(1976); late entry, data have not been discussed in section V.

inspection of the respective average parameters for **71** (R = $SiMe_3$),[278] **72** (R = $SiMe_3$),[278] **80**,[101] **84**,[279] and **89**[110,280] reveals that in the complexes under consideration C(CBD)-C(CBD) > $C(C_p)$-C(Cp) and M-C(CBD) < $M\text{-}C(C_p)$. Interestingly, these findings are highly suggestive of a stronger metal-to-cyclobutadiene than metal-to-cyclopentadienyl bonding interaction. It should be pertinent to mention that this conclusion is consistent with the 1956 theoretical prediction by Longuet-Higgins and Orgel.[26] An interesting example which demonstrates the lower C-C bond order of a cyclobutadiene ligand as compared with that of an uncoordinated conjugated diene can be found in the available data on the benzocyclobutadieneiron complex **390**.[281] The bonds corresponding to b, c, and b' in this iron complex display distinct alternation and have lengths typical of carbon sp^2-sp^2 double bonds and carbon sp^2-sp^2 single bonds. By contrast, the individual C(CBD)-C(CBD) bond distances [1.47, 1.45, 1.49, and 1.46 Å; average 1.47 (2) Å] are significantly longer compared with the bonds *a* (1.40 Å), *a*' (1.41 Å), *b* (1.36 Å), and *b*' (1.33 Å), and are only slightly shorter than bond *c* (1.48 Å).

The geometry of the substituents on the coordinated cyclobutadiene is an issue to be examined next. Studies performed on the parent iron tricarbonyl complex **3** yielded inconclusive results concerning the relative orientation of the C(CBH)-H bonds. For example, the average angle between the C-H bond and the planar cyclobutadiene ring in this complex was reported by the various investigators to be as follows: 0°,[229] 8.6 ± 6.3° (endo to the Fe atom)[282] and 6.5 ± 0.5° (exo to the Fe atom).[283] The C-C bond distances in the cyclobutadiene ligands (already discussed) indicate a considerable sp^3 character for the ring carbon atoms; in light of this observation, the indicated exo C-H configuration[283] in **3** appears most plausible. Evidently, this conclusion is also consistent with the available structural data for the majority of the tetrasubstituted cyclobutadiene metal complexes. Except in the instances of **56**[86] and **269** (R = Ph),[228] for which a reference shall be made at a later stage, the substituents (Ph, Me, *t*-Bu, and $SiMe_3$ as appropriate) in tetrasubstituted cyclobutadienemetal complexes (listed in Table III) have been shown to assume an exo configuration in relationship to the metal atom. Incidentally, phenyl substituents are both bent (exo to the metal atom) and twisted to varying degrees from the cyclobutadiene planes in these complexes. In **269** (R = Ph),[228] the exo cyclic carbon atom lies very nearly in the plane of the cyclobutadiene rings, and this taken in the context of the short C(exocyclic)-C(CBD) distances (~1.40 Å) implies a special case where an α-carbonium ion substituent is being stabilized by an effective interaction with the π-network of the coordinated ligands. Noteworthy in particular is the geometry of the substituents in the iron complex **56**.[86] The two vicinal phenyl substituents are exo bent and twisted in the usual manner. By contrast, the *o*-phenylene substituents in this complex exhibit a slight endo configuration as evident by the ~0.045 Å inward (toward the iron

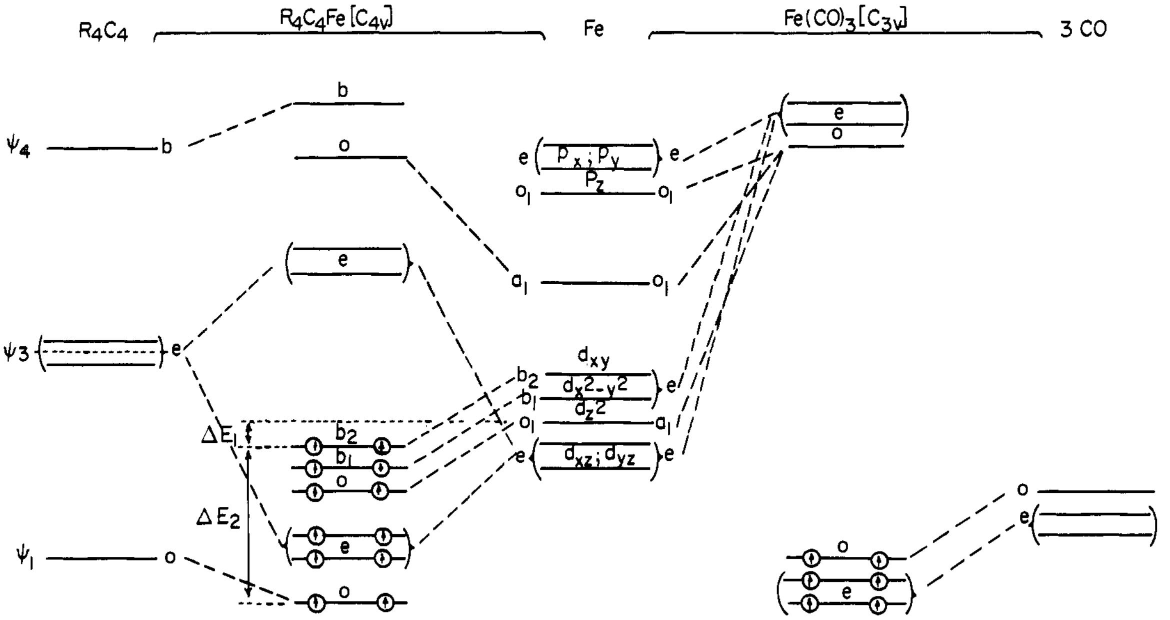
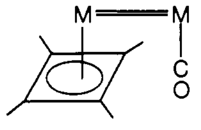


Figure 3. A schematic MO energy level diagram for the $R_4C_4Fe(CO)_3$ system.

atom) displacement of their carbon atoms from the plane of the cyclobutadiene ring to which they are bonded. Evidently, the endo configuration found in this particular complex is the result of a steric constraint imposed by the common attachment of the phenylene substituents to both the ferracyclopentadiene and cyclobutadiene ligands.

Lastly to be examined are the main structural features of the novel molybdenum complexes **59**[88] and **62**.[89] The structure of **59**, the only biscyclobutadienemetal complex known, consists of a tilted biscyclobutadiene geometry with the local point symmetry about the molybdenum atom being approximately C_{2v}. Assuming that each cyclobutadiene ligand occupies one coordination site, the gross geometry around the molybdenum atom is that of a distorted tetrahedron as evident from the interligand angles: CR-Mo-C'R' (CR corresponds to the center of the cyclobutadiene ring), 140.8 (1)°; CR-Mo-CO, average angle 104.5 (2.0)°; and OC-Mo-C'O', 83.4 (6)°. The geometry of the binuclear complex **62** is particularly interesting since it consists of a novel intermediate-like structure. The main structural features of this green diamagnetic complex include the following: (i) a short Mo-Mo distance which has been assigned a double bond multiplicity; (ii) a nearly symmetrically bridging diphenylacetylene ligand; (iii) one of the molybdenum atoms being nearly symmetrically bonded to a tetraphenylcyclobutadiene ligand, whereas the other metal atom is coordinated to a tetraphenylcyclopentadienone ligand; (iv) the keto oxygen of the tetraphenylcyclopentadienone ligand being coordinated to the adjacent molybdenum atom; and (v) the terminal carbonyls being arranged to permit each of the molybdenum atoms to attain an effective atomic number electronic configuration. The presence of the bridging acetylene might suggest that the coordinated cyclobutadiene in this complex was formed by a concerted dimerization of bisacetylene via multimetal centers intermediates, a process which is symmetry allowed according to Mango's theory.[124,125] Especially significant is the observation that the origin of the keto group of the tetraphenylcyclopentadienone ligand can be traced to a vacated terminal carbonyl position on the adjacent molybdenum atom. The saturation of this empty site, after the carbonyl insertion process had been completed, is achieved by a (tetraphenylcyclopentadienone)O → Mo coordination. In the system under consideration, the formation of the doubly coordinated cyclopentadienone, which is in effect a bridging ligand, can be described in terms of intermediates of the types **391**, **392**, and **393**. Based on the premise that the molybdenum complex **62** is a genuine kinetically stabilized intermediate, the structural features of this novel complex might suggest that electronically and coordinatively saturated bi- and polynuclear intermediates, some of which also contain metal-metal multiple bonds, are likely to play an important role in the transition metal catalyzed reactions of acetylenes at large. This implication in the instances of **62** and some other related complexes is currently being tested in our laboratory.[187]



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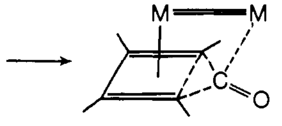

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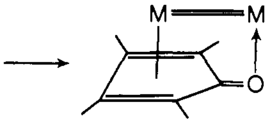

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VI. Bonding in Cyclobutadienemetal Complexes

Molecular orbital (MO) descriptions of the bonding in cyclobutadienemetal complexes have been reported by Longuet-Higgins and Orgel,[26] Green,[284] and Cotton.[285] Bonding concepts in such complexes will be demonstrated by examining a specific system, that of $R_4C_4Fe(CO)_3$ (R = Me, Ph, etc.). In spite of the low symmetry (C_s) observed in such complexes, to a first approximation the bonding in this system can be examined in two parts by separately considering the local symmetries of the R_4C_4Fe (C_{4v}) and $Fe(CO)_3$ (C_{3v}) units. By treating the bonding in the above units separately, it would be necessary to assume, inter alia, that degeneracies permitted in the C_{4v} symmetry will not be greatly split by the influence of the C_{3v} symmetry of the other unit, and vice versa. The two-part, schematic MO energy level diagram for $R_4C_4Fe(CO)_3$ shown in Figure 3 was constructed by the matching of plausible orbitals of the iron atom and ligands according to their symmetry classification. Shown in the center of the diagram are the valence shell orbitals of the iron atom, and given to their immediate left and right are the MOs generated by considering the local symmetries C_{4v} and C_{3v}, respectively. The energy levels of the LCAO-MO of R_4C_4 [ψ_1, ψ_2, ψ_3, ψ_4] labeled according to their symmetries in C_4 and those of the symmetry adapted linear combinations of the filled σ hybrids of the three carbonyl groups labeled according to C_3, appear at the extreme left- and right-hand sides of the diagram, respectively. In the diagram (Figure 3), no account has been taken of $d\pi(Fe) \rightarrow p\pi^*(CO)$ back bonding for clarity reasons, although such interactions are known to be significant.

According to Figure 3, the cyclobutadiene-to-iron bond consists essentially of a π-type interaction between the metal orbitals d_{xz} and d_{yz} and the ring LCAO-MOs ψ_2 and ψ_3; the resulting MOs transform as the irreducible E in the C_{4v} point group. Presuming a triplet ground-state electronic configuration for the free ligand, this bonding interaction neutralizes the diradical character of the ring and provides extra stabilization as a result of bond formation which compensates for the lack of resonance stabilization energy in the free cyclobutadiene ligand. Excluded from the diagram (Figure 3) are the symmetry-allowed σ-type bonding interactions between ψ_1 and the iron orbitals s, p_z, and d_{z^2}, as well as the δ-type bonding interaction between ψ_4 and $d_{x^2-y^2}$. The omission of these symmetry allowed combinations, especially those involving the iron orbitals d_{z^2} and $d_{x^2-y^2}$, is justified to some degree since their contributions to the overall metal-ring bonding are not expected to be as significant as those which have been included in the diagram.

The association of the highest filled nonbonding MO level (b_2) with the d_{xy} orbital of the iron has been based on symmetry considerations. In the absence of suitable ligand orbitals with which d_{xy} could have interacted, the character of the nonbonding MO derived from it is expected to be that of a slightly perturbed atomic orbital, and this would suggest that the b_2 level is the highest in energy among the filled MOs.

The schematic energy level diagram shown in Figure 3 facilitates the "bookkeeping" of the different symmetry derived components which have been utilized in the construction of a plausible set of MOs to describe bonding in the system under consideration. All of the 18 available electrons in the system can be accommodated in nine bonding and nonbonding MOs, thus explaining the diamagnetism and stability of the derivatives $R_4C_4Fe(CO)_3$ (R = H, Me, Ph, etc.). A tentative insight into the relative energies of some of the MO levels, described in Figure 3, can be obtained from ionization data. The first and second ionization potentials (in parentheses) of certain cyclobutadieneiron tricarbonyl derivatives such as $C_4H_4Fe(CO)_3$ (**3**; 8.04 and 9.02 eV), $(CH_3COC_4H_3)Fe(CO)_3$ (**233**; 8.27 and 9.23 eV), $(OHCC_4H_3)Fe(CO)_3$ (**234**; 8.32 and 9.27 eV), and $(H_2NC_4H_3)Fe(CO)_3$ (**248** ($R_1 = R_2$ = H); 7.77 and 8.91 eV) were obtained from the photoelectron spectra[286,287] of these complexes. The first ionization potentials of these complexes differ by only little from that of iron (7.87 eV).[288] This was interpreted on the basis of removal of the first electron from a slightly perturbed atomic orbital (AO) of iron. The second ionization potential of the complexes under consideration has been attributed to the loss of an electron from a perturbed π MO of the ligand. The highest and lowest filled MO energy levels of the R_4C_4Fe unit, both of which are essentially of a nonbonding character according to Figure 3, are evidently the most plausible candidates to match the perturbed AO (iron atom) and π-MO (ligand), respectively. Presuming the validity of these assignments, it should now be possible to estimate the energy difference (ΔE_1) between the degenerate d levels in the free iron atom and the highest filled nonbonding MO level (b_2), as well as that between the highest (b_2) and lowest (a) filled nonbonding MOs (ΔE_2). Moreover, since the first ionization potential of the parent cyclobutadiene (C_4H_4) ligand was determined by an electron impact (~8.4 eV)[289] and photoelectron (8.50 eV)[286] studies, it should now be possible to estimate the energy difference between the ψ_2 and ψ_3 degenerate levels and that of the degenerate d levels of the iron atom. For example, in the parent iron complex **3** the estimated values of ΔE_1 and ΔE_2 are 0.17 and 0.98 eV, respectively. In this particular case, the energy level of ψ_2 and ψ_3 should have appeared approximately 0.4 eV below the MO (b_2) level; however, this relationship is expected to vary depending on the nature of the substituents in the complexes under consideration.

VII. Spectroscopic Properties of Cyclobutadienemetal Complexes

A. Vibrational Spectroscopy

Infrared spectral data are available for the majority of the cyclobutadienemetal complexes. The stretching carbonyl frequencies of cyclobutadienemetal carbonyl derivatives, whose values and pattern provided a considerable amount of structural and bonding information, were examined for most of the complexes in this specific category. In this context, noteworthy in particular is the reported study by Brune and Wolff[290] on a variety of substituted cyclobutadieneiron tricarbonyl derivatives.

The first vibrational analysis of a cyclobutadienemetal complex was reported by Fritz[291] on the infrared spectrum of the nickel complex $[Me_4C_4NiCl_2]_2$ (**1**). More recently, Andrews and Davison have reported the vibrational spectrum (infrared and Raman) of the parent cyclobutadieneiron complex $C_4H_4Fe(CO)_3$ (**3**) and made the appropriate assignment of bands.[292] The investigation of **3** has also been reported, independently, by Aleksanyan et al.[293] Very recently, Andrews and Davison reported a detailed normal coordinate analysis of $C_4H_4Fe(CO)_3$ (**3**).[294] In this elegant study, a valence force field has been calculated for **3** by the use of judicious approximations and local symmetry arguments.

B. Ultraviolet Spectroscopy

The ultraviolet spectra of only few cyclobutadienemetal complexes have so far been reported. None of those spectra have been subjected to a rigorous study. In most instances these spectra were used as a diagnostic tool, although the correlation between the spectra of certain tetraphenylcyclobutadienemetal complexes had been attempted.[290,295]

C. Mössbauer Effect Spectroscopy

The ^{57}Fe Mössbauer effect spectra of the neutral cyclobutadieneiron derivatives $R_4C_4Fe(CO)_3$ [**3** (R = H),[296] **2** (R = Ph),[297] and **9** (R_4C_4 = benzocyclobutadiene)[297]] and the cationic complexes $[C_4H_4Fe(CO)(NO)L]^+PF_6^-$ [**181** (L = CO); **184** (L = Ph_3P, Ph_3As, and Ph_3Sb)][186] were reported in terms of isomer shifts and quadrupole splitting parameters. These spectral parameters were used, primarily, for diagnostic purposes. In this context, noteworthy is the study by Herber, King, and Ackermann[297] which permitted the resolution of two slightly nonequivalent iron atoms in certain ferrole carbonyl derivatives.

D. NMR Spectroscopy

The PMR spectra of the parent cyclobutadienemetal complexes and those of their symmetrically tetrasubstituted analogues do reveal that the four ring positions are magnetically equivalent. These findings could probably be explained in terms of a low-energy barrier of rotation about the center of the coordinated cyclobutadiene-to-metal axis in the complexes. This plausible explanation could, in fact, be ascertained by investigating the variable-temperature PMR spectra of these complexes; such studies which, among other, might permit a quantitative assessment of the energy barrier of rotation about the indicated axis are clearly warranted. The PMR spectra of tetrakis(*p*-tolyl)cyclobutadienemetal complexes have been shown by Maitlis and his co-workers[158,165] to exhibit a nearly perfect AB quartet pattern for the aromatic protons. This feature, used as a diagnostic test to infer the presence of the cyclobutadiene ligand in a variety of such complexes, suggests rather strongly

TABLE IV. PMR Resonances of Cyclobutadiene Protons in the Spectra of Some Unsubstituted and Partially Substituted Cyclobutadienemetal Complexes

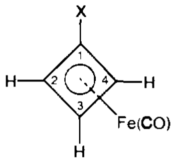
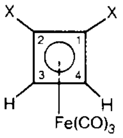
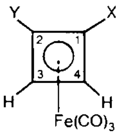
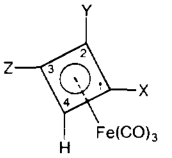
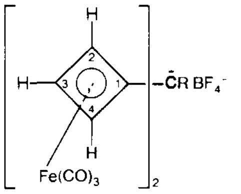
Complex	Cyclobutadiene protons Chemical shifts (τ)[a]		Conditions[b]	Ref
	A. Some Unsubstituted Cyclobutadienemetal Complexes			
$C_4H_4Fe(CO)_3$	6.09 (s)			7, 49
	6.00 (s)		CCl_4	14
$[C_4H_4Fe(CO)(NO)L]^+PF_6^-$				
L = CO	3.86 (s)		Acetone-d_6	186
L = Ph_3P	4.60 (d, 4 H, J(P–H) = 2.0 Hz)		Acetone-d_6	186
L = Ph_3As	4.45 (s, 4 H)		Acetone-d_6	186
L = Ph_3Sb	4.35 (s, 4 H)		Acetone-d_6	186
$(C_4H_4Fe)_2(CO)_3$	5.87 (s)		Toluene-d_8	189
$C_4H_4Fe(C_6H_6NCOOEt)$[c]	6.3 (s, 4 H)			181
$C_4H_4Co(CO)_2I$	5.42 (s)			50
$C_4H_4CoC_5H_5$[d]	6.39 (s, 4 H)			50
	6.34 (s, 4 H)		CCl_4	15
$C_4H_4RhC_5H_5$[e]	5.95 (d, 4 H, J(Rh–H) = 1.6 Hz)		CCl_4	77
$C_4H_4Ru(CO)_3$	5.87 (s)			49
$C_4H_4Cr(CO)_4$	6.12 (s)			51
$C_4H_4Mo(CO)_4$	5.94 (s)			49
$C_4H_4W(CO)_4$	5.98 (s)			49
	B. Some Monosubstituted Cyclobutadienemetal Complexes			
	H(3), s, 1 H	H(2) + H(4), s, 2 H		
X = COOMe	5.72	5.49	$CDCl_3$	75
X = COOH	5.65	5.45	$CDCl_3$	214
X = CH_2COOH	5.73	5.66	Acetone-d_6	214
X = Cl	5.78	6.10	CCl_4	66
X = Br	5.70	5.80	CCl_4	68
X = Ph	5.83	5.53	CCl_4	62
	C. Some Disubstituted Cyclobutadienemetal Complexes (i) Identical Vicinal Substituents			
	H(3) + H(4), s, 2 H			
X = COOH	4.82		Me_2SO-d_6	71
X = COOMe	5.23		$CDCl_3$	71
X = CN	4.62		Acetone-d_6	71
X = t-Bu	5.88		$CDCl_3$	71
X = Me	6.10		CCl_4	54
$[(1\text{-Ph})(2\text{-Ph})C_4H_2]CoCp$	5.70			98
$C_8H_6Fe(CO)_3$[f]	5.98			7
$[C_8H_6Fe(CO)_2NO]^+PF_6^-$[f]	4.48			192
$C_8H_6Cr(CO)_4$[f]	5.65			51
	(ii) Identical Trans Substituents			
$[(1\text{-Ph})(3\text{-Ph})C_4H_2]CoC_5H_5$	5.18			98
	(iii) Nonidentical Vicinal Substituents			
	H(3) [or H(4)], s, 1 H	H(4) [or H(3)], s, 1 H		
X = COOMe, Y = COOH	5.06	5.22	$CDCl_3$	71
X = COOMe, Y = COCl	5.03	5.11		71
X = COOMe, Y = CON_3	5.13	5.21	$CDCl_3$	71
X = COOMe, Y = NH_2	5.78	6.11	Acetone-d_6	71
X = COOMe, Y = NMe_2	5.85	6.31	$CDCl_3$	71

TABLE IV (Continued)

Complex	Cyclobutadiene protons Chemical shifts (τ)[a]		Conditions[b]	Ref
X = COOH, Y = NMe_2	5.73	5.98	Acetone-d_6	71
X = COCl, Y = NMe_2	5.66	6.24	$CDCl_3$	71
X = CN, Y = NMe_2	5.83	6.50	$CDCl_3$	71
X = Me, Y = **Et**	6.38	6.42	C_6D_6	231
	(iv) Some Trisubstituted Cyclobutadienemetal Complexes			
	H(4), S, 1 H			
X = Y = Z = Me	6.08		CCl_4	54
X = Y = Z = *t*-Bu	6.10		C_6D_6	69
X = **Et**; Y = Z = Me	6.03		CCl_4	57
$[(Me_3C_4H)NiCl_2]_2$	3.35		DCl/D_2O	59
	D. Some Binuclear Cyclobutadieneiron Tricarbonyl Derivatives with α-Carbonium			
				
R = H[g]	H(3), 4.40 (s, 2 H) H(2) + H(4), 4.67 (s, 4 H)		SO_2: 40 °C	228
R = H[h]	H(3), 4.38 (s, 2 H) H(2) [or H(4)], 4.63 (d, 2 H; *J* = 9 Hz) H(4) [or H(2)], 4.77 (d, 2 H; *J* = 9 Hz)		−50 °C	228
R = Me	H(3), 4.33 (s, 2 H) H(2) + H(4), 4.76 (s, 4 H)		40 °C	228
R = Me	H(3), 4.43 (s, 2 H) H(2) [or H(4)], 4.66 (d, 2 H, *J* = 9 Hz) H(4) [or H(2)], 4.78 (d; 2 H, *J* = 9 Hz)		10 °C	228
R = Ph	H(3), singlet H(2) and H(4), doublets		Up to 50 °C	228

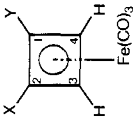
[a] The indicated integration ratios are those in reference to the other protons in the complexes for which spectral data are not provided in this table, except in few cases. [b] Unless stated otherwise, the data presented in the table pertain to spectra obtained at ambient temperature. In some instances, the solvents used in the obtainment of the spectra have not been reported. [c] $C_6H_6NCOOEt$, *N*-carboethoxyazepine. [d] C_5H_5: τ 5.14 (s, 5 H).[50] [e] C_5H_5: τ 4.75 (d, 5 H); *J*(Rh–H) = 1.0 Hz).[77] [f] C_8H_6, benzocyclobutadiene. [g] H-Bonded to carbonium: τ 2.74 (s, 1 H).[228] [h] H-Bonded to carbonium: τ 2.77 (s, 1 H).[228]

that the *p*-tolyl substituents undergo rapid rotation about their bonds to the coordinated cyclobutadiene.

The PMR spectra of partially substituted cyclobutadiene ligands are noteworthy in particular. The dominant feature in the spectra of such complexes is the absence of any detectable H–H couplings between vicinal and/or transannular (diagonal) protons. Accordingly, with very few exceptions the protons of the four-membered ring give rise to singlets whose intensity depends on the number of magnetically equivalent protons of each type. The resonances due to the ring protons in a variety of unsubstituted and partially substituted cyclobutadienemetal complexes are given in Table IV. In the majority of the complexes the cyclobutadiene ring proton resonances appear in the region τ 4.50–6.50. A particularly strong deshielding effect has been observed in the spectra of the cationic cyclobutadieneiron nitrosyl complexes $[C_4H_4Fe(CO)(NO)L]^+PF_6^-$ [186] and $[C_8H_6Fe(CO)_2NO]^+PF_6^-$.[192] The relationship between the chemical shifts of coordinated cyclobutadiene and cyclopentadienyl is perhaps another point of interest. In instances where these ligands coexist in the same complex (e.g., $C_4H_4MC_5H_5$, M = Co[15,50] and Rh[77]), the protons of the five-membered ring are significantly deshielded as compared with those of the four-membered ring. The cyclopentadienyl protons in the complexes under consideration are also considerably deshielded compared with those of ferrocene (τ 5.96 in CCl_4). The splittings of resonances of the coordinated cyclobutadiene protons have been encountered in few instances only. Long-range couplings of the type $J(^{31}P–H)$ and $J(^{103}Rh–H)$ have been shown (see Table IV) to cause splittings of 1.0 to 2.0 Hz. Extremely long-range $J(^{31}P–H)$, involving methyl protons, have been found in certain tetramethylcyclobutadienemetal complexes.[140,298] Especially interesting are the PMR spectra of the binuclear cyclobutadieneiron tricarbonyl derivatives **269,** having carbonium in the α position to the rings (Table IV, section D).[228] The apparent equivalence of the four cyclobutadiene ring protons ortho (adjacent) to the point of substitution which is evident from the spectra, run at 40 °C, of the parent and methyl analogue (**269,** R = H and Me) has been attributed to rapid rotation about the carbon(CBD)–carbon(exocyclic) bonds. This was inferred by variable-temperature PMR studies; upon lowering the temperature the spectra first coalesced and then resolved with the main difference being that the ortho protons now appear as two doublets. The transannular H(2)–H(4) coupling constant, in both the parent (**269,** R = H) and its methyl analogue (**269,** R = Me), has been shown to be 9 Hz.

In 1966, Preston and Davis reported[299] a detailed NMR (^{1}H

TABLE V. Coupling Constants in the NMR Spectra of Some Cyclobutadieneiron Tricarbonyl Derivatives.[a]

Complex	Coupling constants, Hz, and assignments													Ref
	$J[H(n)-H(m)]$			$J[^{13}C(n)-H(n)]$			$J[^{13}C(n)-H(m)], \|n-m\| = 1, 2$							
	2–3	3–4	|2–4|[b]	2–2	3–3	4–4	2–4	4–2	1–3	1–2	3–4	2–3	4–3	
X = Y = H	0.0	0.0	8.9	191.0	191.0	191.0	12.8	12.8	12.8	4.2	4.2	4.2	4.2	300, 301, 303
X = H; Y = Cl	0.0	0.0	8.6	196.8	195.7	196.8	11.5	11.5	23.0	3.9	3.9	5.7	5.7	303
X = H; Y = Br	0.0	0.0	8.9	198.1	196.0	198.1	12.9	12.9	23.0	3.5	3.5	5.7	5.7	303
X = H; Y = Me	0.0	0.0	9.3	188.9	191.3	188.9			13.1			4.6	4.6	303
X = Y = Me	0.0	0.0	(—)	(—)	189.2		12.8	(—)	12.8	(—)	4.2	4.2	4.2	300, 303
X = H; Y = Ph	0.0	0.0	9.3	189.5	190.7	189.5	12.1	12.1	13.3	3.7	3.7	4.7	4.7	304, 303
X = Y = Ph	0.0	0.0	(—)	(—)	189.5		12.8	(—)	12.8	(—)	4.2	4.2	4.2	302, 303

[a] Values noted (—), not expected (empty spaces indicate unavailable data). [b] Coupling involving magnetically nonequivalent protons.

NMR and ^{13}C NMR) study of $C_4H_4Fe(CO)_3$ (**3**). The ^{13}C NMR spectrum of this complex [given in reference to CS_2 (0.0 ppm)] was shown to consist of a singlet at −16.2 ± 1.0 ppm and a doublet centered at +131.8 ± 1.0 ppm (J = 191 ± 1 Hz). The singlet and doublet appear in regions characteristic of metal-carbonyl and metal-olefin complexes, respectively, and therefore, their assignments were rather straightforward. The coupling of 191 Hz, assigned as $J(^{13}C-^{1}H)$, was shown to be identical with the ^{13}C satellites splitting in the ^{1}H NMR spectrum of **3**. Incidentally, each satellite is split into a doublet (J = 9 Hz) due to transannular $^{1}H-^{1}H$ coupling involving magnetically nonequivalent protons, namely long-range coupling between a proton bonded to ^{12}C and a proton bonded to ^{13}C in a diagonal position to the former. Transannular $^{1}H-^{1}H$ couplings having the same value of 9 Hz have already been cited earlier in this section in conjunction with the low-temperature ^{1}H NMR spectra of **269** (R = H and Me).[228] In recent years, Brune and his co-workers[300-304] reported the results of an exhaustive analysis of the coupling constants from the ^{13}C NMR and/or ^{1}H NMR spectra of a large variety of cyclobutadieneiron tricarbonyl derivatives. The different couplings observed in the spectra of some of the complexes are given in Table V. Especially significant are the ranges of the ^{13}C-H coupling constants: $J[^{13}C(n)\text{-}H(n)]$ = 188.9–198.1 Hz; $J[^{13}C(n)\text{-}H(m)]$ ($|n - m| = 2$) = 11.5–23.0 Hz, and $J[^{13}C(n)\text{-}H(m)]$ ($|n - m| = 1$) = 3.5–5.7 Hz. In the above-cited studies the coupling constants were utilized for the evaluation of bonding. It should, however, be pointed out that coupling constants, when considered in the context of chemical shifts, may also be utilized for the making of structural assignments.

Very recently, Nielsen, Hansen, and Jakobsen have reported[305] an interesting ^{13}C NMR study of the $^{57}Fe-^{13}C$ satellites in the spectrum of **3**. The Fourier transform spectrum of this complex permitted the assignment of $J[^{57}Fe-^{13}C(\text{cyclobutadiene})]$ (3.62 Hz) and $J[^{57}Fe-^{13}C(\text{carbonyl})]$ (28.73 Hz). In another noteworthy study, Eschbach, Seyferth, and Reeves have recently described[306] the ^{13}C NMR spectra of the (hydroxymethyl)-, (α-hydroxyethyl)-, and (α-hydroxybenzyl)cyclobutadieneiron tricarbonyl complexes (in $CDCl_3$) and their derived α-carbonium ions (in H_2SO_4). The spectral data suggest extensive migration of electron density from the iron, via the ring, to the exocyclic, electron-deficient carbon atom. In the system under consideration, such an electron delocalization process is evidently consistent with the formation of highly stabilized carbonium ions.

The ^{1}H NMR spectrum of $C_4H_4Fe(CO)_3$ (**3**), measured in nematic media, was examined in detail by two groups of investigators.[307,308] These studies have suggested that under the conditions of the experiments the symmetry of the cyclobutadiene ligand is slightly lower than D_{4h}, for reasons that are not immediately apparent.

E. Mass Spectrometry

Mass spectral data have been reported for the majority of the cyclobutadienemetal complexes which exhibit either high or sufficient volatility. In general, complexes of the type of $[R_4C_4MX_n]_2$ do not exhibit sufficient volatility to obtain their mass spectra. In most instances the mass spectra of cyclobutadienemetal complexes were obtained in order to establish the molecular weight from the molecular ions (MI), although in few isolated cases brief discussions pertaining to some of the other spectral features have also been reported. More detailed studies of fragmentations taking place under electron-impact conditions were reported for complexes such as $Ph_4C_4Fe(CO)_3$ (**2**),[309] Ph_4C_4CoQ [Q = cyclopentadienyl (**63**) and indenyl],[309] $C_8H_6Fe(CO)_2L$ [L = CO, Ph_3P, Ph_3As, and Ph_3Sb],[191] $(Ph_4C_4)_2Mo(CO)_2$ (**59**),[88] and $C_8H_8TiC_4Ph_4$ (**119**).[143]

Under electron impact conditions, the primary fragmentation

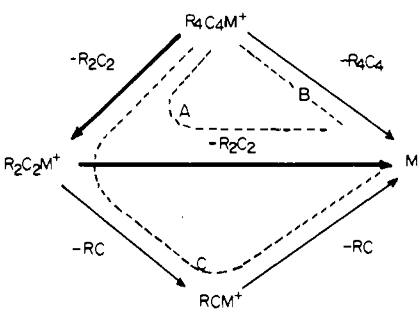


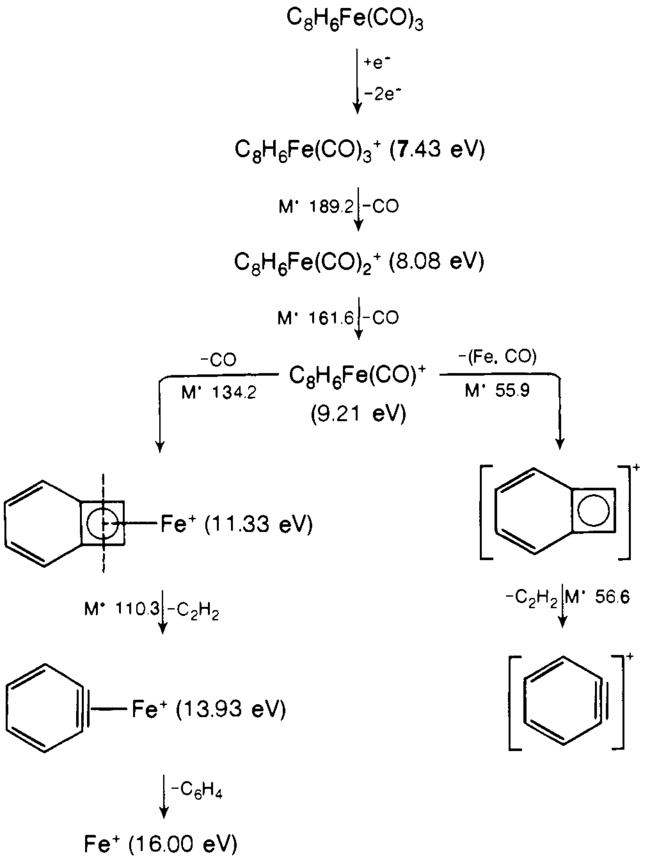
Figure 4. Primary (—) and secondary (—) mode of fragmentations of coordinated cyclobutadiene under electron-impact conditions.

of a coordinated cyclobutadiene [$R_4C_4M^+$, where M indicates either metal and/or metal bonded to some other ligand(s)] occurs by a two-step sequence involving successive losses of two acetylene (R_2C_2) fragments. This characteristic fragmentation pattern, pathway A in Figure 4, has been found in virtually all of the available mass spectra of cyclobutadienemetal complexes. Furthermore, in many of the spectra under consideration, such a fragmentation mode was shown to be supported by the presence of appropriate metastable peaks. The coexistence of the secondary fragmentation modes B and C (Figure 4) has also been considered in certain isolated instances, to be examined next. The mass spectrum of the titanium complex **119**[143] has been reported to contain metastable peaks in support of the following processes: (i) MI → [MI − Ph_2C_2] (M*, 214.4) → [MI − $2Ph_2C_2$] (M*, 70.0), and (ii) MI → [M − Ph_4C_4] (M*, 45.5). The second process (ii) implies the possibility that the rupture of the coordinated cyclobutadiene could occur in one step (Figure 4, B). The detection of a metastable ion which is consistent with process ii does not automatically validate its authenticity. Evidently, the summation of the two steps in pathway A (Figure 4) should give the same metastable ion as that of pathway B. Therefore, in the absence of any additional information the claim made concerning process ii should be viewed with utmost caution. The three-step sequence described by pathway C has been suggested based on the finding of significant amounts of $PhCMo^+$(*m/e* 187) ions in the mass spectrum of the biscyclobutadienemolybdenum complex **59**.[88]

Conspicuously absent from the mass spectra of cyclobutadienemetal complexes are the peaks corresponding to ions derived from the free ligands (R_4C_4). For instance, the mass spectra of tetraphenylcyclobutadienemetal complexes show, rather clearly, the absence of $[Ph_4C_4]^+$ (*m/e* 356). The absence of $[Ph_4C_4]^{2+}$ (*m/e* 178) must be inferred by an indirect method, since all of these spectra also show the presence of considerable amounts of $[Ph_2C_2]^+$ (*m/e* 178). However, the failure to detect any peak at *m/e* 178.5 due to $[Ph_4C_4]^{2+}$ containing one ^{13}C atom provides a rather clear demonstration of the absence of the dipositive ion.[309] These observations imply that fragmentations of the type $R_4C_4M^{n+} \rightarrow R_4C_4^{n+}$ ($n = 1, 2$) + M are highly unfavorable. By contrast with the hypothetical cyclobutadiene ion, the benzocyclobutadiene ion is expected to exhibit a significantly greater stability due to its fused ring structure. In fact, the detection of $C_8H_6^+$ has been claimed in a recent study of the mass spectra of $C_8H_6Fe(CO)_3$ (**9**) and some of its derivatives.[191] The mass spectrum of **9** had been examined in great detail, and thus, it would be instructive to consider some of its main features as an example, to be discussed next.

The main fragmentations of **9**[191] under electron-impact conditions are described in Scheme LI. These fragmentations are supported by the presence of the appropriate metastable ions (M*), as well as by the appearance potential data. The tentative structures of some of the ions have been assigned by carefully considering their modes of production and decay. The three-step unimolecular carbonyl dissociation sequence leading to the formation of the carbonyl-free ion $C_8H_6Fe^+$ is characteristic of the decay of the molecular ions of other metal carbonyl derivatives of the type $QM(CO)_3$ [e.g., M = Fe, Q = R_4C_4 (R = H, Me, Ph, etc.);[310] M = Mn, Q = cyclopentadienyl, indenyl, fluorenyl, pyrrolyl, etc.[311]]. According to Scheme LI, the benzocyclobutadieneiron ion undergoes the elimination of C_2H_2 to afford benzyneiron ion, which then degrades further to free benzyne and Fe^+. Incidentally, this mode of fragmentation of the coordinated benzocyclobutadiene is entirely consistent with the general pathway (Figure 4, A) by which all other coordinated cyclobutadienes have been found to rupture. The appearance potentials of the metal-containing ions described in Scheme LI are similar to those of the related metal-containing ions found in the mass spectra of $R_4C_4Fe(CO)_3$ [R = H, Me, and Ph].[310] This analogy suggests that related fragmentations in the mass spectra of these complexes proceed with similar energetics. Particularly interesting in the mass spectrum of **9** is the fragmentation involving the simultaneous elimination of CO and Fe from $C_8H_6Fe(CO)^+$ by which the monopositive ion of the free ligand ($C_8H_6^+$) was presumed[191] to be formed. In view of the absence of mass spectral data to support a similar process for any of the other cyclobutadieneiron tricarbonyl derivatives, or related complexes of the general type QM $(CO)_3$, it has to be concluded that the formation of $C_8H_6^+$ by the indicated fragmentation is unique in many respects. By analogy with the coordinated ligands, the rupture of acetylene from $C_8H_6^+$ was presumed to afford free benzyne ion.

SCHEME LI. Primary Fragmentations in the Mass Spectrum of $C_8H_6Fe(CO)_3$ (9) and the Appearance Potentials of the Metal-Containing Ions Involved



Mass spectrometry was also used as an analytical tool for the identification of the products obtained from the decomposition of **3**. In 1969, Li and McGee[312] claimed the formation of cyclobutadiene (C_4H_4) by the pyrolysis of **3**. Their primary evidence for the formation of this novel molecule was based on the detection of an ion at *m/e* 52 (9.55 eV) in the mass spectrum of the pyrolyzate. The mass spectrum of the pyrolyzate obtained by the flash vacuum pyrolysis[313] of **3** was also shown to exhibit a band at *m/e* 52 (9.8 eV); however, in contrast with the earlier assignment[312] this was attributed to the presence of vinylacetylene (9.9 eV) among the products. In this context, noteworthy is the flash vacuum pyrolysis of photo-α-pyrone which gave a product C_4H_4 whose ionization potential was found to be 8.2 eV;[314] this value is clearly more consistent with the first ionization potential calculated for the free cyclobutadiene by Worley.[286] In view of the foregoing, the claim made by Li and McGee[312] appears to be in doubt. In another study, the flash photolysis[315] of **3**, in the gas phase, was monitored by means of mass spectrometry. The primary photolytic step was presumed to involve the displacement of free cyclobutadiene [$C_4H_4Fe(CO)_3 + h\nu \rightarrow C_4H_4^* + Fe(CO)_3$]. The fast decay of the free cyclobutadiene [$C_4H_4^* \rightarrow 2C_2H_2$; $2C_4H_4^* \rightarrow C_6H_6 + C_2H_2$] encountered in this experiment was attributed to an excess of energy carried over from the photolytic decomposition. A subsequent study[316] of the vapor-phase photolysis of **3** in the presence of $C^{18}O$ has revealed that the primary photolytic step is reversible; this was inferred by the detection of ions corresponding to $C_4H_4Fe(CO)_n(C^{18}O)_{3-n}$ (n = 0-3). At this stage, it would perhaps be pertinent to mention that the photolysis of **3** (−20 °C) in ethereal solution and in the presence of dienophiles led to the generation and trapping of cyclobutadiene.[315] Incidentally, the photolysis of **3** at 77 K ($\lambda > 2200$ Å), both pure and in matrices of C_3F_8 and neopentane, led to the generation of C_4H_4 and $Fe(CO)_3$, whereas a similar experiment[317] carried out at 8 K ($\lambda > 2800$ Å), in a krypton matrix, gave $C_4H_4Fe(CO)_2$ and co whose recombination to **3** was observed to take place by warming the matrix to 35 K. It has subsequently been argued[318] that the failure to generate cyclobutadiene from a matrix (krypton) isolated **3** might be due to a cage effect. This was taken to exemplify a general limitation of matrix photochemistry as a test of vapor-phase or solution reaction mechanisms.

Lastly, tetraarylcyclobutadieneiron ions were presumed to be implicated in the fragmentation of certain tetraarylcyclopentadienoneiron tricarbonyl derivatives[319] under electron-impact conditions. Evidence based on the relative intensity ratios of certain metastable peaks was presented in support of this assignment.

VIII. Concluding Remarks

In this review, the scope of the field of cyclobutadienemetal complexes has been examined in detail. The subject under consideration has been reviewed according to reactions or other common features. Among the topics discussed in this review, noteworthy in particular is the section (IV.B) describing the use of cyclobutadienemetal complexes as reagents in organic synthesis, a subject of considerable interest which has been investigated rather extensively in recent years. Generalizations concerning the properties of coordinated cyclobutadienes should be made with utmost caution, since they depend to a large degree on the nature of the complexes. For instance, the susceptibility of the four-membered ring in $C_4H_4Fe(CO)_3$ (**3**) toward electrophilic substitution reactions, typical of an aromatic system, contrasts rather dramatically with the failure to observe similar reactions with $C_4H_4Mo(CO)_4$ (**12**). Nevertheless, a limited comparison between the coordinated cyclobutadiene and other π ligands in well-defined systems might to a certain extent be justified. The evaluation of the reactions between d^8 metal cationic complexes of the type $[(\pi\text{-}Ph_4C_4)M(\pi\text{-ligand})]^+$ (M = Co, Ni, and Pd) and nucleophiles has revealed the following decreasing order of ligand susceptibility toward an attack;[320] cycloheptatriene > benzene > tetraphenylcyclobutadiene > cyclopentadienyl. By contrast, in neutral sandwich complexes of the type $(\pi\text{-}C_4H_4)M(\pi\text{-}C_5H_5)$ [M = Co and Rh] the susceptibility of the four-membered ring toward an attack by electrophilic reagents is distinctly greater than that of the five-membered ligand. Very recently, self-consistent charge and configuration MO calculations (SCCC-MO) have been reported[321] for the isoelectronic series $\pi\text{-}LM(CO)_3$ [π-LM = C_6H_6Cr, C_5H_5Mn, C_4H_4Fe, C_3H_5Co, and C_2H_4Ni]. The parameters obtained in this study have revealed that the overlap population associated with $Fe\text{-}C(C_4H_4)$ is the highest among the series members, whereas the charge on C_4H_4 was shown to be next lowest to that of C_2H_4. However, it should be pointed out again that these theoretical observations pertain to an intimately related series of complexes, and therefore, the above cited results should not be viewed out of context.

Lastly, it should be appropriate to remark in brief concerning the postulation of cyclobutadienemetal complexes as reaction intermediates. Reactions between alkynes and metal carbonyls or related complexes have been known to afford a variety of organic products such as benzenes, cyclopentadienones, cyclooctatetraenes, etc. In certain instances such reactions led to the simultaneous formation of both the organic products and cyclobutadienemetal complexes. Moreover, the formation of the organic products directly from the cyclobutadienemetal complexes has also been encountered in numerous reactions. For example, the reaction of $[Ph_4C_4PdX_2]_2$ (**111**) with $Ni(CO)_4$ in benzene at 80 °C gave a good yield of tetraphenylcyclopentadienone.[149,322] In another example the tetraphenylcyclobutadieneniobium complex **89** has been reported to undergo thermal decomposition to afford hexaphenylbenzene.[108] At this stage, it should be pertinent to mention that the issue of intramolecular conversion of cyclobutadiene to cyclopentadienone has already been discussed elsewhere in this review, in the context of the molecular structure of the novel intermediate-like molybdenum complex **62**[89] (section V). The above cited results appear to provide some circumstantial evidence in support of the participation of cyclobutadienemetal complexes and/or intermediates during certain metal-catalyzed reactions involving alkynes. In fact, the intermediacy of cyclobutadienemetal complexes has either been postulated or considered in certain processes involving the cyclotrimerization[323-328] and cyclotetramerization[329,330] of alkynes. In the context of cyclotrimerization processes, noteworthy in particular is the study by Whitesides and Ehmann[331] which describes an ingenious test for the intermediacy of cyclobutadienemetal complexes in the metal-catalyzed formation of benzenes from 1,1,1-trideuterio-2-butyne. This test is particularly effective for establishing the absence of such intermediates. Finally, Schrauzer, Glockner, and Eichler[332] have carefully examined the various kinetic aspects of the Reppe reaction and concluded that the intermediate in the cyclooctatetraene synthesis was a complex containing four acetylenes arranged in such a manner as to permit a concerted ring closure. It should, however, be pointed out that the participation of intermediates containing coordinated cyclobutadiene in this reaction cannot be ruled out entirely, since it has been shown in recent years that a large number of cyclobutadienemetal complexes do react under suitable conditions to afford tricyclooctadienes or cyclooctatetraenes. The implication of cyclobutadienemetal intermediates in catalytic processes is a subject of considerable interest; however, this aspect despite its importance is beyond the immediate scope of the current review.

IX. Addendum

In order to update this review, several noteworthy investigations, most of which have appeared in recent literature, will be cited briefly in this section. King and Harmon[333] reported the reaction of bicyclo[3.2.0]hepta-1,4,6-triene (C_7H_6) with $Fe_3(CO)_{12}$ in boiling benzene by which the novel complex $C_7H_6Fe(CO)_3$ (**394**), containing a novel bicyclic cyclobutadiene ligand was obtained in 41% yield by a process involving hydrogen migration. The chemical properties of **394** were investigated by Bamberg and Bergman.[334] This complex was shown to readily undergo ligand substitution reactions (e.g., with $P(OR)_3$)

including nitrosation with NO^+PF_6. The organic chemistry of the coordinated ligand in **394** was also investigated. For example, removal of a methylene proton from the five-membered ring of the ligand with *n*-BuLi or KCH_2SOCH_3 gave an air-sensitive anion which reacted with various reagents such as D_2O, CH_3I, Me_3SiCl, and CH_3COCH_3 to afford the respective exo-substituted D, CH_3, Me_3Si, and $Me_2C(OH)$ derivatives of **394**. Annelation of tricarbonyliron complexes of ortho-disubstituted [4]annulenes was investigated independently by two groups. Wittig cycloolefination of *o*-dialdehyde cyclobutadieneiron tricarbonyl (**294**) with $[Ph_3P^+{-}CH_2C({=}O)CH_2{-}{}^+PPh_3]2Cl^-$,[335,336] and $[Ph_3P^+{-}(CH_2)_n{-}{}^+PPh_3]2Cl^-$ (**395,** $n = 3$,[335] $n = 4$[336]) gave the expected ring-closure products. The product obtained from the reaction with **395,** $n = 3$, was reported[335] by Stringer and Wege to undergo hydride abstraction on treatment with trityl hexafluorophosphate to afford tricarbonyl(1,2,2a,7a-η-cyclobutatropylium)iron hexafluorophosphate. In a different study, Kaplan and Roberts reported[337] the cyclobisacylation of para-,para′-disubstituted biphenyls with the diacid chloride **285**. Acetylation of the parent complex **3** was reported[338] by Dinulescu et al., to afford the mono- and *o*-diacetyl derivatives; the latter derivative on reaction with hydrazine gave a pyridazinocyclobutadieneiron tricarbonyl complex. A new synthesis of benzocyclobutadieneiron tricarbonyl (**9**) by the reaction of 1,4-dibromocyclooctatetraene with $Fe(CO)_4{}^{2-}2Na^+$ was reported[339] by Harris et al. Among the recently reported studies on cyclobutadieneiron tricarbonyl derivatives, the investigation of the mechanism of oxidative decomposition of certain such complexes by Grubbs and Pancoast[340] is noteworthy. This work describes the synthesis of the optically active ortho-substituted derivative $[(CH_3)(CH_2OCH_2C{\equiv}CCH_3)H_2C_4]Fe(CO)_3$ and its oxidative decomposition with Ce(IV) to afford the expected phthalan derivative (75% yield) as well as a minor carbon monoxide insertion product (20% yield). Significantly, the retention of optical activity was only observed in the instance of the minor product, and this led to the suggestion of an intramolecular trapping mechanism for its formation. By contrast the racemic mixture of the major product from this reaction was most probably formed via a free cyclobutadiene pathway. Starting with the appropriate carbonyldioxycyclobutene and $Fe(CO)_4{}^{2-}2Na^+$, Carrol, Seltman and Hauser reported[341] the stereospecific synthesis of tricarbonyl(*A*-bisnor-17β-acetoxy-1,5(10)-estradieneiron. The photochemical reactions of *o*-dimethylcyclobutadieneiron tricarbonyl (**23**) with a variety of acetylenes (e.g., acetylene, propyne, and 2-butyne), investigated by Bruitt, Biehl and Reeves,[342] gave benzenoid compounds, and the mechanistic routes to such products were evaluated. Weber and Brintzinger reported[343] the isolation of a very small amount of the tetramethylcyclobutadieneiron complex $(Me_6C_6)Fe(C_4Me_4)$ from the reaction of $(Me_6C_6)_2Fe$ and 2-butyne. The structural assignment of this novel complex was claimed on the basis of a peak at *m*/*e* 326 in its mass spectrum and, therefore, should be viewed with utmost caution. The activation of the tetraphenylcyclobutadieneiron complex **180** using cyclic voltammetric technique was reported[344] by Connelly and Kelly to afford the stable paramagnetic cation $[Ph_4C_4Fe(CO)_2(PPh_3)]^+$ by a one-electron oxidation process. In concluding the part dealing with cyclobutadieneiron complexes, it should also be pointed out that several recent papers describe the oxidative displacement of free cyclobutadiene from **3** and its use in organic synthesis.[345–347]

Numerous noteworthy investigations have been reported on cyclobutadienemetal complexes other than those of iron. The preparation of (cyclopentadienyl)(substituted cyclobutadiene)cobalt derivatives containing unusual complexed metal substituents was reported[348,349] by Yasufuku and Yamazaki. For example, the reactions of $CpCo(PPh_3)(RC{\equiv}CR')$ (R, R′ = Ph, COOMe) with the ethynyl complexes $R''C{\equiv}CM$, where R″ = Ph for M = CpFe(CO)(L) (L = CO, Ph_3P) and R″ = Ph and COOMe for M = $CpNi(PPh_3)$, gave[348] cyclobutadienecobalt products having M as one of their substituents. In a similar study, the reactions of mono- and bis(phenylethynyl)ferrocenes with $CpCo(PPh_3)(RC{\equiv}CR')$ (R, R′ = Ph, COOMe) or $CpCo(PPh_3)_2$ at 80 °C were reported[349] to afford ferrocenylcyclobutadienecobalt derivatives. In a somewhat related study, Lee and Brintzinger reported[350] the formation of Ph_4C_4CoCp (**63**) in 78% yield by the reaction of the binuclear complex $Cp_2Co_2(\mu\text{-}CO)(\mu\text{-}Ph_2C_2)$ with Ph_2C_2 in refluxing toluene. In a recent review[351] Vollhardt described the reactions of 1,5-hexadiyne, 1,6-heptadiyne, and 1,7-octadiyne with monoacetylenes in the presence of $CpCo(CO)_2$ which afford general synthetic routes to benzocyclobutenes, indans, and tetralins, respectively. These cobalt-catalyzed cooligomerization reactions gave as by-products several novel (cyclopentadienyl) (substituted cyclobutadiene)cobalt derivatives. Structural data have been reported on the 1,2-dicyano-, 1,2-diiodo-, and iodocyclopentadienylcobalt complexes $[C_5H_3(CN)_2]Co(C_4Ph_4)$, $(C_5H_3I_2)Co(C_4Ph_4)$, and $(C_5H_4I)Co(C_4Ph_4)$. In an extension of an earlier study, King and Ackermann reported[353] the syntheses of the rhodium analogues of the tricyclic cyclobutadienecobalt complexes **101** by the reactions of $CpRh(CO)_2$ with the macrocyclic alkadiynes **100**.

During the past year, little attention was given to the study of cyclobutadienepalladium complexes. The syntheses of certain ortho-substituted diphenylacetylenes and their reactions with dichlorobis(benzonitrile)palladium to afford the corresponding substituted cyclobutadienepalladium chloride derivatives was reported[354] by Staicu et al. Especially noteworthy was the development in the chemistry of cyclobutadienenickel which was reported[355] by Hoberg, Krause-Going, and Kruger. The reaction of pentaphenylaluminacyclopentadiene with lithium gave a dianion which on treatment with $NiBr_2$ yielded the binuclear complex $(Ph_5C_5)Ni(Ph_3C_3)Ni(C_4Ph_4)$, containing an unusual open allylic bridge, as well as a second product whose elemental analysis and mass spectrum are consistent with a bis(tetraphenylcyclobutadiene)nickel(0) structure. Incidentally, the structure of the binuclear complex was determined by crystallographic means.

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X. *References and Notes*

(1) A. Kekulé, *Justus Liebigs Ann. Chem.*, **162,** 77 (1872).
(2) R. Willstätter and W. von Schmaedel, *Ber.*, **38,** 1992 (1905).
(3) M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds", Academic Press, New York, N.Y., 1967.
(4) W. Baker and J. F. W. McOmie, *Chem. Soc., Spec. Publ.*, **No. 12,** 49–67 (1958).
(5) W. Baker and J. F. W. McOmie in "Non-Benzenoid Aromatic Compounds", D. Ginsburg, Ed., Wiley (Interscience), New York, N.Y., 1959.
(6) L. Watts, J. D. Fitzpatrick, and R. Pettit, *J. Am. Chem. Soc.*, **87,** 3253 (1965).
(7) G. F. Emerson, L. Watts, and R. Pettit, *J. Am. Chem. Soc.*, **87,** 131 (1965).
(8) G. Schmid, *Chem. Unserer Zeit.*, **8,** 26 (1974), and pertinent references therein.
(9) A. Nakamura, *Kagaku No Ryoiki Zokan*, **89,** 258 (1970); *Chem. Abstr.*, **73,** 55–213j (1970).
(10) G. Mair, *Angew. Chem., Int. Ed. Engl.*, 13, 425 (1974).
(11) K. P. C. Vollhardt, *Top. Curr. Chem.*, **59,** 113 (1975).
(12) C. Y. Lin and A. Krantz, *J. Chem. Soc., Chem. Commun.*, 1111 (1972).
(13) O. L. Chapman, C. L. McIntosh, and J. Pacansky, *J. Am. Chem. Soc.*, **95,** 614 (1973).
(14) M. Rosenblum and C. Gatsonis, *J. Am. Chem. Soc.*, **89,** 5079 (1967).
(15) M. Rosenblum and B. North, *J. Am. Chem. Soc.*, **90,** 1060 (1968).
(16) E. Hückel, *Z. Phys.*, **70,** 204; **72,** 310 (1931).
(17) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists", Wiley, New York, N.Y., 1961, p 261.
(18) R. J. Buenker and S. D. Peyerimhoff, *J. Chem. Phys.*, **48,** 354 (1968); *J. Am. Chem. Soc.*, **91,** 4342 (1969).
(19) M. J. S. Dewar, M. C. Kohn, and N. Trinajstic, *J. Am. Chem. Soc.*, **93,** 3437

(1971).

(20) M. J. S. Dewar and H. W. Kollmar, *J. Am. Chem. Soc.*, **97**, 2933 (1975); R. C. Haddon and G. R. J. Williams, *ibid.*, **97**, 6582 (1975).

(21) W. T. Borden, *J. Am. Chem. Soc.*, **97**, 5968 (1975).

(22) A. Krantz, C. Y. Lin, and M. D. Newton, *J. Am. Chem. Soc.*, **95**, 2744 (1973).

(23) O. L. Chapman, D. D. La Cruz, R. Roth, and J. Pacansky, *J. Am. Chem. Soc.*, **95**, 1337 (1973).

(24) R. Pettit, *Pure Appl. Chem.*, **17**, 253 (1969).

(25) P. Reeves, T. Devon, and R. Pettit, *J. Am. Chem. Soc.*, **91**, 5890 (1969); P. Reeves, Ph.D. Dissertation, The University of Texas in Austin, 1969.

(26) H. C. Longuet-Higgins and L. E. Orgel, *J. Chem. Soc.*, 1969 (1956).

(27) R. Criegee and G. Schröder, *Justus Liebigs Ann. Chem.*, **623**, 1 (1959); *Angew. Chem.*, **71**, 70 (1959).

(28) W. Hübel and E. H. Braye, *J. Inorg. Nucl. Chem.*, **10**, 250 (1959).

(29) W. Hübel, E. H. Braye, A. Clauss, E. Weiss, U. Kruerke, D. A. Brown, G. S. D. King, and C. Hoogzand, *J. Inorg. Nucl. Chem.*, **9**, 204 (1959).

(30) J. D. Dunitz, H. C. Mez, O. S. Mills, and H. M. M. Shearer, *Helv. Chim. Acta*, **45**, 647 (1962).

(31) R. D. Dodge and V. Schomaker, *Nature (London)*, **186**, 798 (1960).

(32) R. D. Dodge and V. Schomaker, *Acta Crystallogr.*, **18**, 614 (1965).

(33) P. M. Maitlis, *Adv. Organometal. Chem.*, **4**, 95 (1966).

(34) A. Efraty, *J. Organomet. Chem.*, **57**, 1 (1973).

(35) J. D. Fitzpatrick, L. Watts, G. F. Emerson, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 3254 (1965).

(36) A. Sanders, C. V. Magatti, and W. P. Giering, *J. Am. Chem. Soc.*, **96**, 1610 (1974).

(37) A. Sanders and W. P. Giering, *J. Am. Chem. Soc.*, **96**, 5247 (1974).

(38) P. M. Maitlis and K. W. Eberius in "Nonbenzenoid Aromatics", J. P. Snyder, Ed., Academic Press, New York, N.Y., 1971.

(39) R. Pettit, *J. Organometal. Chem.*, **100**, 205 (1975), and pertinent references therein.

(40) R. Criegee and A. Moschel, *Chem. Ber.*, **92**, 2181 (1959); R. Criegee, *Org. Synth.*, **46**, 34 (1966).

(41) J. P. Pfrommer, Ph.D. Dissertation, Karlsruhe, 1961.

(42) R. Criegee, *Angew. Chem., Int. Ed. Engl.*, **1**, 519 (1962).

(43) G. Henrici-Olivé and S. Olivé, *Angew. Chem.*, **79**, 897 (1967).

(44) R. Pettit and J. Henery, *Org. Synth.*, **50**, 21 (1970).

(45) M. Avram, J. Dinulescu, M. Elian, M. Farcasiu, G. Mateescu, and C. D. Nenitzescu, *Chem. Ber.*, **97**, 372 (1964).

(46) R. Pettit and J. Henery, *Org. Synth.*, **50**, 36 (1970).

(47) M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **79**, 1701 (1957).

(48) L. Watts and R. Pettit, *Adv. Chem. Ser.*, **No. 62**, 549 (1967).

(49) R. G. Amiet, P. C. Reeves, and R. Pettit, J. Chem. Soc., *Chem. Commun.*, 1208 (1967).

(50) R. G. Amiet and R. Pettit, *J. Am. Chem. Soc.*, **90**, 1059 (1968).

(51) J. S. Ward and R. Pettit, *J. Chem. Soc., Chem. Commun.*, 1419 (1970).

(52) W. D. Huntsman, *J. Am. Chem. Soc.*, **82**, 6389 (1960); W. D. Huntsman and H. J. Wristers, *ibid.*, **85**, 3308 (1963); W. D. Huntsman, J. A. DeBoer, and M. H. Woosley, *ibid.*, **88**, 5846 (1966); W. D. Huntsman and H. J. Wristers, *ibid.*, **89**, 342 (1967).

(53) R. Criegee, W. Eberius, and H. A. Brune, *Chem. Ber.*, **101**, 94 (1968).

(54) H. A. Brune, W. Eberius, and H. P. Wolff, *J. Organomet. Chem.*, **12**, 485 (1968).

(55) H. A. Brune, H. P. Wolff, and H. Hüther, *Tetrahedron*, **27**, 3949 (1971).

(56) H. A. Brune, H. P. Wolff, and H. Hüther, *Z. Naturforsch., Teil B*, **26**, 765 (1971).

(57) H. A. Brune and H. P. Wolff, *Tetrahedron*, **24**, 4861 (1968).

(58) H. A. Brune, H. P. Wolff, and H. Hüther, *Tetrahedron*, **25**, 1089 (1969).

(59) H. A. Brune, H. P. Wolff, W. Schwab, and H. Hüther, *Tetrahedron*, **27**, 4361 (1971).

(60) H. A. Brune, H. P. Wolff, W. Klein, and U. I. Záhorszky, *Z. Naturforsch.*, Teil **B**, **27**, 639 (1972).

(61) H. P. Wolff, P. Müller, and H. A. Brune, *Z. Naturforsch., Teil B*, **27**, 915 (1972).

(62) H. A. Brune, H. Hanebeck, and H. Hüther, *Tetrahedron*, **26**, 3099 (1970).

(63) H. A. Brune, G. Horlbeck, H. Röttele, and U. Tanger, *Z. Naturforsch., Teil B*, **28**, 68 (1973).

(64) E. J. Smutny, M. C. Caserio, and J. D. Roberts, *J. Am. Chem. Soc.*, **82**, 1973 (1960); E. J. Smutny and J. D. Roberts, *ibid.*, **77**, 3420 (1955).

(65) M. Avram, G. D. Mateescu, I. G. Dinulescu, I. Pogany, and C. D. Nenitzescu, *Rev. Roum. Chim.*, **13**, 1085 (1968).

(66) H. A. Brune, G. Horlbeck, and H. P. Wolff, *Z. Naturforsch., Teil B*, **25**, 326 (1970).

(67) H. A. Brune, G. Horlbeck, and U. I. Záhorszky, *Z. Naturforsch., Teil B*, **26**, 222 (1971).

(68) H. A. Brune, G. Horlbeck, and H. Röettele, *Z. Naturforsch., Teil B*, **27**, 505 (1972).

(69) A. E. Feiring and J. Ciabattoni, *J. Am. Chem. Soc.*, **95**, 5266 (1973).

(70) B. W. Roberts, A. Wissner, and R. A. Rimerman, *J. Am. Chem. Soc.*, **91**, 6208 (1969).

(71) G. Berens, F. Kaplan, R. Rimerman, B. W. Roberts, and A. Wissner, *J. Am. Chem. Soc.*, **97**, 7076 (1975).

(72) E. K. G. Schmidt, *Chem. Ber.*, **107**, 2440 (1974).

(73) H. D. Scharf and K. R. Stahlke, *Angew. Chem., Int. Ed. Engl.*, **9**, 810 (1970).

(74) H. E. Zimmerman, G. L. Grunewald, and R. M. Paufler, *Org. Synth.*, **46**, 101 (1966).

(75) J. Agar, F. Kaplan, and B. W. Roberts, *J. Org. Chem.*, **39**, 3451 (1974).

(76) M. Rosenblum, B. North, D. Wells, and W. P. Giering, *J. Am. Chem. Soc.*, **94**, 1239 (1972).

(77) S. A. Gardner and M. D. Rausch, *J. Organomet. Chem.*, **56**, 365 (1973).

(78) R. H. Grubbs, *J. Am. Chem. Soc.*, **92**, 6693 (1970).

(79) R. H. Grubbs, T. A. Pancoast, and R. A. Grey, *Tetrahedron Lett.*, 2425 (1974).

(80) R. H. Grubbs and R. A. Grey, *J. Chem. Soc., Chem. Commun.*, 76 (1973).

(81) F. L. Bowden and A. B. P. Lever, *Organomet. Chem. Rev.*, 3, 227 (1968).

(82) L. P. Motz, J. Merritt and R. P. Pinnell, *Synthesis*, 305 (1971).

(83) A. Nakamura and N. Hagihara, *Nippon Kagaku Zasshi*, **84**, 339 (1963).

(84) R. Buehler, R. Geist, R. Muendnich, and H. Plieninger, *Tetrahedron Lett.*, 1919 (1973).

(85) H. W. Whitlock and P. E. Sandvick, *J. Am. Chem. Soc.*, **88**, 4526 (1966).

(86) E. F. Epstein and L. F. Dahl, *J. Am. Chem. Soc.*, **92**, 493 (1970).

(87) W. Hübel and R. Merényi, *J. Organomet. Chem.*, **2**, 213 (1964).

(88) A. Efraty, J. Potenza, L. Zyontz, J. Daily, and M. H. A. Huang, *J. Organomet. Chem.*, in press.

(89) A. Efraty, J. Potenza, and R. Johnson, unpublished results.

(90) A. Nakamura, and N. Hagihara, *Bull. Chem. Soc. Jpn.*, **34**, 452 (1961).

(91) A. Nakamura, *Mem. Inst. Sci. Ind. Res., Osaka Univ.*, **19**, 81 (1962).

(92) J. L. Boston, D. W. Sharpe, and G. Wilkinson, *J. Chem. Soc.*, 3488 (1962).

(93) M. D. Rausch and R. A. Genetti, *J. Am. Chem. Soc.*, **89**, 5502 (1967).

(94) R. Markby, H. W. Sternberg, and I. Wender, *Chem. Ind. (London)*, 1381 (1959).

(95) H. Yamazaki and N. Hagihara, *J. Organomet. Chem.*, **7**, P22 (1967).

(96) H. Yamazaki and N. Hagihara, *J. Organomet. Chem.*, **21**, 431 (1970).

(97) M. D. Rausch and R. A. Genetti, *J. Org. Chem.*, **35**, 3888 (1970).

(98) J. F. Helling, S. C. Rennison, and A. Merijan, *J. Am. Chem. Soc.*, **89**, 7140 (1967).

(99) G. E. Herberich, H. J. Becker, *Z. Naturforsch., Teil B*, **28**, 828 (1973).

(100) W. G. L. Aalbersberg, A. J. Berkovich, R. L. Funk, R. L. Hillard, III, and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, **97**, 5600 (1975).

(101) G. G. Cash, J. F. Helling, M. Mathew, and G. J. Palenik, *J. Organomet. Chem.*, **50**, 227 (1973).

(102) S. A. Gardner, P. S. Andrews, and M. D. Rausch, *Inorg. Chem.*, **12**, 2396 (1973).

(103) J. F. Nixon and M. Kooti, *J. Organomet. Chem.*, **104**, 231 (1976).

(104) M. Kooti and J. F. Nixon, *Inorg. Nucl. Chem. Lett.*, **9**, 1031 (1973).

(105) A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and A. A. Pasynskii, *Dokl. Akad. Nauk SSSR*, **182**, 112 (1968).

(106) A. A. Pasynskii, K. N. Anisimov, N. E. Kolobova, and A. N. Nesemeyanov, *Dokl. Akad. Nauk SSSR*, **185**, 610 (1969).

(107) A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and A. A. Pasynskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 774 (1966).

(108) A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and A. A. Pasynskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 100 (1969).

(109) A. N. Nesmeyanov, A. I. Gusev, A. A. Pasynskii, K. N. Anisimov, N. E. Kolobova, and Yu. T. Struchkov, *J. Chem. Soc., Chem. Commun.*, 277 (1969).

(110) A. N. Nesmeyanov, A. I. Gusev, A. A. Pasynskii, K. N. Anisimov, N. E. Kolobova and Yu. T. Struchkov, *J. Chem. Soc., Chem. Commun.*, 739 (1969).

(111) F. Canziani, P. Chini, A. Quarta, and A. Dimartin, *J. Organometal. Chem.*, **26**, 285 (1971).

(112) F. Canziani and M. C. Malatesta, *J. Organometal. Chem.*, **90**, 235 (1975).

(113) S. M. Kim, Yu. A. Kushnikov, L. V. Levchenko and N. N. Paramonova, *Dokl. Vses., Konf. Khim. Atsetilena, 4th*, **2**, 272 (1972); *Chem. Abstr.*, **79**, 105-384n (1973).

(114) R. B. King and A. Efraty, *J. Am. Chem. Soc.*, **92**, 6071 (1970).

(115) R. B. King and A. Efraty, *J. Am. Chem. Soc.*, **94**, 3021 (1972).

(116) R. B. King, I. Haiduc and A. Efraty, *J. Organomet. Chem.*, **47**, 145 (1973).

(117) R. B. King and C. W. Eavenson, *J. Organomet. Chem.*, **16**, P75 (1969).

(118) R. B. King and I. Haiduc, *J. Am. Chem. Soc.*, **94**, 4044 (1972).

(119) R. B. King, I. Haiduc, and C. W. Eavenson, *J. Am. Chem. Soc.*, **95**, 2508 (1973).

(120) Henceforth, for clarity reasons, the symbols *n* and *m* in the structures of metal complexes derived from macrocyclic alkadiynes stand for the methylene chains $-(\mathrm{CH_2})_n-$ and $-(\mathrm{CH_2})_m-$, respectively.

(121) H. B. Chin and R. Bau, *J. Am. Chem. Soc.*, **95**, 5068 (1973).

(122) R. Victor and R. Ben Shoshan, *J. Chem. Soc., Chem. Commun.*, 93 (1974).

(123) R. E. Davis, B. L. Barnett, R. G. Amiet, W. Mark, J. S. McKennis, and R. Pettit, *J. Am. Chem. Soc.*, **96**, 7108 (1974).

(124) F. D. Mango and J. H. Schachtschneider, *J. Am. Chem. Soc.*, **91**, 1030 (1969).

(125) F. D. Mango, Proceedings of the first Japanese-American seminar on "Prospects in Organotransition-Metal Chemistry," University of Hawaii, Honolulu, May 1-3, 1974, pp 169-177, and pertinent references therein.

(126) W. Hübel in "Organic Syntheses via Metal Carbonyls", I. Wender and P. Pino, Ed., Wiley (Interscience), New York, N.Y., 1968, pp 273 and 288.

(127) P. M. Maitlis, D. F. Pollock, M. L. Games, and W. J. Pryde, *Can. J. Chem.*, **43**, 470 (1965).

(128) D. F. Pollock and P. M. Maitlis, *J. Organomet. Chem.*, **26**, 407 (1971).

(129) R. Hüttel and H. J. Neugebauer, *Tetrahedron Lett.*, 3541 (1964).

(130) M. Avram, I. G. Dinulescu, G. D. Mateesu, E. Avram, and C. D. Nenitzescu, *Rev. Roum. Chem.*, **14**, 1181 (1964).

(131) L. Malatesta, G. Santarella, L. M. Vallarino, and F. Zingales, *Angew. Chem.*, **72**, 34 (1960).

(132) A. T. Blomquist and P. M. Maitlis, *J. Am. Chem. Soc.*, **84**, 2329 (1962).

(133) L. M. Vallarino and G. Santarella, *Gazz. Chim. Ital.*, **94**, 252 (1964).

(134) R. C. Cookson and D. W. Jones, *J. Chem. Soc.*, 1881 (1965).

(135) P. M. Maitlis and M. L. Games, *Can. J. Chem.*, **42**, 183 (1964).
(136) L. F. Dahl and W. E. Oberhansli, *Inorg. Chem.*, **4**, 629 (1965).
(137) T. Hosokawa and I. Moritani, *Tetrahedron Lett.*, 3021 (1969).
(138) E. Müller, K. Munk, P. Ziemek and M. Sauerbier, *Justus Liebigs Ann. Chem.*, **713**, 40 (1968).
(139) M. H. Chisholm and H. C. Clark, *J. Chem. Soc., Chem. Commun.*, 1484 (1971).
(140) M. H. Chisholm and H. C. Clark, *J. Am. Chem. Soc.*, **94**, 1532 (1972).
(141) D. B. Crump and N. C. Payne, *Inorg. Chem.*, **12**, 1663 (1973).
(142) W. Winter, *Angew. Chem., Int. Ed. Engl.*, **14**, 170 (1975).
(143) H. O. Van Oven, *J. Organomet. Chem.*, **55**, 309 (1973).
(144) L. I. Smith and H. H. Hoehn, *J. Am. Chem. Soc.*, **63**, 1184 (1941).
(145) W. Hübel, Lecture at Conference, "Current Trends in Organometallic Chemistry", Cincinnati, 1963.
(146) F. C. Leavitt, T. A. Manuel, F. Johnson, L. U. Matternas, and D. S. Lehman, *J. Am. Chem. Soc.*, **82**, 5099 (1960).
(147) H. H. Freedman, *J. Am. Chem. Soc.*, **83**, 2194, 2195 (1961).
(148) H. Sakurai and J. Hayashi, *J. Organomet. Chem.*, **63**, C10 (1973).
(149) P. M. Maitlis and M. L. Games, *J. Am. Chem. Soc.*, **85**, 1887 (1963).
(150) A. Z. Rubezov and S. P. Gubin, *Adv. Organomet. Chem.*, **10**, 347 (1972).
(151) D. F. Pollock and P. M. Maitlis, *Can. J. Chem.*, **44**, 2673 (1966).
(152) C. T. Sears, Jr., and F. G. A. Stone, *J. Organomet. Chem.*, **11**, 644 (1968).
(153) P. M. Maitlis and M. L. Games, *Chem. Ind. (London)*, 1624 (1963).
(154) A. Efraty, *Can. J. Chem.*, **47**, 4695 (1969).
(155) M. Mathew and G. L. Palenik, *Can. J. Chem.*, **47**, 705 (1969).
(156) M. Mathew and G. L. Palenik, *J. Organomet. Chem.*, **61**, 301 (1973).
(157) P. M. Maitlis and A. Efraty, *J. Organomet. Chem.*, **4**, 172 (1965).
(158) A. Efraty and P. M. Maitlis, *J. Am. Chem. Soc.*, **89**, 3744 (1967).
(159) P. M. Maitlis and A. Efraty, *J. Organomet. Chem.*, **4**, 175 (1965).
(160) P. M. Maitlis, A. Efraty, and M. L. Games, *J. Organomet. Chem.*, **2**, 284 (1964).
(161) P. M. Maitlis, A. Efraty, and M. L. Games, *J. Am. Chem. Soc.*, **87**, 719 (1965).
(162) R. Bruce, K. Moseley and P. M. Maitlis, *Can. J. Chem.*, **45**, 2011 (1967).
(163) E. F. Epstein and L. F. Dahl, *J. Am. Chem. Soc.*, **92**, 502 (1970).
(164) R. Bruce and P. M. Maitlis, *Can. J. Chem.*, **45**, 2017 (1967).
(165) A. Efraty, Ph.D. Dissertation, McMaster University, Hamilton, Ontario, Canada, 1967.
(166) R. E. Davis, *J. Chem. Soc., Chem. Commun.*, 1218 (1968).
(167) M. R. Churchill, J. Wormald, W. P. Giering, and G. F. Emerson, *J. Chem. Soc., Chem. Commun.*, 1217 (1968).
(168) M. R. Churchill and J. Wormald, *Inorg. Chem.*, **8**, 1936 (1969).
(169) C. H. Campbell and M. L. H. Green, *J. Chem. Soc., Chem. Commun.*, 1009 (1970).
(170) W. P. Giering, *J. Chem. Soc., Chem. Commun.*, 4 (1971).
(171) R. B. King, A. Efraty, and W. C. Zipperer, *J. Organomet. Chem.*, **38**, 121 (1972).
(172) T. Bauch, A. Sanders, C. V. Magatti, P. Waterman, D. Judelson, and W. P. Giering, *J. Organomet. Chem.*, **99**, 269 (1975).
(173) A. Sanders, L. Cohen, W. P. Giering, D. Kenedy, and C. V. Magatti, *J. Am. Chem. Soc.*, **95**, 5430 (1973).
(174) A. Sanders and W. P. Giering, *J. Am. Chem. Soc.*, **97**, 919 (1975).
(175) A. Sanders and W. P. Giering, *J. Organomet. Chem.*, **104**, 49 (1976).
(176) A. Sanders and W. P. Giering, *J. Organomet. Chem.*, **104**, 67 (1976).
(177) R. B. King and A. Efraty, *Inorg. Chem.*, **10**, 1376 (1971).
(178) A. N. Nesmeyanov, V. A. Sazonova, and V. N. Drozd, *Dokl. Akad. Nauk SSSR*, **130**, 1030 (1960).
(179) E. G. Perevalova, K. I. Grandberg, N. A. Zharikova, S. P. Gubin, and A. N. Nesmeyanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 832 (1966).
(180) P. Reeves, J. Henery and R. Pettit, *J. Am. Chem. Soc.*, **91**, 5888 (1969).
(181) J. S. Ward and R. Pettit, *J. Am. Chem. Soc.*, **93**, 262 (1971).
(182) A. Bond and M. Green, *J. Chem. Soc., Chem. Commun.*, 12 (1971).
(183) A. Bond and M. Green, *J. Chem. Soc., Dalton Trans.*, 763 (1972).
(184) F. M. Chaudhari and P. L. Pauson, *J. Organomet. Chem.*, 5, 73 (1966).
(185) A. Efraty, R. Bystrek, J. A. Geaman, M. H. A. Huang, and R. H. Herber, *J. Organomet. Chem.*, **55**, C33 (1973).
(186) A. Efraty, R. Bystrek, J. A. Geaman, S. S. Sandhu, Jr., M. H. A. Huang, and R. H. Herber, *Inorg. Chem.*, **13**, 1269 (1974).
(187) A. Efraty, unpublished results.
(188) A. Efraty and D. Liebman, unpublished results.
(189) I. Fischler, K. Hildenbrand, and E. K. von Gustorf, *Angew. Chem., Int. Ed. Engl.*, **14**, 54 (1975).
(190) S. I. Murahashi, T. Mizoguchi, T. Hosokawa, I. Moritani, Y. Kai, M. Kohara, N. Yasuoka, and N. Kasai, *J. Chem. Soc., Chem. Commun.*, 563 (1974).
(191) A. Efraty, M. H. A. Huang, and C. A. Weston, *J. Organomet. Chem.*, **91**, 327 (1975).
(192) A. Efraty, D. Liebman, J. Sikora, and D. Z. Denney, *Inorg. Chem.*, **15**, 886 (1976).
(193) E. J. Wharton, *Inorg.-Nucl. Chem. Lett.*, **7**, 307 (1971).
(194) P. A. Wegner and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 861 (1966).
(195) M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, Jr., and P. A. Wegner, *J. Am. Chem. Soc.*, **90**, 879 (1968).
(196) R. B. King and A. Efraty, *J. Chem. Soc., Chem. Commun.*, 1370 (1970).
(197) R. Criegee, F. Förg, H. A. Brune, and D. Schönleber, *Chem. Ber.*, **97**, 3461 (1964).
(198) R. Criegee and P. Ludwig, *Chem. Ber.*, **94**, 2038 (1961).
(199) W. Oberhansli and L. F. Dahl, *Inorg. Chem.*, **4**, 150 (1965).
(200) R. B. King, *Inorg. Chem.*, **2**, 530 (1963).
(201) H. Takahashi and J. Tsuji, *J. Am. Chem. Soc.*, **90**, 2387 (1968).
(202) T. H. Whitesides, R. W. Arhart, and R. Slaven, *J. Am. Chem. Soc.*, **95**, 5792 (1973).
(203) J. Evans, D. V. Howe, B. F. G. Johnson, and L. Lewis, *J. Organomet. Chem.*, **61**, C48 (1973).
(204) A. Efraty, J. Potenza, S. S. Sandhu, Jr., R. Johnson, D. Mastropaolo, R. Bystrek, D. Z. Denney, and R. H. Herber, *J. Organomet. Chem.*, **70**, C24 (1974).
(205) A. Bond, M. Green, and S. H. Taylor, *J. Chem. Soc., Chem. Commun.*, 112 (1973).
(206) M. Green, N. Mayne, and F. G. A. Stone, *J. Chem. Soc. A*, 902 (1968).
(207) W. T. Miller, J. H. Fried, and H. Goldwhite, *J. Am. Chem. Soc.*, **82**, 3091 (1960).
(208) R. E. Davis, P. Reeves, and R. Pettit, to be published—quotation of ref 20 in a recent review[39] by R. Pettit.
(209) R. E. Davis, N. Grice and R. Pettit, submitted for publication—quotation of ref 16 in a recent review[39] by R. Pettit.
(210) G. Amiet and R. Pettit, to be published—quotation of ref 18 in a recent review[39] by R. Pettit.
(211) J. Fitzpatrick, Ph.D. Dissertation, University of Texas, Austin, 1970.
(212) M. Rosenblum "Chemistry of the Iron Group Metallocenes", Wiley, New York, N.Y., 1965.
(213) P. Marcincal and E. Cuingnet, *Tetrahedron Lett.*, 1223 (1975).
(214) D. Stierle, E. R. Biehl, and P. C. Reeves, *J. Organomet. Chem.*, **72**, 221 (1974).
(215) G. F. Emerson and R. Pettit, *J. Am. Chem. Soc.*, **84**, 4591 (1962).
(216) G. F. Emerson, J. E. Mahler, and R. Pettit, *Chem. Ind. (London)*, 836 (1964).
(217) E. R. Biehl and P. C. Reeves, *Synthesis*, No. 12, 883 (1974).
(218) Y. Fujiwara, R. Asano, I. Moritani, and S. Teranishi, *Chem. Soc. Jpn., Chem. Lett.*, 1061 (1975).
(219) Y. Fujiwara, R. Asano, I. Moritani, and S. Teranishi, *J. Org. Chem.*, **41**, 1681 (1976).
(220) J. Henery, Ph.D. Dissertation, University of Texas, Austin, 1970.
(221) P. Marcincal and E. Cuingnet, *Tetrahedron Lett.*, 3827 (1975).
(222) P. Marcincal, N. Hannoir-Guisz, and E. Cuingnet, *Trav. Soc. Pharm. Montpellier*, 33, 281 (1973).
(223) C. H. Mauldin, E. R. Biehl, and P. C. Reeves, *Tetrahedron Lett.*, 2955 (1972).
(224) H. Dieck, Ph.D. Dissertation, University of Texas, Austin, 1968.
(225) G. Amiet, K. Nicholas, and R. Pettit, *J. Chem. Soc., Chem. Commun.*, 161 (1970).
(226) J. Broussard, Ph.D. Dissertation, University of Texas, Austin, 1970.
(227) J. D. Fitzpatrick, L. Watts, and R. Pettit, *Tetrahedron Lett.*, 1299 (1966).
(228) R. E. Davis, H. D. Simpson, N. Grice, and R. Pettit, *J. Am. Chem. Soc.*, **93**, 6688 (1971).
(229) M. I. Davis and C. S. Speed, *J. Organomet. Chem.*, **21**, 401 (1970).
(230) M. Cais, *Organomet. Chem. Rev.*, 1, 435 (1966).
(231) E. K. G. Schmidt, *Angew. Chem., Int. Ed. Engl.*, **12**, 777 (1973).
(232) H. W. Whitlock, Jr., and P. L. Markezich, *J. Am. Chem. Soc.*, **93**, 5290 (1971).
(233) B. W. Roberts and A. Wissner, *J. Am. Chem. Soc.*, **92**, 6382 (1970).
(234) B. W. Roberts and A. Wissner, *J. Am. Chem. Soc.*, **94**, 7168 (1972).
(235) R. Criegee, J. Dekker, W. Engel, P. Ludwig, and K. Noll, *Chem. Ber.*, **96**, 2362 (1963).
(236) H. H. Freedman and D. R. Peterson, *J. Am. Chem. Soc.*, **94**, 2837 (1962).
(237) G. S. Pawley, W. N. Lipscomb, and H. H. Freedman, *J. Am. Chem. Soc.*, **86**, 4725 (1964).
(238) P. J. Wheatley, *J. Chem. Soc.*, 3136 (1965).
(239) J. H. Beynon, R. C. Cookson, R. R. Hill, D. W. Jones, R. A. Saunders, and A. E. Williams, *J. Chem. Soc.*, 7052 (1965).
(240) V. R. Sandel and H. H. Freedman, *J. Am. Chem. Soc.*, **90**, 2059 (1968).
(241) W. Eberius, Ph.D. Dissertation, Karlsruhe, 1967.
(242) H. H. Freedman, G. A. Doorakian, and V. R. Sandel, *J. Am. Chem. Soc.*, **87**, 3019 (1965).
(243) H. H. Freedman and G. A. Doorakian, *Tetrahedron*, **20**, 2181 (1964).
(244) H. H. Freedman and A. M. Frantz, *J. Am. Chem. Soc.*, **84**, 4165 (1962).
(245) D. J. Severn and E. M. Kosower, *Tetrahedron Lett.*, 2119 (1968).
(246) P. M. Maitlis and F. G. A. Stone, *Proc. Chem. Soc.*, 330 (1962).
(247) R. C. Cookson and D. W. Jones, *Proc. Chem. Soc.*, 115 (1963).
(248) L. Watts, J. D. Fitzpatrick and R. Pettit, *J. Am. Chem. Soc.*, **88**, 623 (1966).
(249) G. D. Burt and R. Pettit, *J. Chem. Soc., Chem. Commun.*, 517 (1965).
(250) H. D. Martin and M. Hekman, *Synthesis*, 667 (1973).
(251) J. Meinwald and J. Mioduski, *Tetrahedron Lett.*, 3839 (1974).
(252) J. Meinwald and J. Mioduski, *Tetrahedron Lett.*, 4137 (1974).
(253) J. C. Barborak, L. Watts and R. Pettit, *J. Am. Chem. Soc.*, **88**, 1328 (1966).
(254) L. Brener, J. S. McKennis, and R. Pettit, *Org. Synth.*, **55**, 43 (1976).
(255) E. Vedejs and E. S. C. Wu, *J. Am. Chem. Soc.*, **97**, 4706 (1975).
(256) J. C. Barborak and R. Pettit, *J. Am. Chem. Soc.*, **89**, 3080 (1967).
(257) M. Avram, I. G. Dinulescu, F. Chiraleu, and C. D. Nenitzescu, *Rev. Roum. Chim.*, **18**, 863 (1973).
(258) L. A. Paquette and J. C. Stowell, *J. Am. Chem. Soc.*, **93**, 5735 (1971).
(259) S. Masamune, N. Nakamura, and J. Spadaro, *J. Am. Chem. Soc.*, **97**, 918 (1975).
(260) L. A. Paquette and L. M/ Leichter, *J. Am. Chem. Soc.*, **93**, 5128 (1971).
(261) L. A. Paquette, M. R. Short, and J. F. Kelly, *J. Am. Chem. Soc.*, **93**, 7179 (1971).
(262) T. L. Gilchrist, E. E. Munn, and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1262 (1974).

(263) E. K. G. Schmidt, L. Brener, and R. Pettit, *J. Am. Chem. Soc.*, **92**, 3240 (1970).
(264) E. K. G. Schmidt, *Chem. Ber.*, **108**, 1598 (1975).
(265) L. A. Paquette and L. D. Wise, *J. Am. Chem. Soc.*, **89**, 6659 (1967).
(266) W. Merk and R. Pettit, *J. Am. Chem. Soc.*, **89**, 4787 (1967).
(267) J. Sauer, H. Wiest and A. Mielert, *Chem. Ber.*, **97**, 3183 (1964).
(268) J. Sauer and B. Schroder, *Angew. Chem., Int. Ed. Engl.*, **4**, 711 (1965).
(269) R. H. Grubbs and R. A. Grey, *J. Am. Chem. Soc.*, **95**, 5765 (1973).
(270) E. K. G. Schmidt, *Chem. Ber.*, **108**, 1609 (1975).
(271) J. Ciabattoni and A. E. Feiring, *J. Am. Chem. Soc.*, **94**, 5113 (1972).
(272) E. E. van Tamelen and T. H. Whitesides, *J. Am. Chem. Soc.*, **93**, 6129 (1971).
(273) J. S. McKennis, L. Brener, J. S. Ward, and R. Pettit, *J. Am. Chem. Soc.*, **93**, 4957 (1971).
(274) E. Vedejs, *J. Chem. Soc., Chem. Commun.*, 536 (1971).
(275) P. E. Eaton and S. A. Cerefice, *J. Chem. Soc., Chem. Commun.*, 1494 (1970).
(276) J. Rebek and F. Gavina, *J. Am. Chem. Soc.*, **96**, 7112 (1974).
(277) J. Rebek and F. Gavina, *J. Am. Chem. Soc.*, **97**, 3453 (1975).
(278) C. Kabuto, J. Hayashi, H. Sakurai, and Y. Kitahara, *J. Organomet. Chem.*, **43**, C23 (1972). Similar data for the trans isomer (**72**, R = SiMe$_3$) were also reported by M. D. Rausch, I. Bernal, B. R. Davies, A. Siegel, F. A. Higbie, and G. F. Westover, *J. Coord. Chem.*, 3 149 (1973).
(279) A. I. Gusev, G. G. Aleksandrov, and Yu. T. Struchkov, *Zh. Strukt. Khim.*, **10**, 665 (1969).
(280) A. I. Gusev and Yu. T. Struchkov, *Zh. Strukt. Khim.*, **10**, 515 (1969).
(281) R. E. Davis and R. Pettit, *J. Am. Chem. Soc.*, **92**, 716 (1970).
(282) H. Oberhammer and H. A. Brune, *Z. Naturforsch., Teil A*, **24**, 607 (1969).
(283) E. A. C. Lucken, R. Pozzi, and K. R. Ramaprasad, *J. Mol. Struct.*, **18**, 377 (1973).
(284) G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds", Vol. 2, M. L. H. Green, Ed., 3rd ed, Methuen, London, 1968, pp 68–70.
(285) F. A. Cotton, "Chemical Application of Group Theory", 2nd ed, Wiley, New York, N.Y., 1971, pp 239–241.
(286) S. D. Worley, *J. Chem. Soc., Chem. Commun.*, 980 (1970).
(287) M. J. S. Dewar and S. D. Worley, *J. Chem. Phys.*, **50**, 654 (1969).
(288) C. E. Moore, *Natl. Bur. Stand.* (*U.S.*), *Circ.*, No. 467, 3, 34 (1957).
(289) E. Hedaya, R. D. Miller, D. W. McNeil, P. E. D'Angelo, and P. Schissel, *J. Am. Chem. Soc.*, **91**, 1875 (1969).
(290) H. A. Brune and H. P. Wolff, *Z. Naturforsch., Teil B*, **26**, 68 (1971).
(291) H. P. Fritz, *Adv. Organomet. Chem.*, 1, 239 (1964); H. P. Fritz, Habil. Thesis, University of Munich, 1962.
(292) D. C. Andrews and g. Davison, *J. Organomet. Chem.*, **36**, 349 (1972).
(293) V. T. Aleksanyan and M. N. Nefedova, *Zh. Strukt. Khim.*, **14**, 839 (1973).
(294) D. Andrews and G. Davison, *J. Organomet. Chem.*, **76**, 373 (1974).
(295) H. P. Fritz, *Z. Naturforsch., Teil B*, **16**, 415 (1961).
(296) R. Grubbs, R. Breslow, R. Herber, and S. J. Lippard, *J. Am. Chem. Soc.*, **89**, 6864 (1967).
(297) R. H. Herber, R. B. King, and M. N. Ackermann, *J. Am. Chem. Soc.*, **96**, 5437 (1974).
(298) E. O. Greaves, R. Bruce, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 860 (1967).
(299) H. G. Preston, Jr., and J. C. Davis, Jr., *J. Am. Chem. Soc.*, **88**, 1585 (1966).
(300) H. A. Brune, H. P. Wolff, and H. Hüther, *Chem. Ber.*, **101**, 1485 (1968).
(301) H. A. Brune, H. P. Wolff, and H. Hüther, *Z. Naturforsch., Teil B*, **23**, 1184 (1968).
(302) H. A. Brune, H. Hüther, and H. Hanebeck, *Z. Naturforsch., Teil B*, **26**, 570 (1971).
(303) H. A. Brune, H. Hanebeck, G. Horlbeck, and H. Hüther, *Z. Naturforsch., Teil B*, **29**, 219 (1974).
(304) H. A. Brune and G. Horlbeck, *Z. Naturforsch., Teil B*, **28**, 656 (1973).
(305) P. S. Nielsen, R. S. Hansen, and H. J. Jakobsen, *J. Organomet. Chem.*, **114**, 145 (1976).
(306) C. S. Eschbach, D. Seyferth, and P. C. Reeves, *J. Organomet. Chem.*, **104**, 363 (1976).
(307) C. S. Yannoni, G. P. Ceasar, and B. P. Daily, *J. Am. Chem. Soc.*, **89**, 2833 (1967).
(308) J. W. Emsley and J. C. Lindon, *Mol. Phys.*, **28**, 1373 (1974).
(309) R. B. King and A. Efraty, *Org. Mass Spectrom.*, 3, 1233 (1970).
(310) A. Efraty, M. H. A. Huang, and C. A. Weston; a manuscript describing in detail the primary fragmentations of these complexes under electron-impact conditions and their energetics, is currently under preparation.
(311) R. B. King and A. Efraty, *Org. Mass Spectrom.*, 3, 1227 (1970).
(312) P. H. Li and H. A. McGee, Jr., *J. Chem. Soc., Chem. Commun.*, 592 (1969).
(313) E. Hedaya, I. S. Krull, R. D. Miller, M. E. Kent, P. F. D'Angelo, and P. Schissel, *J. Am. Chem. Soc.*, **91**, 6880 (1969).
(314) E. Hedaya, R. D. Miller, D. W. McNeil, P. F. D'Angelo, and P. Schissel, *J. Am. Chem. Soc.*, **91**, 1875 (1969).
(315) W. J. R. Tyerman, M. Kato, P. Kebarle, S. Masamune, O. P. Strausz, and H. E. Gunning, *J. Chem. Soc., Chem. Commun.*, 497 (1967).
(316) J. Font, S. C. Barton, and O. P. Strausz, *J. Chem. Soc., Chem. Commun.*, 499 (1970).
(317) O. L. Chapman, J. Pacansky, and P. W. Wojtkowski, *J. Chem. Soc., Chem. Commun.*, 681 (1973).
(318) J. D. Black, M. J. Boylan, P. S. Braterman, and W. J. Wallace, *J. Organomet. Chem.*, **63**, C21 (1973).
(319) M. M. Bursey, F. E. Tibbetts, and W. F. Little, *J. Am. Chem. Soc.*, **92**, 1087 (1970).
(320) A. Efraty and P. M. Maitlis, *Tetrahedron Lett.*, 4025 (1966).
(321) D. A. Brown, N. J. Fitzpatrick, and N. J. Mathews, *J. Organomet. Chem.*, **88**, C27 (1975).
(322) D. F. Pollock, Ph.D. Dissertation, McMaster University, Hamilton, Canada, 1969.
(323) U. Krüerke and W. Hübel, *Chem. Ber.*, **94**, 2892 (1961).
(324) E. M. Arnett and J. M. Bollinger, *J. Am. Chem. Soc.*, **86**, 4729 (1964).
(325) T. L. Cairns, V. A. Engelhardt, H. L. Jackson, G. H. Kalb, and J. C. Sauer, *J. Am. Chem. Soc.*, **74**, 5636 (1952).
(326) J. C. Sauer and T. L. Cairns, *J. Am. Chem. Soc.*, **79**, 2659 (1957).
(327) T. J. Bieber, *Chem. Ind.* (*London*), 1126 (1957).
(328) M. Tsutsui and H. Zeiss, *J. Am. Chem. Soc.*, **82**, 6255 (1960).
(329) E. D. Bergmann, "Chemistry of Acetylenes and Related Compounds", Wiley, New York, N.Y., 1948, p 93.
(330) W. Reppe, "Neue Entwicklungen auf dem Gebiete der Chemie des Acetylenes und Kohlenoxyds", Springer, Berlin, 1949, p 68.
(331) G. M. Whitesides and W. J. Ehmann, *J. Am. Chem. Soc.*, **90**, 804 (1968); **91**, 3800 (1969).
(332) G. N. Schrauzer, P. Glockner, and S. Eichler, *Angew. Chem., Int. Ed. Engl.*, 3, 185 (1964).
(333) R. B. King and C. A. Harmon, *J. Am. Chem. Soc.*, **98**, 2409 (1976).
(334) J. T. Bamberg and R. G. Bergman, *J. Am. Chem. Soc.*, **99**, 3173 (1977).
(335) M. B. Stringer and D. Wede, *Tetrahedron Lett.*, 65–68 (1977).
(336) F. A. Kaplan and B. W. Roberts, *J. Am. Chem. Soc.*, **99**, 513 (1977).
(337) F. A. Kaplan and B. W. Roberts, *J. Am. Chem. Soc.*, **99**, 518 (1977).
(338) I. G. Dinulescu, E. G. Georgescu, and M. Avram, *J. Organometal. Chem.*, **127**, 193 (1977).
(339) P. J. Harris, J. A. K. Howard, S. A. R. Knox, R. P. Phillips, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 377 (1976).
(340) R. H. Grubbs and T. A. Pancoast, *J. Am. Chem. Soc.*, **99**, 2382 (1977).
(341) F. I. Carrol, H. H. Seltman, and F. M. Hauser, *Tetrahedron Lett.*, 4237 (1976).
(342) P. L. Bruitt, E. R. Biehl, and P. C. Reeves, *J. Organometal. Chem.*, **134**, 37 (1977).
(343) S. R. Weber and H. H. Brintzinger, *J. Organometal. Chem.*, **127**, 45 (1977).
(344) N. G. Connelly and R. L. Kelly, *J. Organometal. Chem.*, **120**, C16 (1976).
(345) Y. Kobayashi, I. Kumadaki, A. Ohsawa, Y. Hanzawa, M. Honda, and W. Miyashita, *Tetrahedron Lett.*, 1795–1798 (1977).
(346) Y. Kobayashi, I. Kumadaki, A. Ohsawa Y. Hanzawa, H. Hamana, and S. Fujio, *Heterocycles*, **4**, 1833 (1976).
(347) R. N. Warrener, E. E. Nunn, and M. N. Paddon-Row, *Tetrahedron Lett.*, 2639 (1976).
(348) K. Yasufuku and H. Yamazaki, *J. Organometal. Chem.*, **121**, 405 (1976).
(349) K. Yasufuku and H. Yamazaki, *J. Organometal. Chem.*, **127**, 197 (1977).
(350) W. S. Lee and H. H. Brintzinger, *J. Organometal. Chem.*, **127**, 93 (1977).
(351) K. P. C. Vollhardt, *Acc. Chem. Res.*, **10**, 1 (1977).
(352) A. C. Villa, L. Coghi, A. G. Manfredoti, and C. Gustini, *Acta Crystallogr., Sect. B*, **30**, 2101 (1974).
(353) R. B. King and M. N. Ackermann, *J. Organometal. Chem.*, **67**, 431 (1974).
(354) S. Staicu, I. G. Dinulescu, F. Chiraleu, and M. Avram, *J. Organometal. Chem.*, **117**, 385 (1976).
(355) H. Hoberg, R. Krause-Going, and C. Kruger, *Angew Chem., Int. Ed. Engl.*, **16**, 183 (1977).