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Review Paper

Polyolefin Carbonyl Derivatives of Iron, Ruthenium and Osmium

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I. Introduction

Transition metal polyolefin–carbonyl derivatives have been the subject of extensive investigations in the past fifteen years. Three main features may be recognized in the development of topics and scopes related to this field.

First, preparative reactions involving polyolefin metal carbonyls as substrates were exploited for the synthesis of novel and often versatile derivatives based on the easy displacement of the olefin by neutral ligands. The synthetic aspects of these reactions were implemented by kinetic and mechanistic studies.[a] Polyolefin metal carbonyls owed much of their interest also to the activation of reactivity centers in the polyolefin caused by coordination, which made possible its conversion to otherwise inaccessible substituted polyolefin derivatives.

Then there was another upsurge of interest in these derivatives when a peculiar feature of their behaviour was discovered, that is, the fluxional character that most of them display in solution.[b] Investigations in this regard involved structural studies in solution by extensive application of NMR spectroscopy and entailed an impressive amount of crystal and molecular X-ray structure determinations. Mechanistic aspects of fluxional behaviour were also tackled to provide a clearer understanding of the phenomenon.

The latest development of research concerning polyolefin metal carbonyls originated from the application of the Woodward–Hoffmann rules to the rearrangement of unsaturated organic molecules promoted by transition metals.[c] The interest of chemists centered about the way of affecting the course of thermal or photochemical rearrangements of such moieties by the presence of transition metals. As a matter of fact, the mechanism and actual course of a rearrangement appear to be markedly influenced by the intermediacy of metal *d* orbitals.

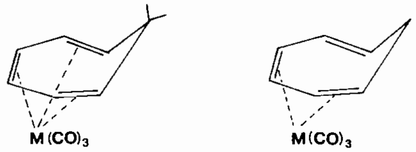
This challenging field of research has both theoretical and practical implications. On one hand, the stabilization of otherwise labile intermediates by metal coordination offers new opportunities to the study of mechanistic pathways. On the other hand, the influence of the metal on reaction courses allows the preparation of novel organic moieties, thereby expanding the frontier of synthetic organic chemistry.

In the light of the ever-increasing interest and importance of this active research topics, we felt it worth while and timely to present a survey of most significant achievements in the field. In this article–review we shall deal with Iron, Ruthenium and Osmium carbonyl derivatives of cyclic polyolefins containing more than six carbon atoms in the ring and at least three carbon–carbon double bonds. In fact, it is with these species that most prominent results were obtained.

II. Preparations and Structures

1. Cycloheptatriene

Cycloheptatriene, C_7H_8, can give two types of complexes: those in which C_7H_8 is bonded to the metal with all the three double bonds, and those in which C_7H_8 is linked to the metal as a butadiene-like unit. Significant examples are the $M(CO)_3(C_7H_8)$ complexes:



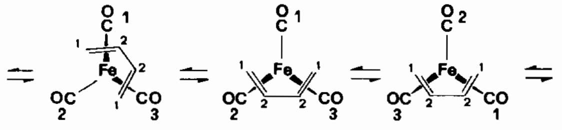
C_7H_8 has a non-planar configuration in its complexes and thus it is hardly justified to consider it as a quasi-aromatic system.[1]

A. Iron Carbonyl Complexes

Cycloheptatriene readily gives two types of complexes of formula $C_7H_8(Fe(CO)_3)_n$ (n = 1, 2) upon coordination to iron carbonyls.

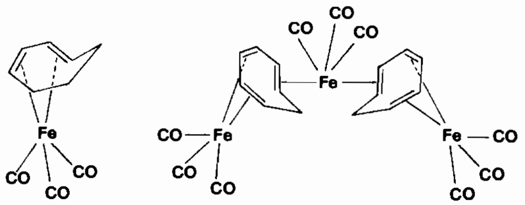
$(C_7H_8)Fe(CO)_3$, a low melting solid prepared by reaction of C_7H_8 with $Fe(CO)_5$ at 110° C for seven days which was previously formulated as $(C_7H_8)Fe(CO)_2$,[2,3] in the i.r. spectrum shows the usual three C=O stretching bands at 2050, 1989 and 1975 cm^{-1} and a medium intensity absorption at 1660 cm^{-1}, attributable to $\nu(C=C)$ of the uncoordinated double bond.[4] Its pmr spectrum is fully consistent with a $Fe(CO)_3$ group bonded to a 1,3-diene unit with an uncoordinated olefinic bond.

^{13}C NMR spectra at room temperature of this and other $(diene)Fe(CO)_3$ complexes show a single peak for the three CO.[5] This finding is not consistent with the square-pyramidal structure of these compounds[6] from which three or at least two peaks should be found. Two resonances in the ratio 2:1 are indeed found at lower temperature. The molecules are fluxional and the simplest way to explain this behaviour is the interchange of the basal and apical CO through a simultaneous rotation of the carbonyl groups and the diene system:[5]



Ia I Ia

If the reaction of C_7H_8 with $Fe(CO)_5$ is carried out at 135–140° C two additional products are obtained:[4]



The formation of the cycloheptadiene iron tricarbonyl complex may involve an iron tricarbonyl hydride intermediate.[7]

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[a] R.J. Angelici, *Organometal. Chem. Rev., 3,* 173 (1968).

[b] F.A. Cotton, *Acc. Chem. Res., 1,* 283 (1968).

[c] J.S. Ward and R. Pettit, *J. Am. Chem. Soc., 93,* 262 (1971); R.H. Grubbs and T.K. Brunk, *ibid., 94,* 2538 (1972).

The compound obtained from the reaction of C_7H_8 with $Fe_2(CO)_9$ is $(C_7H_8)Fe_2(CO)_6$.[8] A similar complex is obtained when 7-methoxy-1,3,5-cycloheptatriene is used. On the basis of i.r. (ν(CO) at 2058, 2015, 1995, 1975, 1960 cm^{-1}), pmr[9] and Mössbauer spectra (two symmetric peaks of equal width at half height) this complex has been suggested to have a bis-π-allyl structure.[8]

The pmr spectrum is typical of a symmetric species. Also, no change was observed at –100° C. This suggests no fluxional behaviour, at variance with the spectra of several other complexes of the type $(polyolefin)M_2(CO)_6$ (M = Fe, Ru).[10]

The presence of an approximate plane of symmetry passing through the Fe_1–Fe_2 and C_4–C_5 bonds and C_1 is confirmed by an X-ray structural analysis (Figure 1):[9]

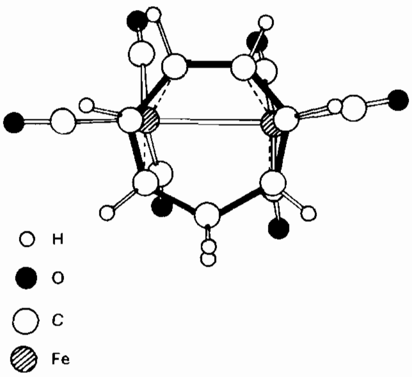


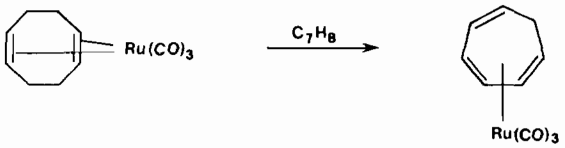
Figure 1. A view of the X-ray molecular structure of $(C_7H_8)Fe_2(CO)_6$ showing the symmetry plane bisecting the Fe_1–Fe_2 and C_4–C_5 bonds and passing through C_1.

This situation fits well in the anticipated bis-π-allyl configuration of such a complex. The two ends of the $Fe_2(CO)_6$ "sawhorse" are twisted by 9° about the Fe_1–Fe_2 axis, and by 8° about the axis normal to the Fe_1–Fe_2 bond and to the plane of the organic unit. However, there is likely to be some degree of electronic coupling between the two allyl groups. The symmetric configuration is also confirmed by the proton decoupled ^{13}C nmr spectrum both in the polyolefin and in the metal carbonyl region (three peaks for the three carbon–carbon pairs C_4–C_5, C_3–C_6, C_2–C_7, two peaks of *ca.* 1:2 relative intensity for the three carbonyl pairs, with accidental superposition of two pairs).[11]

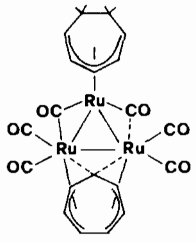
B. Ruthenium Carbonyl Complexes

Complexes of ruthenium carbonyls with cycloheptatriene have received less attention than their iron analogs.

A very simple route to prepare (1-4η-cycloheptatriene)rutheniumtricarbonyl involves ligand displacement from 1,5-cyclooctadiene ruthenium tricarbonyl:[12]



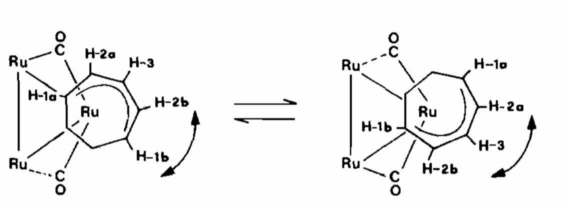
The same compound is probably the first product in the reaction of C_7H_8 with $Ru_3(CO)_{12}$ in heptane at reflux. In this case, however, further reactions with C_7H_8 and ruthenium carbonyls occur to give a number of other complexes.[13] Some of these, $(C_7H_{10})Ru(CO)_3$ and $(C_7H_8)Ru_2(CO)_6$, are analogous to the iron complexes and probably have the same configurations. Two complexes which have no iron counterparts, $(C_7H_8)Ru(CO)_2$ and $(C_7H_7)(C_7H_9)Ru_3(CO)_6$, have been also isolated. The trinuclear complex, which is the major product in the reaction (62% yield), has been fully characterized by an X-ray study:



The ^1H nmr spectrum at room temperature shows a single peak for the seven protons of the C_7H_7 ring (τ = 6.86) which is fluxional, and signals attributable to a symmetrically bonded 1-5η-C_7H_9 ring (τ = 4.80 (1,H_3), 5.15 (2,H_2), 5.95 (2,H_1), 7.90(2) and 8.30 (2,H_4 and H_5)).

A low temperature ^1H nmr study has shown that also the C_7H_9 exhibits a fluxional behaviour.[14] While the resonance corresponding to H_3 remains unchanged on lowering the temperature, both the signals corresponding to H_2 and H_1 collapse and then split.

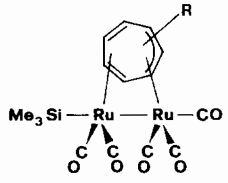
The C_7H_7 ring is still fluxional at –94° C. The proposed interpretation of the behaviour of the C_7H_9 ring in this molecule is a rotation of the C_7H_9 ring relative to the Ru_3 triangle:



It is likely that also an exchange of the bridging carbonyls occurs.

2. Substituted Cycloheptatrienes

The reaction between $[Ru(CO)_4(SiMe_3)]_2$ and cycloheptatriene and its 1-substituted derivatives is a general method for the preparation of the complexes $(C_7H_6R)Ru_2(CO)_5(SiMe_3)$:[15]



R = H, Me, Ph, C_6F_5

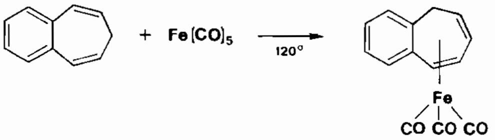
These complexes are fluxional and the presence of R can modify greatly the energy of the process. Thus, when R = H the seven protons of the C_7H_7 ring (τ = 6.14) remain a singlet at –90° C whereas when R = Ph the ^1H nmr spectrum is temperature-dependent between +60° and –90° C.

A minor product of the above reaction involves transfer of one $SiMe_3$ group from Ru to the ring. The X-ray crystal structure of the complex shows that the $SiMe_3$ group is linked to a terminal carbon of the allyl moiety. This does not imply, however, that in the other substituted complexes the R group is located at the same position.

Some complexes of substituted cycloheptatrienes have been prepared for special purposes, such as the obtainment of tropylium complexes or the stabilization of reactive metal carbonyl derivatives by addition of an electron-withdrawing substituent in the 1-position of cycloheptatriene.

Thus, the $Fe(CO)_3$ complexes of 1-methoxy-cycloheptatriene and of a number of 1-substituted cycloheptatrienes have been described.[16,17] Since their characteristics are not drastically changed by the substitution, there is no need to discuss these systems, which will be only described in the section relative to the compounds for which they have been prepared.

The reaction of 4,5-benzo-cycloheptatriene with iron pentacarbonyl involves isomerization of the polyolefin promoted by the strong dienophile $Fe(CO)_3$.[18] Further details will be found in the appropriate section:



A. Tropone Derivatives

Tropone iron tricarbonyl, $(\eta^4\text{-}C_7H_6O)Fe(CO)_3$ was originally prepared either through the reaction of acetylene with $Fe_2(CO)_9$ under pressure[19] or by the direct reaction of tropone with $Fe_3(CO)_{12}$.[20] A better yield is obtained by the use of tropone and $Fe_2(CO)_9$.[21]

This complex should exist in two optically active forms, but resolution was never achieved. Two forms which differ only in melting point (63.5–64.5 and 83–84° C) have been reported.[19,22] An X-ray crystal structure determination of the low-melting form shows that the iron is bonded to a normal butadiene unit.[23] The organic unit is not planar and is quite similar to that found in the 2,4,6-phenyl-substituted complex in which the plane of C4, C5, C6, C7 makes an angle of 139° with the C1, C2, C3 plane[24] (Figure 2):

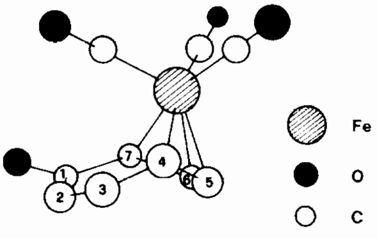
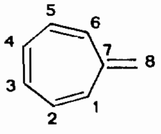


Figure 2. Molecular structure of $(\eta^4\text{-}C_7H_6O)Fe(CO)_3$.

B. Heptafulvene Derivatives

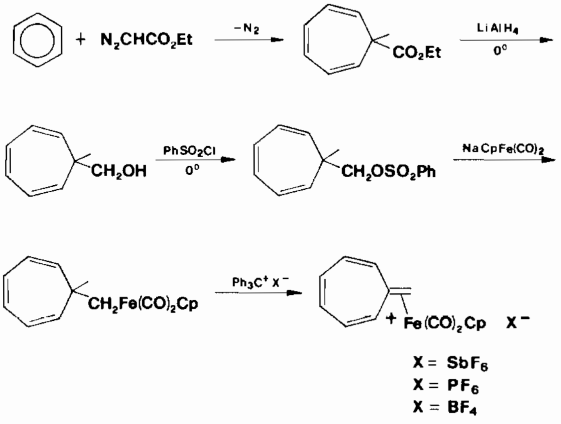
Although heptafulvenes are not usually isolable at room temperature owing to their tendency to polymerize or react with oxygen, they can be stabilized by coordination to metal carbonyls:



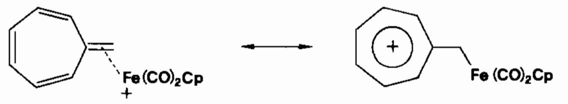
I

In principle, metal coordination to heptafulvene may involve carbons 7,8 as well as the carbons of the cycloheptatriene ring. Both types of complexes have been reported.

The synthesis of $(\eta^2\text{-}7,8\text{-heptafulvene})(\eta^5\text{-cyclopentadienyl})$iron dicarbonyl cation has been accomplished by the following route:[25,26]



This complex is best represented by a participation of two resonance structures

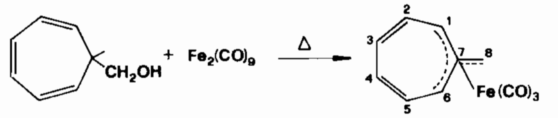


As a matter of fact, the increase in CO stretching frequencies (2033 and 1986 cm^{-1}, $\Delta\nu = 25$; 33) and downfield shift of the cyclopentadienyl protons ($\tau = 4.73$; $\Delta\tau = 0.60$), which are usually observed upon conversion of η^1-alkyl to η^2-alkene iron dicarbonyl complexes occur to a lesser extent (usually $\Delta\nu = 75$; 100; $\Delta\tau = 1.1$–1.3).

Further, the resonances of the other protons in the ring have an intermediate value ($\tau = 2.2$) between the pure delocalized systems (heptafulvene, for instance, has $\tau = 4.09$) and the aromatic systems (tropylium has $\tau = 0.86$). The CH_2 (carbon 8) signal is at τ 6.51.[26]

X-ray analysis favours the tropylium configuration (Fe–C_8 = 2.16 Å ± 0.05, Fe–C_7 = 3.00 Å ± 0.05, C_7 FeC_8 angle = 109°), confirming that the –$Fe(CO)_2(C_5H_5)$ group is bonded almost exclusively to carbon 8.[27]

Another heptafulvene complex can be obtained through the reaction of 7-cycloheptatrienyl-methanol with diiron nonacarbonyl and distillation of the crude product at 115° C:[25,26]



The above configuration is consistent with spectroscopic data such as mass spectra[26] (parent peak at m/e 244), i.r. (ν(CO) at 2049 and 1980 cm^{-1} in CH_2Cl_2)[25,26,28] and pmr ($H_{2,3,4,5} = \tau\,4.13$; $H_{1,6}$ = 6.30 and $H_{8,8'}$ = 8.60, in CS_2) and was confirmed by an X-ray study.[29] The molecule has an approximate C_s symmetry and the $Fe(CO)_3$ group and the trimethylenemethane unit are mutually staggered (Figure 3):

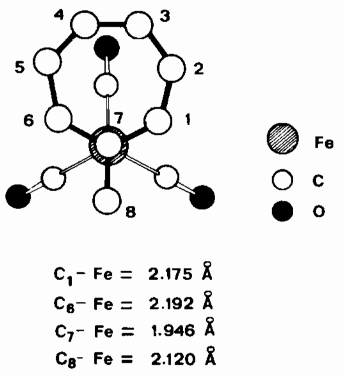
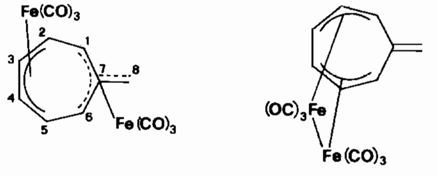


Figure 3. Molecular structure of (η^4-1,6,7,8-heptafulvene) iron tricarbonyl.

Coordination of the metal group induces non-planarity in C_7 and C_8 which lie 0.365 and 0.231 Å above the plane defined by the other carbons of the ligand.

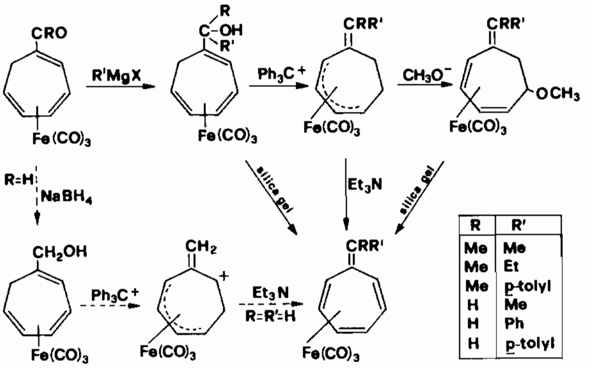
Further reaction of this *tetrahapto*-1,6,7,8 complex with $Fe_2(CO)_9$ allows coordination of a further Fe $(CO)_3$ group in the diene position:



a b

The presence of only two ν(CO) at 2040 and 1980 cm^{-1} rules out the possibility of an Fe–Fe bond. The pmr spectrum displays the characteristic peaks of coordinated diene at $\tau = 4.0$ (inner protons) and $\tau = 8.4$ (outer protons).

Complexes of heptafulvene and 8-substituted heptafulvenes[30a,b] have been prepared in which the metal carbonyl group coordinates only to the olefinic carbons of the ring. The preparative routes are very similar and are condensed in the following scheme:



R	R'
Me	Me
Me	Et
Me	p-tolyl
H	Me
H	Ph
H	p-tolyl

The unsubstituted heptafulvene complex has been obtained only by the route indicated by a dotted line.[30a] Its pmr spectrum has been confirmed by deuteration in the exocyclic methylene.

The solvent seems to have an important role in the dehydrogenation of the alcohol with triethylamine, since the above complex is only obtained in dichloromethane. In diethyl ether, a dimeric complex[30b] is isolated which shows an unexpected structure (Figure 4):[31]

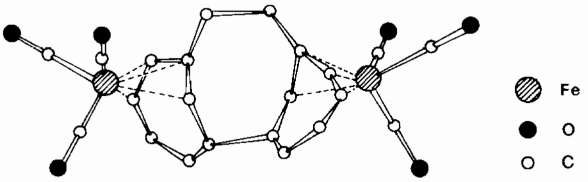
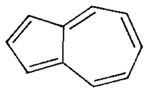


Figure 4. Molecular structure of (η^4-1,2,3,15;η^4-11,12,13,16-tricyclo[9.4.1.1^{1,6}]hexadecahexaene)diiron hexacarbonyl.

Another convenient route to these complexes which can be considered as the key intermediates to heptafulvene complexes is the reaction of (BDA)$Fe(CO)_3$ (BDA = benzylideneacetone) with 7-cycloheptatrienylmethanol.[32]

3. *Azulene and Substituted Azulenes*

The hydrocarbon bicyclo[5.3.0]decapentaene is better known by its trivial name azulene:

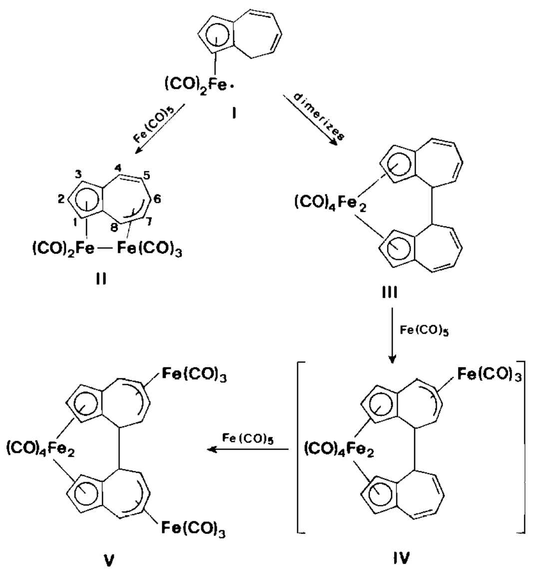


Its ranking in this review as a derivative of cycloheptatriene is due to the presence of its seven-member ring. Its reactivity, however, and its metal complexes, owing to the availability of coordination to both the condensed rings, place azulene in a particular position among substituted cycloheptatrienes.

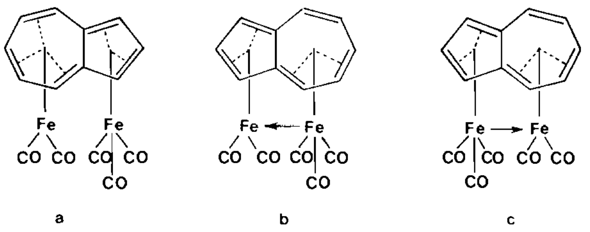
Some of the previously reported azulene complexes, which were investigated by pmr, i.r. and magnetic moment measurements[33] have been reformulated on the basis of X-ray crystal and molecular structure determinations.[34]

Although several complexes of azulene are dimers through a C–C bond between two azulenyl ligands and, therefore, should be discussed in the section dealing with rearrangements of cyclic polyolefin metal derivatives, they are described here together, since they are strictly related in their formation.

The reaction of azulene and iron carbonyls such as $Fe(CO)_5$, $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ gives a series of complexes[2,33,35] which can be rationalized on the basis of the following scheme, as derived from a pseudo-η^5-cycloazulenyl iron dicarbonyl species (I):[36]



The pmr spectrum of II (non equivalence of H_1, H_8, H_7 with H_3, H_4, H_5) shows that the complex does not contain any plane of symmetry passing through C_2 and C_6. The dipole moment measurements indicate a *cis*-configuration of the metal carbonyl groups for II and so three structures were originally proposed:[33]



The above configurations contain localized double bonds whereas an X-ray investigation has shown a delocalization in the cyclopentadienyl ring (Figure 5):[37]

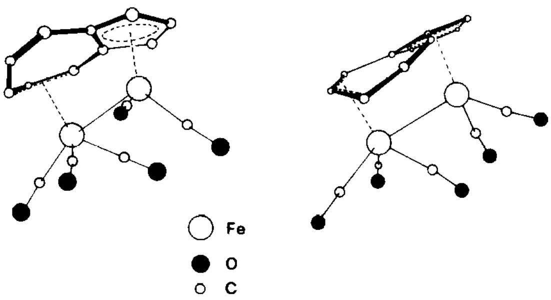


Figure 5. Molecular structure of $(C_{10}H_8)Fe_2(CO)_5$.

There is a metal–metal bond linking an $Fe(CO)_2$ and an $Fe(CO)_3$ group. The $Fe(CO)_2$ group is bonded to a cyclopentadienyl ring and the $Fe(CO)_3$ one to an allyl unit of the larger ring.

The azulene ligand is not planar and a bending of the seven-member ring towards the $Fe(CO)_3$ group is evident. Further, the π-allyl bond is not symmetric (C_6–C_7 = 1.432 Å, C_7–C_8 = 1.391 Å).

The above results suggest that symmetric substitution should give enantiomeric forms and unsymmetrical substitution geometrical isomers.[33] The (guaiazulene) $Fe_2(CO)_5$ complex has been separated in two geometrical isomers which differ in melting point and pmr spectra.

Other substituted (azulene)$Fe_2(CO)_5$ complexes have been reported, namely the 2,4-dideutero-, 4-methyl- and 4,6,8-trymethylazulene complexes.

Complex III has been isolated.[35] So far complex IV has not been isolated but it represents a possible intermediate in the above scheme, since V has been prepared. The complex, previously formulated tentatively as $(C_{10}H_8)Fe_5(CO)_{13}$[33] is actually $(C_{10}H_8)_2Fe_4(CO)_{10}C_2H_4Cl_2$[36,38] (Figure 6):

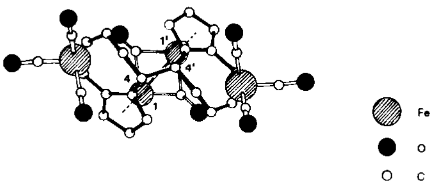


Figure 6. Molecular structure of $(C_{10}H_8)_2Fe_4(CO)_{10}$. Terminal carbonyl groups lie almost immediately under Fe_1 and $Fe_{1'}$.

The two azulene units are linked by a 4–4' endo bond (endo as referred to the $Fe_2(CO)_4$ group which is coordinated to both five-member rings). The other two $Fe(CO)_3$ groups are coordinated to the butadiene units of the seven-member rings. These latter rings are severely distorted. The variety of complexes between the azulene ligand and iron carbonyls suggests an important role of the reaction conditions which favour the formation of one or another complex. However, within the same triad of metals different complexes can be obtained, thereby stressing the added importance of the metal in such reactions. The ruthenium analogs of the above described iron carbonyl complexes of azulene have never been reported. Reaction of $Ru_3(CO)_{12}$ with azulene, or substituted azulene, yields some cluster compounds. Two of these, (4,6,8-trimethylazulene)$Ru_4(CO)_9$ (VI),[39–41] and (azulene) $Ru_3(CO)_7$ (VII)[42,43] have been fully characterized by X-ray crystal and molecular determinations. Although VI can have a different crystal structure (monoclinic and triclinic) these modifications are not distinguishable as far as the molecular structure is concerned. VI has an approximate C_s symmetry with a plane passing through Ru(1), Ru(4) and the midpoint of the Ru(2)–Ru(3) bond (Figure 7).[39–41]

The ruthenium cluster bears a tetrahedral configuration and Ru(1,2,3) are bonded together and to two carbonyls. Ru(4) is linked to the remaining ruthenium atoms and to three CO groups.

The bonding to the organic unit is not simple and a good approximation can be given by two-electron three-center bonds over Ru(1)–C(10)–Ru(2), Ru (1)–C(9)–Ru(3) and Ru(2)–C(6)–Ru(3). The Ru (4) atom is not bonded to the azulene derivative. In the (azulene)$Ru_3(CO)_7$ complex,[42,43] which can be considered as an intermediate to complex VI, the $Ru_3(CO)_7$ cluster is triangular (Figure 8) with the Ru(1) bonded to the five-member ring of the ligand and the other two Ru atoms to the seven-member ring. All the ruthenium atoms bear two terminal CO (i.r. 2050, 2005, 1976, 1958 cm^{-1}), whereas a bridging CO (i.r. 1764 cm^{-1}) links Ru(2) and Ru(3).

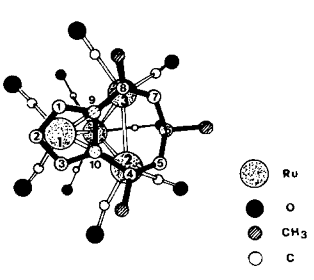


Figure 7. Molecular structure of (4,6,8-trimethylazulene)Ru_4 $(CO)_9$ projected onto the C(8)–C(9)–C(10)–C(4) plane.

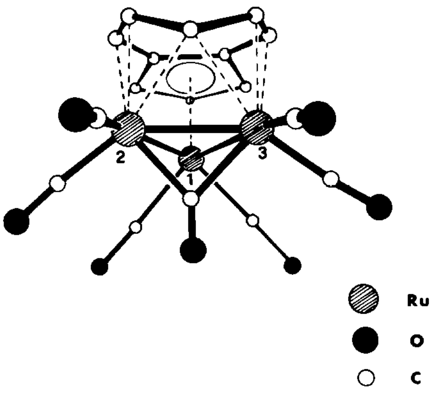
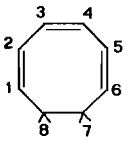


Figure 8. Molecular structure of (azulene)$Ru_3(CO)_7$.

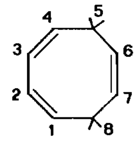
Substitution of bridging CO with a $Ru(CO)_3$ group, together with a reorganization of the metal-azulene bond, can give VI.

4. *Cyclooctatriene*

Two isomers of cyclooctatriene (C_8H_{10}) are known and both can give complexes with metal ions or metal derivatives:



a

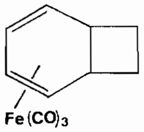


b

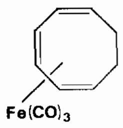
The organometallic chemistry of C_8H_{10} was developed along with that of C_7H_8 and many complexes are of the same type since chemical and physical properties do not differ much among them.

The important difference of this polyolefin is the impossibility of gaining an aromatic stabilization by loss of hydrogen. Thus, no complexes of a planar ligand derived from C_8H_{10} are known, and complexes of the $C_8H_9^+$ cation (homotropylium) are not usually derived from a hydride abstraction from the C_8H_{10} unit but from protonation of cyclooctatetraene.[44]

Reaction of C_8H_{10} with $Fe(CO)_5$ in high boiling solvents gives $(C_8H_{10})Fe(CO)_3$ (I). When C_8H_{10} is reacted under milder conditions with $Fe_3(CO)_{12}$ another $(C_8H_{10})Fe(CO)_3$ complex is obtained (II). Reaction of I with $Fe(CO)_5$ gives II:



I



II

The same reaction in the absence of $Fe(CO)_5$ has been studied kinetically (see further).

Spectroscopic evidence and chemical reactivity agree with the formulation of I and II as the metal derivatives of bicyclo[4.2.0]octa-2,4-diene and 1,3,5-cyclooctatriene respectively.[45–47]

Another complex of iron with C_8H_{10} can be obtained in a low yield from C_8H_{10} and $Fe_3(CO)_{12}$ in refluxing benzene, namely 1,3,5-cyclooctatrienediironhexacarbonyl.[20] The yield can be improved up to 30% by reaction of C_8H_{10} with $Fe_2(CO)_9$ in ether at room temperature.[48]

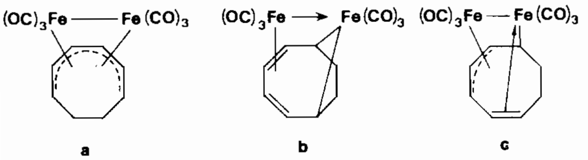


Figure 9. Proposed configurations of $(C_8H_{10})Fe_2(CO)_6$.

For $(C_8H_{10})Fe_2(CO)_6$ the structure a (Figure 9) was originally proposed[20], then b was preferred on the basis of Mössbauer absorption spectra which give apparently equivalent iron atoms.[8] The true structure was, however, c as determined by an X-ray investigation.[49]

The structure of *cis*(1,2,6-*trihapto*-3,4,5-*trihapto*) 1,3,5-cyclooctatrienediironhexacarbonyl in solution has been studied by variable temperature pmr[50] and the results suggest that the fluxional behaviour of the molecule is due to an oscillatory motion between the enantiomorphs *c* and *d* either directly or through a symmetric structure, *a* or *b* (Figure 10):

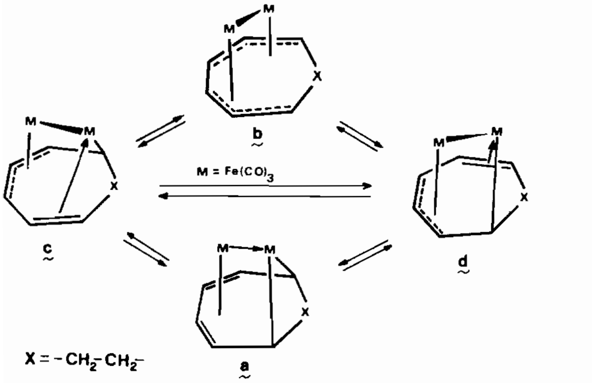
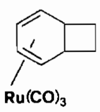
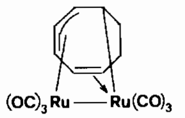


Figure 10. Mechanism of fluxional behaviour in $(C_8H_{10})Fe_2(CO)_6$.

The corresponding complexes of ruthenium with cyclooctatriene have been recently reported. While (η^4-bicyclo[4.2.0]octa-2,4-diene)rutheniumtricarbonyl (I) has been obtained by ligand displacement from (cyclo-octa-1,5-diene)$Ru(CO)_3$ with cycloocta-1,3,5-triene[12] (C_8H_{10}), the reaction of $Ru_3(CO)_{12}$ with C_8H_{10} in boiling heptane gives also (η^6-cyclooctatriene)hexacarbonyldiruthenium (Ru–Ru) (II)[50a]. The



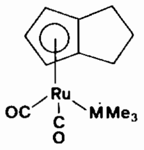
I



II

spectroscopic features of these complexes are very similar to those of the analogous iron complexes[45–47, 50]. The $Ru_2(CO)_6$ derivative shows a temperature dependent pmr spectrum which can be explained in terms of interconversion of its enantiomeric forms[50a] as for the iron analog. Calculations of the free activation energy for the two fluxional processes have established that the energy barrier is higher for the ruthenium compound.

The same ruthenium complexes can been obtained by reaction of $[Ru(MMe_3)_2(CO)_4]$ and $[RuMMe_3(CO)_4]_2$ (M = Si) with C_8H_{10}. In addition, a tetrahydropentalenyl complex (III)



III

is obtained: when M = Ge the cleavage of the Ru–M bond is more difficult and tetrahydropentalenyl complexes (M = Ge) become the major products.

5. *Cyclooctatetraene (COT)*

An important series of COT metal complexes is that containing only carbon monoxide as the additional ligand. We can divide this class of complexes in four types, namely: $(COT)M(CO)_3$, $(COT)M_2(CO)_5$, $(COT)M_2(CO)_6$ and $(COT)_xM_y(CO)_z$.

One peculiar feature of most of these COT metal carbonyl complexes is their "fluxionality" in solution which has recently been found also in the solid state at least for some compounds (see further). The fluxional behaviour will be discussed for at least one compound of each type.

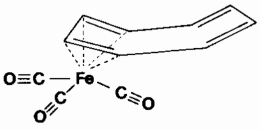
Usually the reaction of COT with a metal carbonyl, even under very mild conditions, gives a number of complexes that depends on the reaction conditions.

Thus, in almost every case chromatography on alumina or silica gel columns is required. Recently very mild absorbers like Florisil have been successfully used for unstable complexes. Separation of the various components of the reaction mixture is sometimes difficult, since a balance between higher selectivity and decomposition due to high activity of the absorber must be achieved. Further, purification of products is usually performed by sublimation and/or by crystallization.

A. Complexes of Type (COT)M(CO)$_3$

This group comprehends those compounds which require four π electrons from COT. The most important complex of this type is (COT)Fe(CO)$_3$ which is very likely to be one of the most studied organometallic compounds since its discovery in 1959.[51–53] (COT)Fe(CO)$_3$ is formed as a major product in the reaction of COT with Fe(CO)$_5$, Fe$_2$(CO)$_9$, or Fe$_3$(CO)$_{12}$. Yields as high as 87% were reported by the use of Stone and Manuel's[3,52] procedure.[54]

At least two structures in the solid state were proposed at the beginning, based on infrared studies[3,51–53] and molecular orbital calculations.[55,56] The controversy arose from the pmr spectrum which shows only one peak. One suggestion was that the complex had a planar COT ring.[3,53,55] Supporting this interpretation was the absence of the C=C stretchings in the i.r. and the lack of evidence of any free double bonds in the chemical reactions. The structure was elucidated by X-ray crystallography[57,58] and it was found to have the Fe(CO)$_3$ group bonded to a butadiene-like residue of the COT molecule, at least in the crystal:



Accurate infrared and Raman spectra later supported this structure.[59] I.r. spectra both in the solid and in solution are comparable (Table I); however, it should be pointed out that the time scale required to obtain equivalence in the i.r. spectra is much higher than that of nmr equivalence.

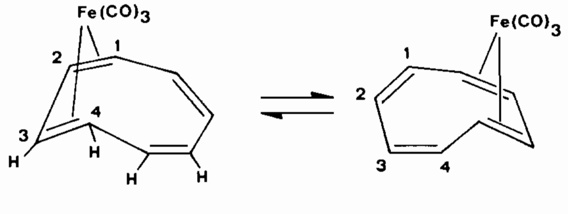
The Fe(CO)$_3$ group is in a C$_s$ symmetry group since there is splitting of the *e*-class CO vibration (1993 and 1976 cm^{-1}). The band at 2061 cm^{-1} is clearly due to an a_1 CO stretching. These data correspond with the X-ray study which indicates a small dissymmetry in the Fe(CO)$_3$ group.[58] However, it is not possible, from i.r. data, to rule out the possibility of a reduced rotation of the Fe(CO)$_3$ group.[59]

TABLE I. Descriptive Assignments of Frequencies of (COT) Fe(CO)$_3$.[59]

Absorptions, cm^{-1}	Descriptive Assignment
3075 3040 3022	CH stretch
2061 1993 1976	CO stretch
1562	Sym C=C stretch
1420	C=C stretch
1460	C=C stretch
1431 1419	Ring deformation
1400–1100	CH deformation
750–500	Fe–C–O angle bending
475–350	Fe–CO stretch
404	Ring tilt
330	Ring metal stretch
137, 100	C–Fe–C angle bending

Although the X-ray crystal structure resolved unequivocally the problem of the configuration in the solid state, a great many attempts to resolve the configuration in solution were carried out by a combination of i.r. and pmr studies. Therefore, the suggestion of a complete equivalence of the eight carbon atoms in a delocalized planar configuration of COT,[3,52,55,56] which might possibly be supported by the first low-temperature pmr study on (COT)Fe(CO)$_3$[60–62] (no broadening down to –60° C), proved to be incorrect. In fact at a lower temperature a neat change in the peak of the pmr[63–65] spectrum is observed, thus ruling out, albeit not completely, the formulation as a 1,5-bonded tub model.[51,64] The 1,5-bonded tub COT should have two distinct sharp peaks in the "frozen" spectrum, corresponding to the four protons of uncomplexed C=C and to the other four protons of the bonded 1,5 C=C double bonds. Arguments favouring this configuration[64] were based on the similarity of i.r. spectra in the C–H stretching region with known compounds of this configuration, and on the assumption that the two broad peaks in the pmr spectrum at –150° C might not be those of the limiting spectrum.

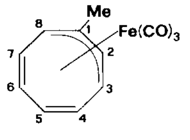
At present, however, every controversy has been settled by the experiments done on (CH$_3$COT)Fe(CO)$_3$,[66] supported by the pmr spectra of (CH$_2$DC$_8$HD$_7$)Fe(CO)$_3$.[67] The previous mechanism[65] suggested to rationalize the pmr spectrum, *i.e.*



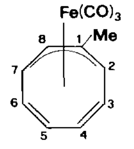
Ia Ib

was shown to be incorrect[66] since it should give a sharper peak, corresponding to the four protons of the C=C bonded to Fe(CO)$_3$.

The mechanism which was derived for (MeCOT) Fe(CO)$_3$ is very likely the same as the one operating in (COT)Fe(CO)$_3$. The following values were calculated for two valency tautomers (IIa and IIb) from plausible chemical shifts,



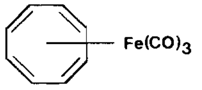
IIa



IIb

and agree fully with experimental results (Table II).

The spectrum at −145° C is given by the "frozen" IIa and IIb configurations, whereas at room temperature the observed chemical shifts are the average of those of IIa and IIb. Similar results were obtained by comparing the room temperature pmr spectra of two disubstituted Fe(CO)$_3$ complexes with the low temperature (−155° C) spectrum of (COT)Fe(CO)$_3$[54] (see Figure 11):



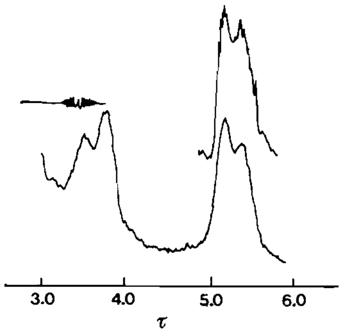


Figure 11. Spin decoupling of the −155° C pmr spectrum of (C$_8$H$_8$)Fe(CO)$_3$ in mixed Freon solvents.

Particularly, at −155° C four resonances appear at 5.22 (H$_{1,8}$), 5.45(H$_{2,7}$), 3.55 and 3.81 (H$_{3,4,5,6}$), thus confirming the 1,3-diene configuration of the complex at low temperature. A comparison with pmr spectra of known 1,3-diene complexes, together with Mössbauer data, completely support this structure.

The fluxional behaviour of (η^4-C$_8$H$_8$)Fe(CO)$_3$ has been confirmed by a ^{13}C nmr study at variable temperature. At room temperature only one single peak is found in the CO region but at temperatures lower than −120° C the carbonyl signal is split into two peaks (intensity ratio 1:2).[68] Since rate constants calculated through simulated spectra for the organic carbons agree with previously reported constants derived from pmr spectra, but are significantly lower than those calculated through simulation of carbonyl signals, the occurrence of an independent carbonyl exchange process is suggested.

The analogous ruthenium complex (η^4-C$_8$H$_8$)Ru (CO)$_3$[69–71] has been fully analyzed in its physicochemical properties and a detailed variable temperature pmr study shows that it has a fluxional behaviour similar to that of the iron tricarbonyl complex but with a somewhat slower rate. Thus, the limiting spectrum at −128° C,[72] unchanged down to −147° C, was recorded. The configuration in the frozen solution corresponds totally to the X-ray crystal structure (Figure 12):[73]

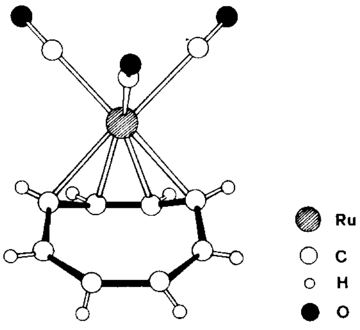


Figure 12. Molecular structure of (η^4-C$_8$H$_8$)Ru(CO)$_3$.

The pmr spectrum at various temperatures will be described in details as an example of the fluxional

TABLE II. Predicted[66] and Experimental Chemical Shifts for IIa and IIb.

Positions	Chemical Shift at −145°C		Average IIa/IIb Ratio (intensity) at Room Temperature	Found
	IIa	IIb		
2 and 8	5.4, 5.4	5.4, 5.4	5.4(2)	5.5
3 and 7	5.4, 4.1	4.1, 5.4	4.75(2)	4.92(2)
4 and 6	4.1, 4.1	4.1, 4.1	4.1 } (3)	
5	4.1	4.1	4.1	

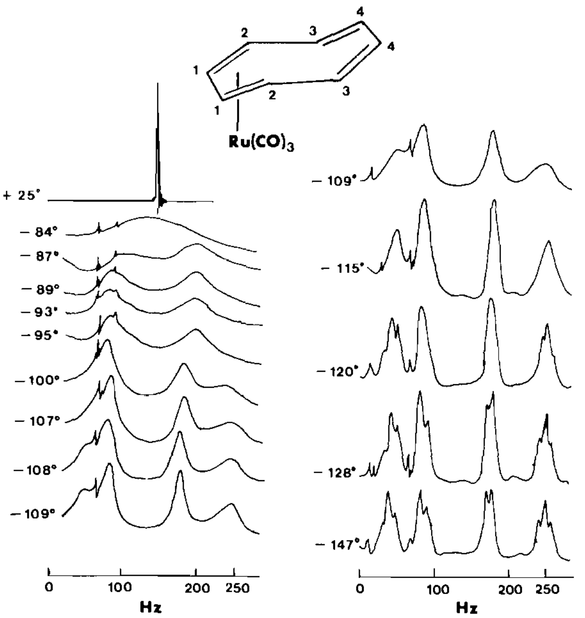


Figure 13. Variable temperature pmr spectra of $(C_8H_8)Ru(CO)_3$.

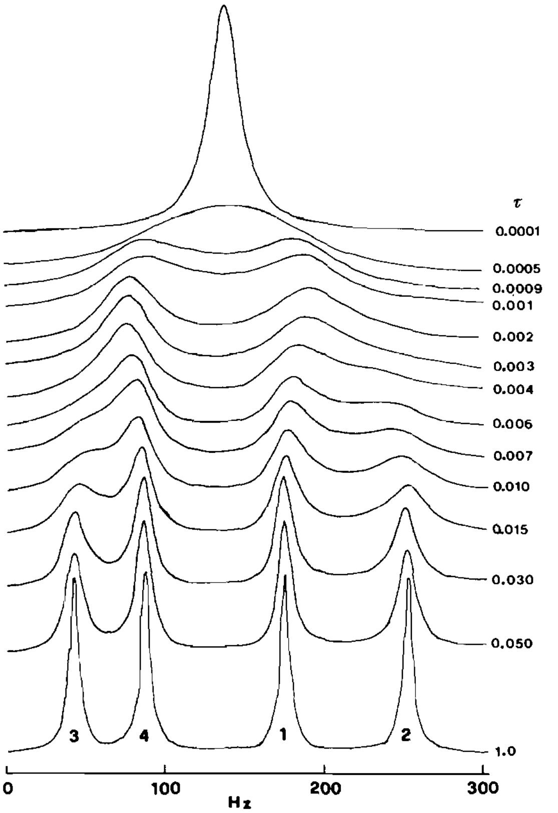


Figure 14. Simulated spectrum for protons in $(C_8H_8)Ru(CO)_3$ as a function of the mean exchange lifetime, τ (sec), between successive 1,2 shifts.

behaviour of $(COT)M(CO)_3$ (M = Fe, Ru, Os) (Figure 13) together with the body of experimental observations, which allow a complete understanding of the mechanism involved in the rearrangement.

The peaks centered at 42, 87, 174 and 251 Hz can easily be ascribed to the 3, 4, 1, 2 protons. In principle several mechanisms might be operating in the rearrangement, namely a) 1,2 shift, b) 1,3 shift, c) 1,4 shift, d) 1,5 shift, e) random shift.

The 1,5 shift can immediately be ruled out by the pmr spectrum at room temperature (one singlet). If we consider the full set of variable temperature pmr spectra of $(COT)Ru(CO)_3$ the 1,4 shift also can be eliminated since it should result in the resonance due to protons 1 collapsing prior to that of protons 2, in contrast with the experimental evidence. Further, the random shift is eliminated since the collapse of every peak in that case should occur at approximately the same rate. Therefore only the 1,2 or 1,3 shift can be responsible for the experimental observations. That the 1,2 shift is indeed almost the only pathway is demonstrated by comparing the experimental spectra, using a computer simulated spectrum obtained by calculating the line shapes for the two possible mechanisms (Figure 14). The line shape analysis was extended also to the other shifts.[74]

$(COT)Os(CO)_3$ also is known.[75] Its formation, however, is somewhat different from the analogous iron and ruthenium complexes. Irradiation of a benzene solution of COT and $Os_3(CO)_{12}$ gave a yellow solid which shows a pmr independent of temperature[76] (Figure 15):

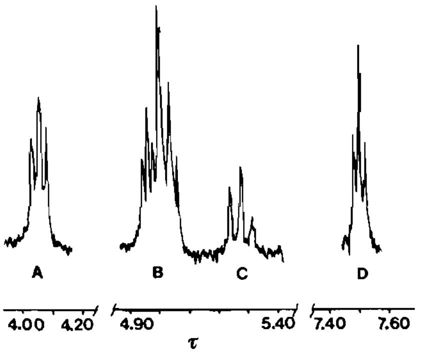
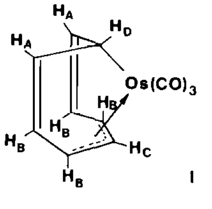
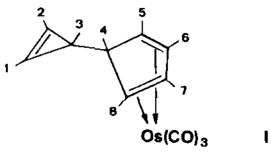


Figure 15. Pmr spectrum of $(C_8H_8)Os(CO)_3$.

On the basis of decoupling experiments and chemical shift two structures were proposed[75–77]:

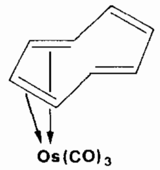


I



II

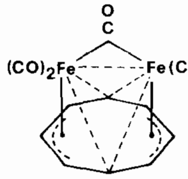
Structure II is, however, unlikely since the reactivity of this complex is somewhat different from that expected for a diene bonded species. The complex easily rearranges to the usual (COT)M(CO)$_3$ derivative on heating[77] (one pmr signal at $\tau = 4.78$):



B. *Complexes of the Type (COT)M$_2$(CO)$_5$*

The iron [78] and ruthenium[71] derivatives of the type (COT)M$_2$(CO)$_5$ have been reported. Although there is a large difference in colour (iron complex is black, ruthenium complex orange) all the spectroscopic features are comparable. The i.r. spectra show the presence for both compounds of a band at $\cong 1800\ \mathrm{cm}^{-1}$, characteristic of a bridging CO. The pmr spectra suggest a fluxional configuration since only one sharp peak at $\cong \tau\ 5.3$ is observed. The "frozen" spectrum, however, could not be realized due to the very low solubility of these compounds. At –80° C no change in the pmr spectra could be noticed. On the basis of the above evidence the solid structure *A* was proposed[78] (Figure 16) which in solution should be converted with a rapid rotation to *B* and other equivalent configurations. This should account for the equivalence of all eight protons.

The X-ray crystal structure of (COT)Fe$_2$(CO)$_5$ has been determined and is rather surprising[79]:



The analogous (COT)Ru$_2$(CO)$_5$ has very likely the same crystal structure.[74]

Reaction of (COT)Fe(CO)$_3$ with Ru$_3$(CO)$_{12}$ in boiling toluene yields a mixed Ru–Fe bonded complex. Analytical and spectroscopic data support a similar formulation as the above described (COT)M$_2$(CO)$_5$ (M = Fe or Ru) complexes.[80] (COT)FeRu(CO)$_5$ is also a fluxional molecule.

C. *Complexes of the Type (COT)M$_2$(CO)$_6$*

As for the (COT)M$_2$(CO)$_5$ the complexes of the type (COT)M$_2$(CO)$_6$ are known for iron and ruthenium. At least two isomers for both metals are known (*trans* and *cis* isomers).

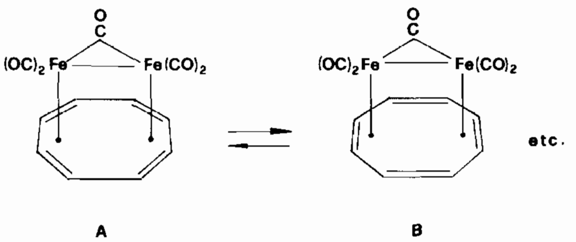
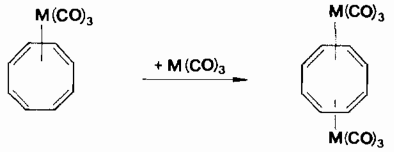


Figure 16. Fluxional behaviour of (C$_8$H$_8$)Fe$_2$(CO)$_5$.

The *trans* isomers are not fluxional. The second M(CO)$_3$ coordinates the opposite side of the molecular plane to the other 1,3 diene moiety available, thereby engaging the free double bonds necessary for the 1,2 shift of the M(CO)$_3$ group. The *trans*-(COT)Ru$_2$(CO)$_6$ complex was obtained only in a very small amount[74] and is not well characterized. The analogous iron[3,53,78] shows the expected pattern in i.r. (three ν(CO) stretchings) and pmr spectrum (two absorptions at τ 4.2 and 6.7). The crystal structure has been determined[58,81] (Figure 17):



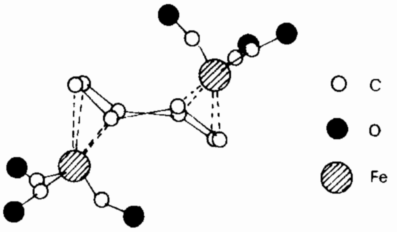


Figure 17. Molecular structure of (η^4, $\eta^{4'}$-C$_8$H$_8$)Fe$_2$(CO)$_6$.

Mössbauer studies, which show identical values for the quadrupole splitting in (C$_8$H$_8$)Fe(CO)$_3$ and (C$_8$H$_8$)Fe$_2$(CO)$_6$, further support the similarity of bonding of the Fe(CO)$_3$ groups.[82]

The *cis* isomers are fluxional molecules and as regards ruthenium a detailed study was carried out in the solid[83] and in solution[71,74] (Figure 18):

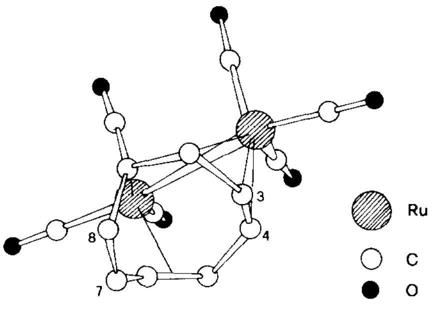
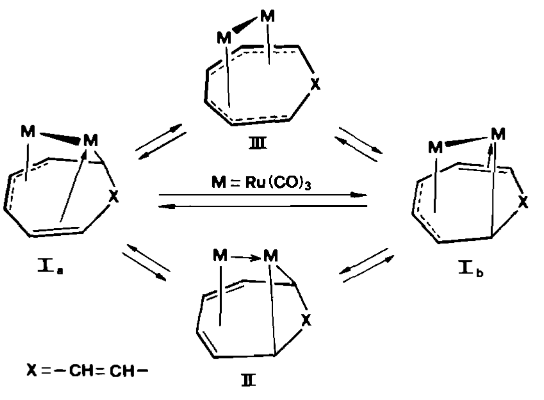


Figure 18. Molecular structure of (η^6-C_8H_8)$Ru_2(CO)_6$ (Ru–Ru).

As shown, the structure in the solid is not that proposed for the analogous iron complex, being a completely asymmetric structure.[83] Again, in (COT)$Ru_2$$(CO)_6$, the room temperature pmr spectrum is not consistent with the solid structure and the molecule must be fluxional. The following mechanism has been proposed to account for the changes in the pmr spectrum with temperature:



Ia and Ib are rapidly interconverting at room temperature and the molecule has a plane of symmetry bisecting the carbons in the 3,4 and 7,8 positions.[74] A choice between II and III as preferred symmetric intermediates in the rearrangement is not easy. Originally II was preferred since it can be easily formed from Ia and Ib without great changes in the bonds. However, in the light of recent studies such as the crystal structure of type III found for (C_7H_8)$Fe_2$$(CO)_6$[9], III must also be considered as a possible intermediate. An analogous mechanism can be well applied to other fluxional (polyolefin)$M_2(CO)_6$ complexes.[10]

Although neither a low temperature pmr nor a X-ray crystal and molecular structure have been reported for *cis*-(COT)$Fe_2(CO)_6$, an equilibrium between an iron–iron bonded species (I) and a complex (II) with two separate $Fe(CO)_3$ groups has been suggested to account for the pmr spectrum at room temperature. Both isomers were separated in a pure solid form[78] (Figure 19):

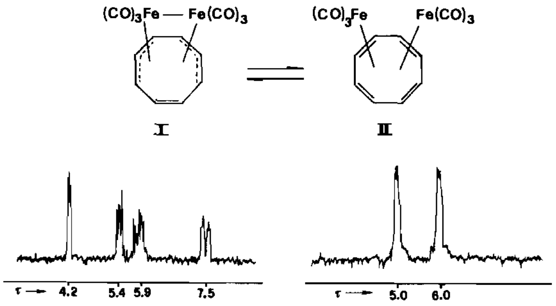


Figure 19. The interconversion of two forms of *cis*-(C_8H_8)$Fe_2(CO)_6$ and their pmr spectra.

In principle two explanations are feasible: (i) I and II are really two symmetric non fluxional complexes in equilibrium as proposed. In this case the equilibrium should be shifted to either form (probably I) at a lower temperature; (ii) I is a fluxional molecule similar to (COT)$Ru_2(CO)_6$ in equilibrium with the non fluxional form II. Should this be the case, lowering the temperature should produce a drastic change in the pmr spectrum. At a very low temperature it should be possible to find a "frozen" configuration for structure II similar to the one of the ruthenium complex.

In both cases a study of the crystal structure, and possibly of variable temperature pmr should be of great help.

At room temperature solutions of either I and II slowly lose CO to give (COT)$Fe_2(CO)_5$.[78]

D. Complexes of the Type (COT)$_x$M$_y$(CO)$_z$

(COT)$_2$$Ru_3(CO)_4$ was prepared in boiling octane from COT and $Ru_3(CO)_{12}$.[71,74] The X-ray crystal structure[84] shows that the Ru_3 moiety maintains the triangular structure of the starting $Ru_3(CO)_{12}$ (Figure 20) but the average Ru–Ru distance is larger (2.89 Å to 2.85 Å). This has been attributed to the

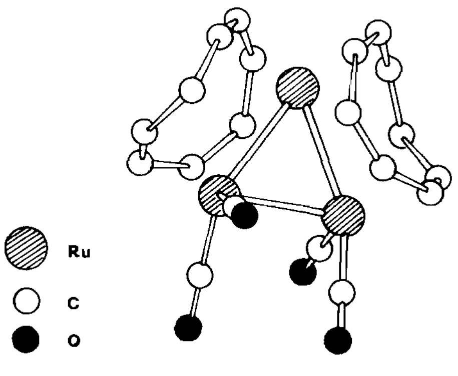


Figure 20. Molecular structure of (C_8H_8)$_2$$Ru_3(CO)_4$.

lower π acceptor ability of COT in comparison with CO.

$(COT)_2Ru_3(CO)_4$ in solution shows fluxional behaviour: at room temperature the 16 hydrogens appear as a singlet at $\tau = 6.26$. The protons behave as equivalent even down to −40° C.[71,74] The low solubility prevented a further lowering of temperature.

E. Fluxional Behaviour in the Solid State

It has been found that all those COT metal carbonyl complexes studied so far which show a dynamic behaviour in solution, will do so also in the solid state.[85] Because no disorder in the crystals was noticed in the X-ray structure determinations, it was suggested that reorientation in the crystal was unfeasible[58,78,79]. This conclusion is not correct if we assume that the motion involves a simultaneous rotation and distortion of the ring in such a way that each carbon in the spatial configuration is substituted by another one so that no disorder can be found in the crystal[85]. If this is the case only nmr spectroscopy could reveal this motion.

It appears that there is a good correspondence between solution and solid fluxionality. $(COT)Fe(CO)_3$ and $(COT)Fe_2(CO)_5$ are fluxional whereas *trans*-$(COT)Fe_2(CO)_6$ is not. From the solid nmr spectrum of $(COT)Fe_2(CO)_5$ it appears also that it will be very difficult to stop the fluxionality of the compound since the ring is still quite mobile. There is, however, a difference between the solution and the solid fluxionality. In solution both the ring and the metal atom must move,[10] whereas in the solid movement involves only the ring (Figure 21):[86]

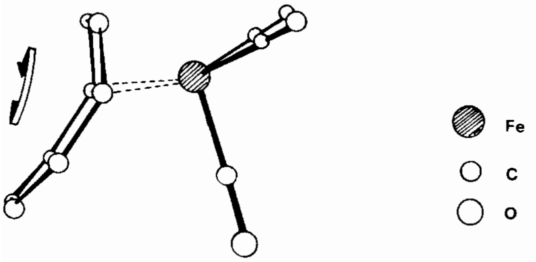


Figure 21. The rotation axis for the C_8H_8 ring in $(C_8H_8)Fe(CO)_3$.

Some pieces of information concerning the type of bonding between the components in those complexes which show motion in the solid can be obtained. This motion in the solid must be quite general since it has been found also in $(C_8H_8)_2Ru_3(CO)_4$ which is the most complex molecule so far studied.

From a comparison between the experimental and the theoretical values of second moment parameters it can be deduced that an independent re-orientation of the rings is very likely to occur through a jumping process.[87]

F. Other COT Complexes

Carbonylation of a n-hexane solution of $Fe(COT)_2$ and 1,3-butadiene affords a compound which has been formulated as $(\eta^4\text{-COT})(\eta^4\text{-butadiene})Fe(CO)$[88]. Its i.r. spectrum shows ν(CO) at 1967 cm^{-1} and uncoordinated olefinic bands at 1571 cm^{-1} (COT). The coordinated double bonds of COT display bands at 1426 and 1412 cm^{-1}, whereas the bands at 1486 and 1476 cm^{-1} can be justified by the olefinic stretching of the butadiene unit. The X-ray analysis confirms the assignment[89] (Figure 22):

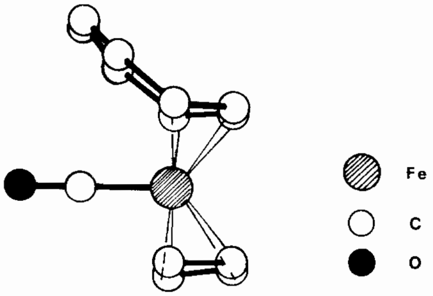
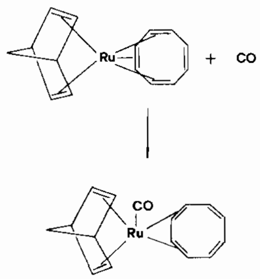


Figure 22. Molecular structure of $(\eta^4\text{-COT})(\eta^4\text{-butadiene})Fe(CO)$.

There is a symmetry plane bisecting the Fe(CO) group and the two organic ligands, forcing coplanarity of the four carbons of butadiene in a *cisoid* form. The pmr at room temperature is, however, inconsistent with the above structure, since it displays only four bands at $\tau = 5.5(8)$, 5.7(2), 8.3(2), and 10.1(2) indicating a fluxional behaviour of the COT unit. With a decrease in temperature the major peak broadens, collapses and then at −65° C it originates three distinct broad bands at $\tau = 4.15(4)$, 6.53(2) and 7.65(2) corresponding to a butadiene-like configuration of the COT unit.

An interesting series of Ru(0) and Os(0) derivatives which do not contain carbonyl groups have been obtained by reduction of the corresponding Ru(II) and Os(II) complexes with $2K^+COT^{2-}$.

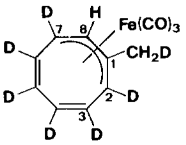
The compound Ru(NBD)(COT) contains a labile tricoordinated COT moiety as shown by the easy reaction with CO:[89a]



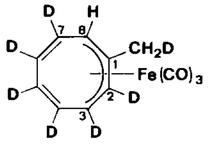
G. Substituted Cyclooctatetraenes

The complexes described in this section have one or more hydrogens in the COT ring substituted by methyl, phenyl or other groups. The structural characteristics of these complexes are quite similar to those of the unsubstituted COT complexes. Their preparations, however, were in many cases extremely useful to the understanding of fluxional behaviour and/or to the availability of the reference complexes in the structural determination in solution by pmr techniques.

We have already described the methyl derivative, namely $(CH_3C_8H_7)Fe(CO)_3$[66,67] and its partially deuterated analog. The pmr spectra of these two substituted COT complexes provided definite clues as to the conformation of $(COT)Fe(CO)_3$ in solution.



I

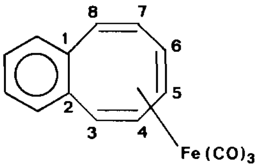


II

At lower temperatures the peak corresponding to proton 8 splits into two distinct sharp peaks whereas the peaks from CH_2D remained unchanged, thus demonstrating that two forms are present in equilibrium (I and II). That the average of the chemical shift of the protons 8 of I and II does not coincide with the point at which the single peak at −100° C appears, substantiates the presence of a small percentage of other tautomers in the region covered by the ^{13}C peak of the solvent. The single peak at temperatures over −100° C is the result of a rapid interconversion of I, II and the other equivalent conformations, through 1,2 shift.

For similar purposes other substituted complexes, *i.e.,* (1,8-dicarbomethoxy-COT)$Fe(CO)_3$ and (furan-1(3H)-one-COT)$Fe(CO)_3$ were prepared and studied by pmr.[54] That no temperature dependence of the pmr spectrum was observed, supports further the idea that a 1,2 shift is responsible for fluxional behaviour. In both complexes the 1,2 shift is relatively blocked. However, the absence of any time average phenomena in these 1,2 substituted complexes cannot be exclusively ascribed to the blocking of the 1,2 positions since structural factors, *i.e.* preferred configurations, must be of importance.

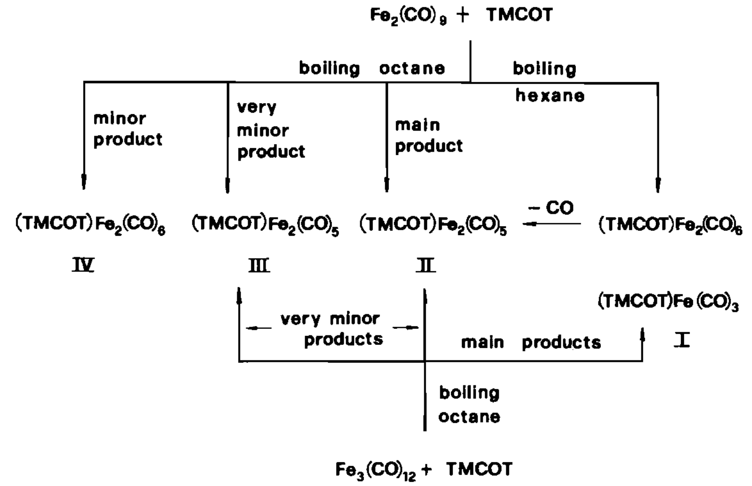
With this in mind it may be interesting to recall that (η^4-3,4,5,6)-benzocyclooctatetraeneirontricarbonyl was reported to be nonfluxional:[90]



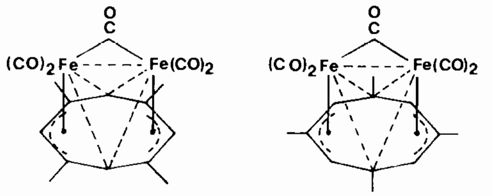
This statement has been revised.[91] Although the frozen spectrum is reached at a relatively high temperature (−15° C) suggesting a higher activation energy for the 1,2 shift interconversion, it appears that the blocking of the 1,2 position, in this case, is not sufficient to stop the fluxional behaviour of the molecule.

The similar naphtho-substituted COT complex is also fluxional; the frozen spectrum is, however, reached only at −70° C.

A series of 1,3,5,7-tetramethyl-COT (TMCOT) complexes which are similar, and in some cases analogous, to the corresponding COT complexes has been reported.[92–94] The iron carbonyl complexes are summarized in the following scheme:



Complex II is fluxional and very similar in its physical and chemical properties to $(COT)Fe_2(CO)_5$.[78,79] An X-ray study has shown that of the two possible structures IIa is the correct one[95] (Figure 23):



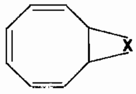
IIa IIb

Figure 23. Possible configurations of $(TMCOT)Fe_2(CO)_5$.

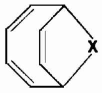
Finally, the complexes IV and V are quite similar to the *trans*- and *cis*-$(COT)Fe_2(CO)_6$ complexes and the analogous $(COT)Ru_2(CO)_6$ complexes.[92] It was suggested that IV in the solid has the same structure as the ruthenium analog,[83] but no X-ray analysis has so far been reported.

6. Bicyclotrienes

This general name is used here to denote those complexes which contain the bicyclic polyolefins of formula C_8H_8X:



I



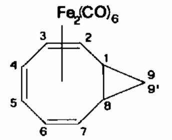
II

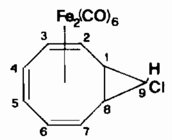
I X = CRR′, R = R′ = H, CH_3; R = H, R′ = Cl
X = O
X = $(CH_2)_n$ with n = 2,3,4
II X = CH_2, PC_6H_5, $NCO_2C_2H_5$

The reaction of I with metal carbonyls usually involves a rearrangement of the organic moiety. In every case, however, complexes of $Fe_2(CO)_6$ groups with the starting ligand could be isolated.

A. Bicyclo[6.1.0.]nonatriene

The formation of complexes of type (polyolefin)$Fe_2(CO)_6$ is quite easy, albeit in low yield (6–30%) because of the extensive rearrangement of the polyolefin promoted by the metal carbonyl. Since an increase in the reaction temperature results in an enhancement of the yield of rearranged products (see further) it is preferable to carry out the reactions at room temperature, with a large excess of the iron carbonyl. The best iron carbonyl as starting material is $Fe_2(CO)_9$. Thus, the orange-red crystals of $(C_9H_{10})Fe_2(CO)_6$,[96] $((CH_3)_2C_8H_8)Fe_2(CO)_6$[97] and $(C_9H_9Cl)Fe_2(CO)_6$[98] have been isolated. The i.r. spectra show five peaks in the region of terminal CO. The pmr spectra indicate perfectly symmetric molecules[96–98], a condition which may or may not be maintained at lower temperatures:[99]

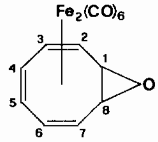




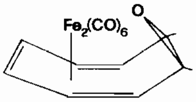
In some cases the solid structures differ from those in solution (by pmr at room temperature) indicating fluxionality of the molecules.[100]

B. 9-Heterosubstituted Bicyclotrienes

The reaction of 9-oxa-bicyclo[6.1.0]nona-2,4,6-triene (COTOX) with $Fe_2(CO)_9$ affords $(COTOX)Fe_2(CO)_6$, together with several complexes of the rearranged ligand.[101] This complex shows some differences from the other complexes of the type (polyolefin) $Fe_2(CO)_6$:

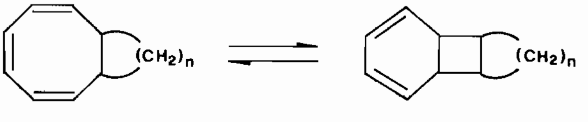


It is pale yellow (the others are orange or red) and its i.r. spectrum shows an extra band in the carbonyl stretching region at 2078 cm^{-1}. The oxyran group is easily lost by simple heating of the compound. This experimental evidence suggests some sort of interaction between the oxygen and the metal carbonyl group, probably through a *cis*-configuration of the ligand:



C. Bicyclo[6.n.0]trienes

When an aliphatic ring larger than a three-atom one is fused to a cyclic octatriene moiety there is an increased stability of the tricyclodiene, (b), relative to the bicyclotriene configuration (a).[102,103] Other factors, however, can contribute to the shift of this equilibrium (see Section III):



a b

n	a	b
= 2	≃100%	≃0%
= 3	≃3%	≃97%
= 4	≃53%	≃47%

By reaction with $Fe_2(CO)_9$ the above equilibria are shifted to the diene form, owing to the well documented dienophilic character of the $Fe(CO)_3$ group. However, a relatively high yield of the $Fe_2(CO)_6$–triene complexes was obtained with 1a and 3a;[102–104] only traces of $(2a)Fe_2(CO)_6$ were isolated. Their i.r. and pmr spectra are very similar to the other (polyolefin)$Fe_2(CO)_6$ complexes previously described, *i.e.* the molecules are symmetric at room temperature. The X-ray crystal and molecular structures of $(C_{10}H_{12})Fe_2(CO)_6$ have been found to be highly unsymmetric[105] (Figure 24):

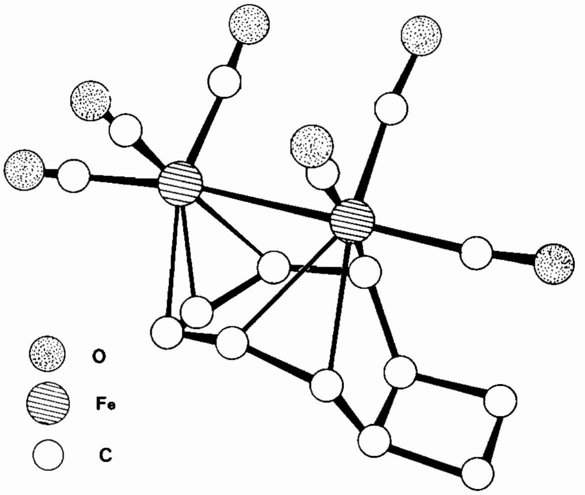


Figure 24. Molecular structure of $(C_{10}H_{12})Fe_2(CO)_6$.

The complex is fluxional and on lowering the temperature its pmr spectrum starts to collapse at –75° C, and at –130° C shows a consistent configuration with the crystal structure.

7. ^{13}C *Nmr Spectra*

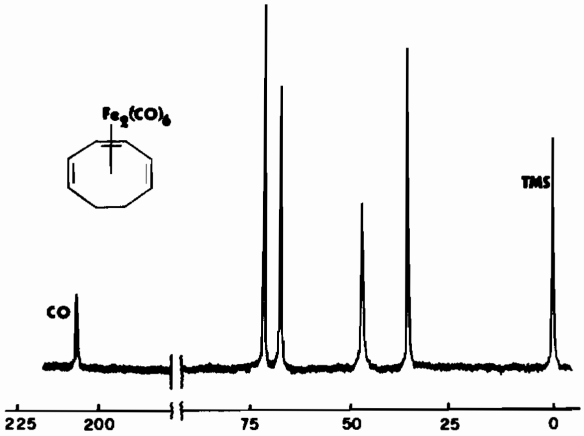
^{13}C nmr techniques are well documented in organic chemistry, whereas very few approaches have been reported in organometallic chemistry. This is mainly due to the relatively large amount of sample and to the fairly good solubility required for this technique. The long relaxation time in the carbonyl complexes which usually are the most interesting systems in organometallic chemistry plays a negative role in ^{13}C nmr spectroscopy. An improvement in the technical aspects of research comes from the addition of inert complexes such as $Cr(acac)_3$ (acac = acetylacetonate), which produces a 40-fold enhancement in the intensity of the signals,[106] and by the Fourier transformer which greatly reduces the time required for scanning a good spectrum.

In the field of polyolefin metal carbonyl complexes this application is becoming quite important since the assignments of ^{13}C in the organic region are much easier than those of the pmr spectra, and the fluxional behaviour can be monitored much better. Further, data relating to carbonyls can also be recorded and studied.

At room temperature the sequences of absorptions of the ^{13}C, proton decoupled, nmr spectra of complexes of the type (polyolefin)$M_2(CO)_6$ (M = Fe, Ru) are very similar to their pmr spectra. Some new informations can be obtained from the observation of the ^{13}CO region.

It is worth recalling that if a molecule (at least of the type of which we are concerned here) displays a symmetric spectrum at room temperature, it has no way of becoming dissymmetric at higher temperatures other than by decomposition or irreversible rearrangement. Only if the molecule shows a dissymmetric spectrum at room temperature is it liable to display changes at higher temperatures, *i.e.*, the molecule may be fluxional. This would be an exception among (polyolefin)$Fe_2(CO)_6$ complexes since it would require a very high activation energy; no such cases have been reported so far.

An attempt to correlate the number of ^{13}CO peaks to the fluxional or non-fluxional behaviour of these molecules has been made.[11] The observation of a single peak in the room temperature ^{13}C nmr spectra of several known fluxional molecules led to the suggestion of independent participation of the carbonyl groups to the fluxional behaviour of these molecules. Although this conclusion is correct, the isolated observation of a single line at r.t. as resulting from a time-average process which makes all six CO groups equivalent can be misleading. Further studies have shown that the single peak at room temperature is due to the carbonyl groups of a single $Fe(CO)_3$ moiety.[107] This point, however, will be described here in detail for $(C_8H_{10})Fe_2(CO)_6$ as an example. In the following figure the room temperature ^{13}C nmr spectra of two complexes of the type (polyolefin)$Fe_2CO)_6$ (where polyolefin is C_8H_{10}, $C_{10}H_{12}$) are reported[11] (Figure 25):



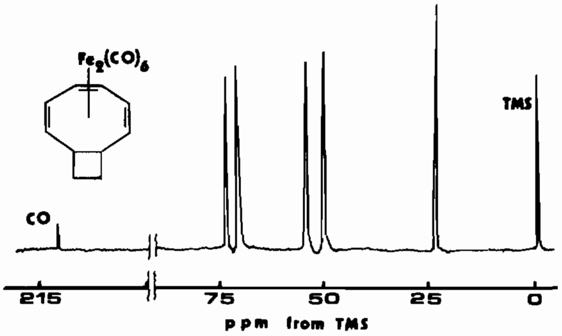
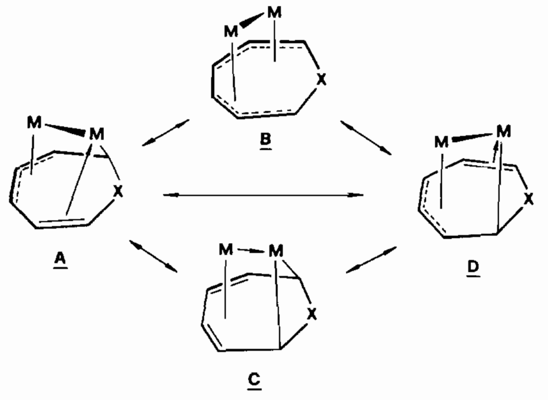


Figure 25. Room temperature ^{13}C nmr spectra of $(C_8H_{10})Fe_2(CO)_6$ and $(C_{10}H_{12})Fe_2(CO)_6$.

The presence of a single line for each couple of resonances of the ring carbon atoms is in agreement with the conclusions previously reached from the ^{1}H nmr spectra. At lower temperatures eight (C_8H_{10}) or ten $(C_{10}H_{12})$ signals appear as expected for an asymmetric configuration of type A or D. The increasingly rapid interconversion of the two enantiomorphs A and D with increasing temperature is completely consistent with the collapse of the eight or ten carbon peaks and with the appearance of four or five peaks at room temperature. The intermediate symmetric forms B or C are not important in the explanation of the behaviour of the ring carbons but will be essential in discussing the mechanism of interchange of carbonyl groups:



The advantages of ^{13}C nmr spectroscopy in the study of this type of molecules become evident when the variable temperature spectra of the carbonyl region are observed. In addition to the interconversion A $\rightleftarrows$ D there is a process in which the three carbonyl groups attached to one iron atom are scrambled among themselves.[107a] As a consequence of these two processes the carbonyl resonances become only three at 8° C with relative intensity 1:3:2 (Figure 26):

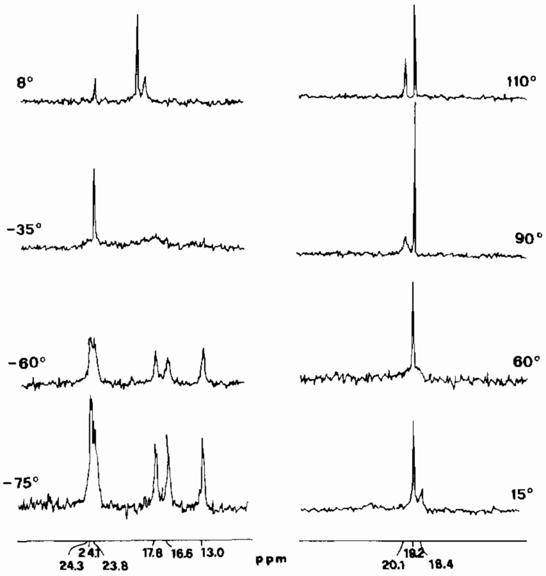
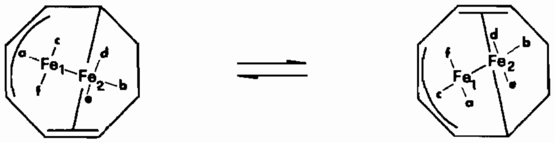


Figure 26. Temperature-dependent ^{13}C nmr spectrum of $(C_8H_{10})Fe_2(CO)_6$ in the carbonyl resonance region.

While the peak of intensity three does not change anymore, the two other peaks collapse at room temperature and then appear above 90° C as a single peak of intensity three. This can be easily rationalized as a scrambling of the three CO groups attached to the second iron atom. On the basis of several considerations the mechanism which best explains the experimental findings is one involving simultaneously a twitching motion and internal scrambling of the CO group attached to the iron atom bonded to the allyl unit:



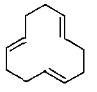
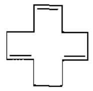
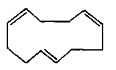
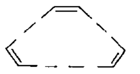
This accounts for the spectrum at 8° C. At higher temperatures the scrambling of the CO groups attached to iron(2) also becomes rapid.

8. *Cyclododecatriene (CDT)*

The discovery of trimerization of butadiene to cyclododeca-1,5,9-triene on a Ziegler-type catalyst,[108, 109] provoked a number of studies on complexes of these macrocyclic ligands.

The Ni–CDT complex proved effective in the cyclo-oligomerisation of butadiene and has been used (owing to the easy replacement of its coordinated CDT) for the synthesis of a number of other olefinic complexes.[108]

CDT $(C_{12}H_{18})$ can be obtained in four isomeric forms:

and complexes of the above isomers have been reported for the Group Ib metals (Cu, Ag, Au)[109–115], the Platinum triad (Ni, Pd, Pt),[108, 116–122] Titanium[123] and Iron.[123a]

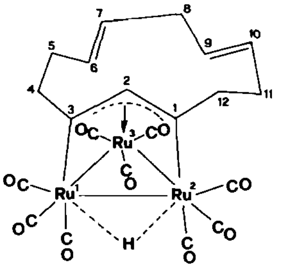
Some other metal ions or metal carbonyls promote the rearrangement of the ligand and will be described in the following sections. CDT complexes of Group Ib metals are usually quite insoluble, thus limiting their characterization to infrared spectra. In addition, the stoichiometry of such complexes changes with the preparation conditions and crystallization solvents.

Although attempts to obtain complexes of Cr, Mo, W with CDT by reacting the polyolefin with the metal hexacarbonyls failed, reaction of $Fe(CO)_5$ gives a stable $(CDT)Fe(CO)_3$ complex. It appears that only two double bonds should be coordinated to the metal in such a complex and indeed the i.r. spectrum shows an uncoordinated double bond stretching frequency in the expected region ($\nu(C{=}C) \simeq 1600\ cm^{-1}$).[123a]

Some very unusual compounds have been obtained from the reaction of $Ru_3(CO)_{12}$ with CDT. The formation of these complexes involves dehydrogenation and hydrogen isomerization of the starting polyolefin. The major product of the reaction is $HRu_3(CO)_9(C_{12}H_{15})$; in addition, other complexes, $HRu_3(CO)_9(C_{12}H_{17})$, $HRu_3(CO)_7(C_{12}H_{17})$ and $Ru_4(CO)_{10}(C_{12}H_{16})$ have been isolated.[124a]

Although some clues as to their configurations were given by spectroscopic data, their bonding features could be determined only by X-ray analysis. So far only $HRu_3(CO)_9(C_{12}H_{15})$ (I)[124b,c] and $Ru_4(CO)_{10}(C_{12}H_{16})$ (II)[124d] have been characterized by X-ray analysis.

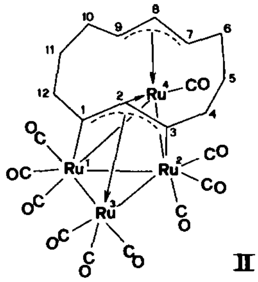
In I the ruthenium atoms are on the corners of an isosceles triangle and three carbonyl groups are bonded to each ruthenium. The hydride atom could not be located with certainty but the length of the Ru_1–Ru_2 bond may indicate a bridge between these two atoms.[124b,c] Interestingly, in the pmr spectrum the hydride appears as a doublet (at τ 30.24, J = 2.5 Hz) coupled to proton in position 2:[124a]



I

Only three carbons (1,2,3) of the ligand are bonded to the Ru_3, while two double bonds (C_6–C_7 and C_9–C_{10}) remain uncoordinated. In addition σ-bonds between C_1 and Ru_2 and C_3 and Ru_1 are present.[124b,c]

The structure of $Ru_4(CO)_{10}(C_{12}H_{16})$ (II) is also very unusual:



II

The Ru_1–Ru_2 atoms can be seen as the basis of two different triangles which have Ru_3 and Ru_4 at the apices. Ru_1 and Ru_2 carry three carbonyls as well as Ru_3, while only one carbonyl group is attached to Ru_4.[124d] Ru_1 and Ru_2 are σ-bonded to the organic ligand. Ru_3 and Ru_4 are bonded to the $C_1C_2C_3$ and $C_7C_8C_9$ allyl units. In addition, Ru_4 is bonded also to $C_1C_2C_3$, thereby making this allyl unit bridge the apical Ru_4.

This complex can be formed also from the above $HRu_3(CO)_9(C_{12}H_{15})$ and $Ru_3(CO)_{12}$. A tentative mechanism involving interaction of a new ruthenium atom with one of the free olefinic bonds of the reacting complex has been proposed. Further steps involve hydrogen isomerization and linkage of the fourth ruthenium to the cluster.

9. Annulenes

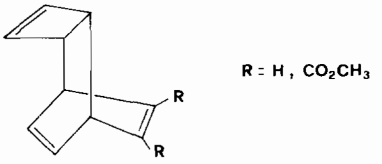
The organometallic chemistry of higher annulenes (*i.e.* with more then eight carbon atoms in their ring) is virtually an unexplored field. This is mainly due to the poor availability of the ligands and to the instability of the complexes.

Attemps to isolate complexes of [14] and [18] annulenes with chromium carbonyl groups failed.[126] Sometimes complexes of the rearranged ligands can be obtained.[127]

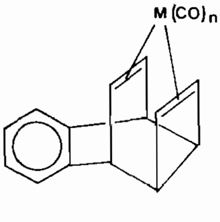
10. Miscellanea

In this section the metal complexes of polycyclic polyolefins, which are somewhat related to the main polyolefins considered earlier, are discussed. These particular hydrocarbons usually contain two or more double bonds which are not conjugated and often the double bonds belong to different cycles. Only ligands containing at least three double bonds will be considered.

The addition of acetylene or acetylenedicarboxylate to cyclooctatetraene involves the formation of these tricyclic hydrocarbons:[128]



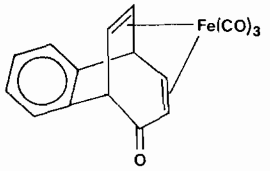
Complexes related to these ligands are:[129]

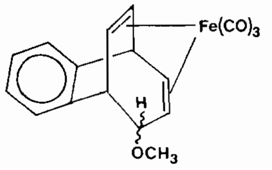


M= Mo, n=4
M= Fe, n=3

The large spin–spin interaction between the junction and vinylcyclobutene protons can be rationalized by the increase of the sp^3 character of the corresponding carbon atoms. There are also up-field shifts of both bridge and cyclobutene double bonds relative to the uncoordinated ligand.

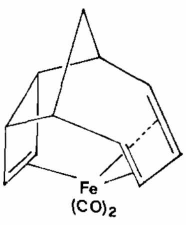
Complexes of 6,7-benzobicyclononatriene substituted in the 4-position with a methoxy or keto group have been prepared:[130]

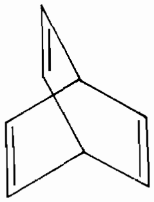




The methoxy derivative complex exists in both isomeric forms.

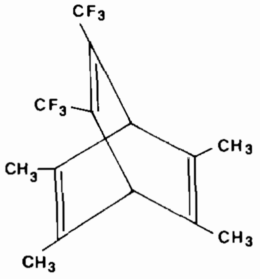
Cycloheptatriene addition on cyclobutadieneirontricarbonyl gives some interesting reaction products. One of these is a complex of an $Fe(CO)_2$ group:[131]





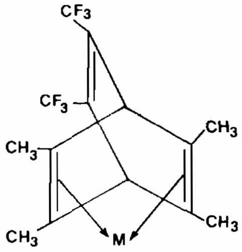
I

Bicyclo[2.2.2]octatriene (I) contains three double bonds capable of coordination to a metal group. In the cases of the metal groups which require four π-electrons for stable coordination, the formation of isomers is expected. Their existence has been verified in the following substituted bicyclo [2.2.2]octatriene (II)[132]:

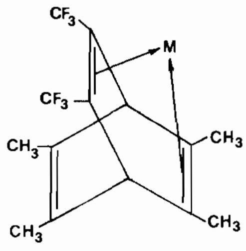


II

Complexes of (II) with M = $Fe(CO)_3$, have been isolated and have the configuration (III) or (IV):



III



IV

III. Rearrangements

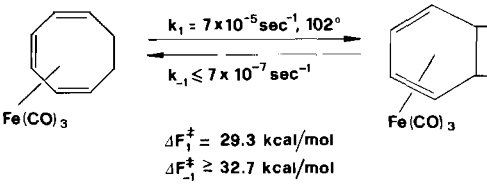
1. *Rearrangement of Cycloheptatriene Complexes*

Rearrangements of cycloheptatriene metal complexes are so far unknown. In the reaction of iron carbonyls with C_7H_8 in high boiling solvents another compound, $(C_7H_{10})Fe(CO)_3$, is separated in addition to $(C_7H_8)Fe(CO)_3$.[4]

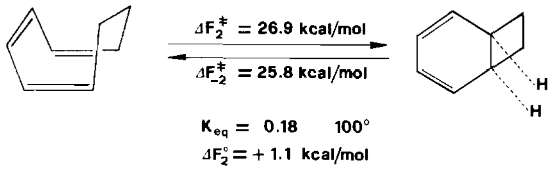
Since cycloheptadieneirontricarbonyl is probably formed by reaction of C_7H_8 in excess with $(C_7H_8)Fe(CO)_3$, this process cannot be considered as originated by thermal rearrangement of $(C_7H_8)Fe(CO)_3$.

2. Rearrangement of Cyclooctatriene Complexes

C_8H_{10} hydrocarbons obtained by reduction of cyclooctatetraene are a mixture of bicyclo[4.2.0]octadiene, cycloocta-1,3,5-triene and cycloocta-1,3,6-triene, depending on the conditions of the reaction. It is not surprising that reactions of metal carbonyls give mixtures of complexes of these ligands.[3,45]. However, when pure cycloocta-1,3,5-trieneirontricarbonyl is heated with $Fe(CO)_5$, isomerization takes place to the bicyclodiene complex.[45] The process, as expected, occurs also without $Fe(CO)_5$ at 102° C:[133]



A kinetic study of this reaction has provided a first order rate constant. In the same process involving the free ligand the equilibrium is shifted in the opposite direction but with a lower value of the activation energy:[134] *



The enhanced ΔF value in the metal complex equilibrium may be accounted for, at least partially, by the occurrcnce of 1,2 shift of thc metal in the cyclization.[133] The driving force of the reaction is very likely due to the distortion provoked by the complexation which forces the coordinated diene unit to be planar. This configuration is favoured only in the bicyclic isomer. Electronic factors, however, may be also important. Energetic considerations (only about 2.4 Kcal/mol = ΔF_1–ΔF_2 available for the activation energy of the dissociation process) exclude the possibility of previous dissociation of the metal group in the reorganization of the polyolefin. A catalytic process promoted by the free diene is also unlikely since this pathway is known to involve second order reactions.[135,136]

Additional rings fused to the cyclooctatriene unit favour the equilibrium displacement towards the diene form in both the complexed and the free ligand cases[102,103] (see section on bicyclotrienes).

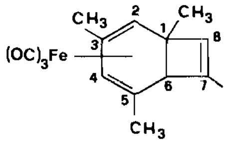
We have described previously that reaction of cycloocta-1,3,5-triene with $Ru_3(CO)_{12}$[50a] or with (cycloocta-1,5-diene)$Ru(CO)_3$[12] involves formation of a $(C_8H_{10})Ru(CO)_3$ complex only in the rearranged form, *i.e.*, bicyclo[4.2.0]octa-2,4-diene. Since these reactions are carried out at temperatures lower than 100° C and the formation of the corresponding iron tricarbonyl complex occurs at 140° C, it appears that the electrocyclic ring closure is facilitated by coordination of the triene moiety to the $Ru(CO)_3$ group.

The formation of tetrahydropentalenyl ruthenium carbonyl complexes when C_8H_{10} is heated with $[Ru(MMe_3)_2(CO)_4]$ or $[RuMMe_3(CO)_4]_2$ (M = Si, Ge) will be discussed in the appropriate section.

3. Rearrangement of Cyclooctatetraene Complexes

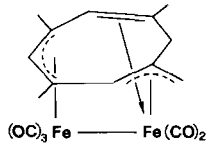
A. Thermal Reaction

Cyclooctatetraene metal complexes are quite stable and no thermal rearrangement has been reported except for that occurring in tetramethyl-substituted COT (however, see Section III. 5. A). Thus, one of the products of the reaction of TMCOT with $Fe_2(CO)_9$ is an oil which by analogy with other similar complexes has been formulated as tetramethylbicyclo[4.2.0]octa-2,4,7-trieneirontricarbonyl:[92]



Since in the above reaction complexes of the starting ligand TMCOT were obtained, whereas no (TMCOT) $Fe(CO)_3$ was isolated, tetramethylbicyclo[4.2.0]octa-2,4,7-trieneirontricarbonyl must be the rearranged product of the thermally unstable (η^4-TMCOT)$Fe(CO)_3$.*

The same reaction gave $(C_{12}H_{16})Fe_2(CO)_5$ in low yield. X-ray crystal structure has shown it to be a complex of 1,3,5-trimethyl-7-methylenecycloocta-1,3,5-triene in which the two metals are linked to two and three carbonyls:[137]



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* In the thermal isomerization of bicyclo[5.1.0]-2,4-octadieneirontricarbonyl to the corresponding bicyclo[4.2.0]-2,4-octadiene complex, (cycloocta-1,3,5-triene)irontricarbonyl is proposed as intermediate on the basis of a kinetic analysis: M. Brookhart, R.E. Dedmond and B.F. Lewis, *J. Organomet. Chem.*, *72*, 239 (1974).

* Recently, other examples of this type of ring closure have been reported to occur in a series of mono- and di-substituted cyclooctatetraene iron tricarbonyl complexes. In contrast, the ruthenium analogs afford polynuclear species; M. Cooke, J.A.K. Howard, C.R. Russ, F.G.A. Stone, and P. Woodward, *J. Organomet. Chem.*, *78*, C43 (1974).

B. Photochemical Reaction

Earlier work suggested that $(COT)Fe(CO)_3$ can be recovered unchanged (80% yield) after U.V. irradiation (20 hr).[3,53] Other authors reported a rapid decomposition in oxygen but a clean reaction in deoxygenated hexane:[138]

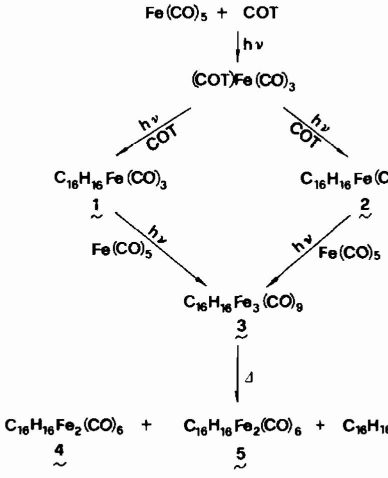
$$2\,(COT)Fe(CO)_3 \xrightarrow{h\nu} (COT)Fe_2(CO)_5 + COT + CO$$

Trans-$(COT)Fe_2(CO)_6$ is similarly converted to $(COT)Fe_2(CO)_5$ when irradiated for short periods in deoxygenated hexane. The possibility that *trans*-$(COT)Fe_2(CO)_6$ may be a photointermediate in the transformation of $(COT)Fe(CO)_3$ to $(COT)Fe_2(CO)_5$ was not proved by experiments. Another interpretation involves the formation of $(COT)Fe(CO)_2$[139] as initial photoproduct, which then undergoes intermolecular reaction with another $(COT)Fe(CO)_3$ molecule to give the final products:[138]

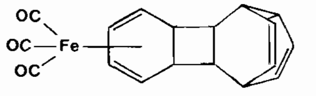
$$(COT)Fe(CO)_3 \xrightarrow{U.V.} (COT)Fe(CO)_2 + CO$$

$$(COT)Fe(CO)_2 \xrightarrow[+(COT)Fe(CO)_3]{U.V.} (COT)Fe_2(CO)_5 + COT$$

The above photochemical reactions do not involve rearrangement of the organic unit, but in the presence of excess COT a number of new complexes of COT dimers have been isolated.[140–142] The following scheme summarizes the products of the reaction of $Fe(CO)_5$ with excess COT:[142]

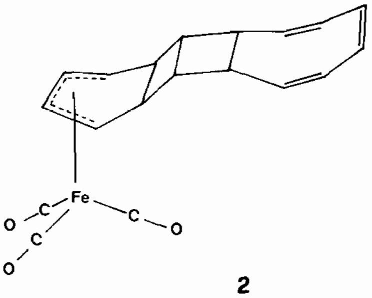


1 is a fluxional compound which has been tentatively formulated as pentacyclo$[6.4.3.0^{3,8}.0^{11,16}]$hexadeca-4,6,12,14-tetraeneirontricarbonyl on the basis of an analogous complex obtained by reaction of the corresponding hydrocarbon with $Fe_3(CO)_{12}$. Its pmr spectrum is, however, too complicated to allow a safe assignment, and the X-ray structure determination is not yet complete.[143]



1

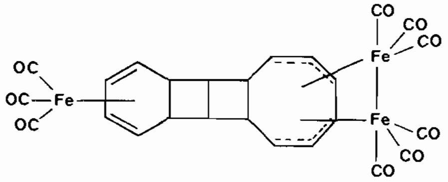
Complex *2* has been fully characterized by pmr[142] and X-ray structural analysis:[144]

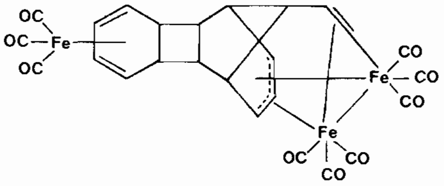


2

The ratio of isomer *1* to *2* depends on the conditions of irradiation, the concentration and the transparency of the reaction flask. Light of the U.V. region favours the formation of *2*.

Complex *3*, erroneously formulated as has been shown to have a rather unusual bond of the organic unit to the iron:[145]

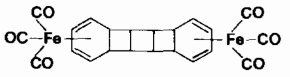


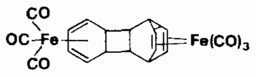


3

Its pmr is still difficult to interprete.

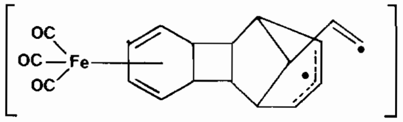
In the light of these results also the formulation of complex *4* may be uncorrect whereas *5* can be a real degradation product:





4 **5**

The configuration of *6* obtained only in trace amount is still inknown.[142] A plausible mechanism for the formation of *3* from *1* involves an hypothetical biradical:



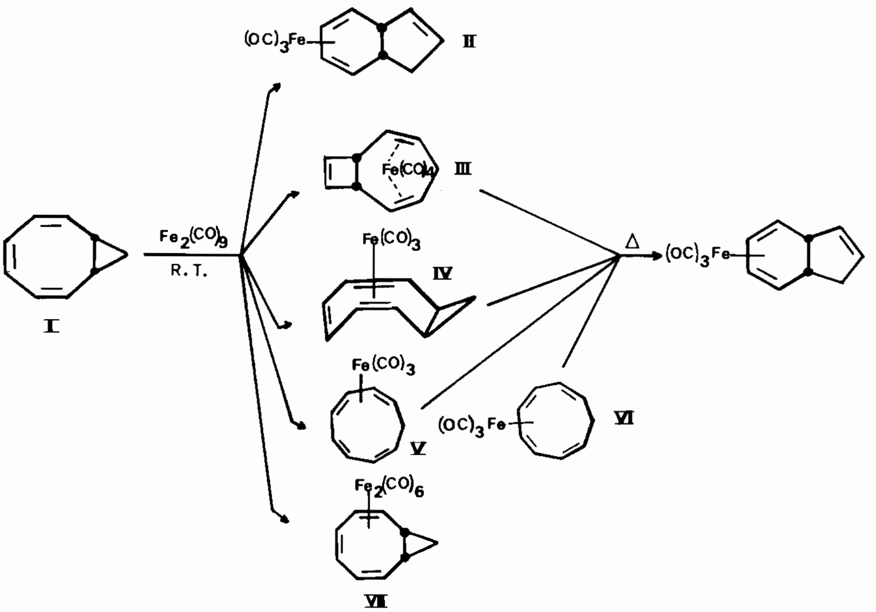
Further, the formation of *3* from *2* suggests an isomerization of *2* to *1* or to a precursor before the reaction with the other iron carbonyl groups.[145]

4. Rearrangement of Bicyclo[6.n.0]trienes

We previously pointed out that at least one compound in the reaction of metal carbonyls with bicyclotrienes contains the ligand in its original diagramatic form, when the reaction is carried out at room temperature. If higher temperatures (80–100° C) are employed all the complexes which can be isolated contain the ligand in a rearranged form. The same rearranged complexes usually are obtained in the thermolysis of the original (polyolefin)$Fe_2(CO)_6$ complex.

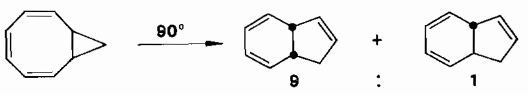
We will now describe the cases of complexes of rearranged ligands obtained at room temperature.

Reaction of *cis*-bicyclo[6.1.0]nona-2,4,6-triene (I) with $Fe_2(CO)_9$ gives a number of complexes which can be separated by careful chromatography on an alumina column.[96] Similar results have been obtained in the U.V. irradiation of the polyolefin in the presence of $Fe(CO)_5$:[146]

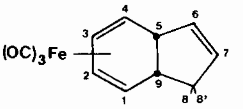


The series of complexes shown in the above scheme needs more discussion since many features are of common occurrence in the chemistry of bicyclotriene complexes. The presence of the metal carbonyl group must play an important role in the rearrangement of I. This appears to be due mostly to a promotion by the metal rather than to a more facile rearrangement of I upon coordination,[96] since the isolated complexes are thermally quite stable and require forcing conditions to rearrange further to the *cis*-dihydroindene complex (II).[96, 146]

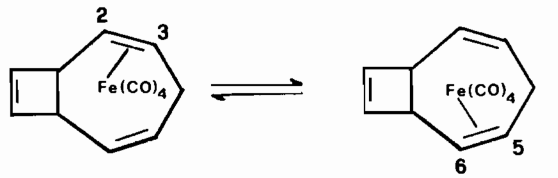
In addition the presence of the metal carbonyl groups forces the reaction pathway in one direction. We have already seen that I, when heated at 90° C, yields a mixture (9 to 1 ratio) of *cis*- and *trans*-bicyclo[4.3.0]nona-2,4,7-triene (8,9-dihydroindene):



whereas only the $Fe(CO)_3$ derivative of the *cis*-isomer has been isolated in the reaction of I with $Fe_2(CO)_9$ at room temperature, or with $Fe(CO)_5$ upon U.V. irradiation. Its pmr spectrum is superimposable to that of the product obtained at room temperature in the reaction of pure *cis*-8,9-dihydroindene with $Fe_2(CO)_9$:

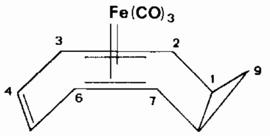


The other complexes which have been isolated in the reaction mixture are iron carbonyl derivatives of those intermediates which have been postulated in the rearrangement of the free polyolefin (I). Complex III has been formulated as (η^2-*cis*-bicyclo[5.2.0]nona-2,5,8-triene)irontetracarbonyl on the basis of mass (molecular ion at 386 m/e and loss of four CO groups), i.r. and pmr spectra:[96]



The symmetry of the pmr spectrum and the broad peaks corresponding to the methylene protons suggest that the spectrum is in an almost frozen configuration of two rapidly interchanging forms. The $Fe(CO)_4$ group should be bonded alternatively to the double bond at C_2–C_3 and to C_5–C_6.

IV was obtained in low yield and formulated as (η^4-*cis*-bicyclo[6.1.0]nona-2,4,6-triene)irontricarbonyl; its pmr spectrum shows that the metal carbonyl group is bonded to two unconjugated double bonds:[146]

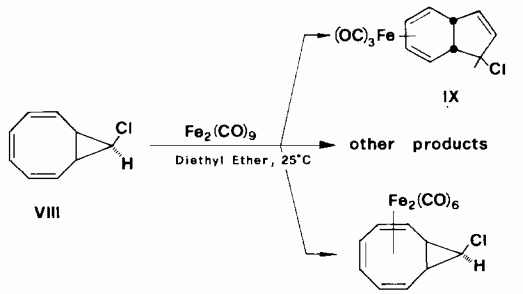


It is most likely that the unusual coordination of the $Fe(CO)_3$ group is due to steric reasons such as the non-planarity of the conjugated diene moiety in the bicyclotriene derivatives. The thermal stability of IV is low, as expected.

The complexes V and VI are the assymmetric and symmetric derivatives of the unstable *cis*^{4}-cyclononatetraene. The assymmetric isomer is obtained in much higher yield than the symmetric one. Their configuration follows from spectroscopic evidence, particularly pmr spectra.

The (η^6-*cis*-bicyclo[6.1.0]nonatriene)diironhexacarbonyl (Fe–Fe) has been described in the previous section. It must be pointed out that different metals can behave differently: in the case of the reaction of $Mo(CO)_3$(diglyme) with I, in fact, only the $Mo(CO)_3$ complex of the starting polyolefin has been obtained.[147]

Beside $(C_9H_9Cl)Fe_2(CO)_6$[98] the reaction of C_9H_9Cl with $Fe_2(CO)_9$ gives some other complexes of the rearranged ligand:[99]



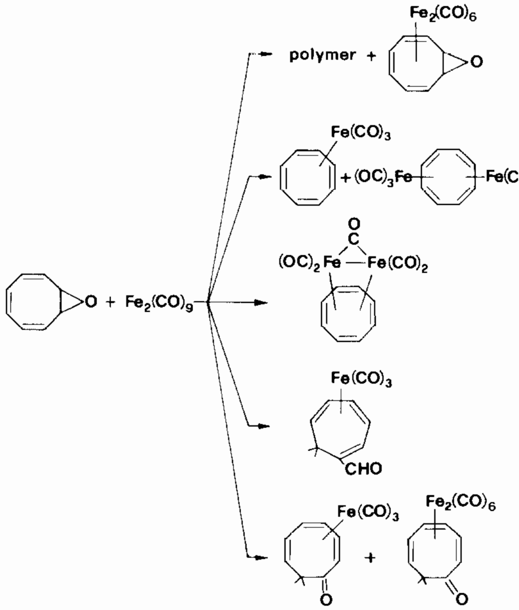
Comparison with the thermal rearrangement of VIII again shows an increasing rate for the formation of the 9-chloro-8,9-dihydroindene species and a selective influence of the metal in giving the *cis*-configuration of IX. In this reaction no cyclononatetraene derivative was isolated.

Preliminary results[148] on the reaction between 9-dimethyl-bicyclo[6.1.0]nona-2,4,6-triene and $Fe_2(CO)_9$ show that the formation of the *cis* dihydroindene complex in the metal promoted rearrangement contrasts with the thermal rearrangement of the free ligand which is completely converted to the *trans* derivative.

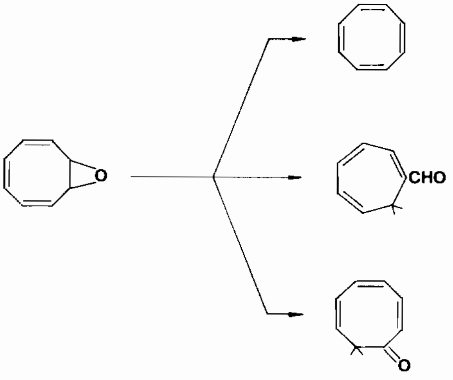
From the above results it appears that $Fe_2(CO)_9$ increases the rate of formation of the 8,9-dihydroindene moiety and selectively favors in any case the *cis* isomer, whereas the thermal rearrangement of the ligands is strongly influenced by the substituents in the 9 position. The driving force of these transformations must be the well documented dienophilic character of the $Fe(CO)_3$ group. Whether this character manifests itself in a promotion of the organic triene→diene rearrangement followed by coordination of $Fe(CO)_3$ to the diene or in a rearrangement of the unstable complex formed by coordination of $Fe(CO)_3$ to the triene ligand, is not at present established.

We favor the former interpretation, since it has been shown that the complexes of the unstable polyolefins are thermally stable and only forcing conditions are required for further rearrangements to the 8,9-dihydroindene moieties.

The reaction of 9-oxa-bicyclo[6.1.0]nona-2,4,6-triene (COTOX) with $Fe_2(CO)_9$ is more complicated since at least four pathways are followed. One, (a), implies the usual formation of the $Fe_2(CO)_6$ complex and of the unstable $Fe(CO)_3$ complex of COTOX which polymerizes; another pathway, (b), is the deoxygenation of the polyolefin; a third one, (c), the contraction of the ring to a seven-member ring carboxaldehyde, and the fourth one, (d), implies a rearrangement to the isomeric keto-polyolefin cyclooctatrienone:



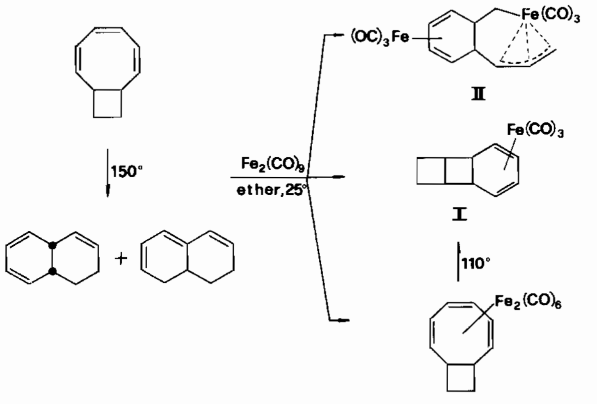
An explanation of the formation of the above complexes can be attempted by considering the different possibilities of stabilization of a derivative obtained upon breaking one C–O bond of the epoxide:



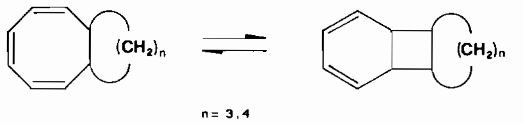
The presence of the metal carbonyl must play an important role in these rearrangements. The formation of γ-carboxaldehyde is now easy; COTOX is converted to the same uncomplexed compound only at 230° C.[149]

Until now we have considered cases in which the metal influences mostly the rate of the rearrangement yielding complexes of the same organic moiety as found in the rearrangement of the polyolefin itself at least in a diagrammatic form.

In the case of the reaction between *cis*-bicyclo[6.2.0]deca-2,4,6-triene[102,104,105] and $Fe_2(CO)_9$, isolation of complexes was achieved in which the rearranged organic moieties are completely different from those obtained in the thermolysis of the ligand:[150]



I is not found in the thermolysis of the ligand but the homologous polyolefins $C_{11}H_{14}$ and $C_{12}H_{16}$ were obtained as mixture of the bicyclotriene and tricyclodiene[102,103]:



Reaction of these ligands with $Fe_2(CO)_9$ shifts the equilibrium to the tricyclodiene form. The formation of I was not completely unexpected since in the light of the results of the preparation of $C_{11}H_{14}$ and $C_{12}H_{16}$ mixtures, its isolation is in line with the expected effect of the coordination of iron.

Pmr spectra of the series of tricyclodiene$Fe(CO)_3$ complexes are very similar if due account is made of the difference in the $(CH_2)_n$ part of the spectrum.

The structures of $(C_{11}H_{14})Fe(CO)_3$[6] and $(C_{12}H_{16})Fe(CO)_3$[151] have been confirmed by X-ray investigations (Figure 27).

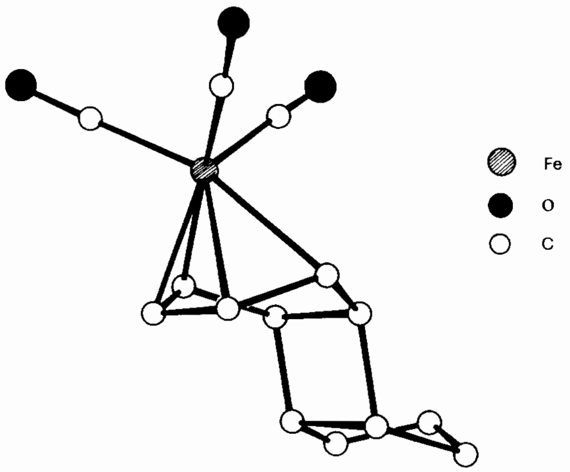


Figure 27. Molecular structure of $(C_{11}H_{14})Fe(CO)_3$.

The four-membered ring is an almost perfect square, whereas the five-membered ring has an envelope configuration in which the methylene carbon is 0.58° Å over the plane defined by the other carbons of the ring.

The irregular stabilization of the tricyclodiene form on going from $C_{10}H_{12}$ to $C_{11}H_{14}$ and to $C_{12}H_{16}$ must depend on steric factors and the formation of crystalline $Fe(CO)_3$ complexes is a good tool for this check through X-ray crystal determinations. The $Fe(CO)_3$ should not modify the configuration of the saturated rings.

The formation of II is quite surprising and was elucidated only after an X-ray crystal structure determination[152] (Figure 28):

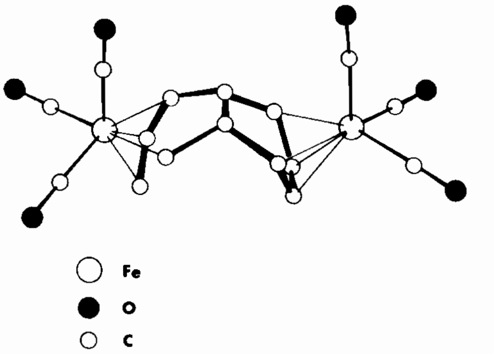
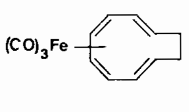


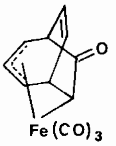
Figure 28. Molecular structure of $(C_{10}H_{12})Fe_2(CO)_6$.

It appears that the formation of II is a consequence of a further reaction with excess of $Fe_2(CO)_9$.[148]

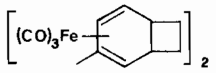
In addition to the major products of the reaction of $C_{10}H_{12}$ with $Fe_2(CO)_9$ other minor products have been characterized by systematic X-ray analysis of the minute amounts of crystals obtained. In this way the following complexes could be fully characterized:[153]



A



B



C

Complex B has been obtained also by direct reaction of barbaralone with $Fe_2(CO)_9$* and in better yield by reaction of (cyclooctatetraene)irontricarbonyl with anhydrous aluminum trichloride.**

Although (η^4-*cis*-cyclodecatetraene)irontricarbonyl may be easily explained as originated by the starting ligand, rationalization of the barbaralone iron tricarbonyl complex and of the dimeric bicyclodiene complex is more difficult. They can be formed also by small impurities of the starting polyolefin.

Finally another complex, $[C_{10}H_{11}Fe(CO)_2]_2$,[154] has been fully characterized. Since it is obtained in relatively higher yield by thermal rearrangement of the (η^6-*cis*-bicyclo[6.2.0]deca-2,4,6-triene)diironhexacarbonyl (Fe–Fe) complex, it will be described in the next section.

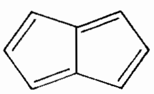
5. *Thermolysis of Cyclic Polyolefin Metal Carbonyl Complexes*

In the previous section we have seen that metal carbonyls can stabilize labile or unstable polyolefins which can derive from ring opening of a small cycle or ring closure of a large cycle. Thus, usually, it is difficult to predict whether the stabilization of the polyolefin is enhanced by a ring opening process or a ring closure process.

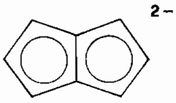
When, however, the temperature of the reaction is increased up to 100° C ring closure is the more favoured process, usually accompanied by dehydrogenation. Another common feature of these high temperature ring closures is the formation of complexes containing two metal groups linked together by a metal–metal bond.

A. Pentalene Complexes

One of the most interesting hydrocarbons which has been stabilized by high temperature reaction of a metal carbonyl with a cyclic polyolefin containing at least eight carbon atoms is bicyclo[3.3.0] octatetraene or pentalene (I):



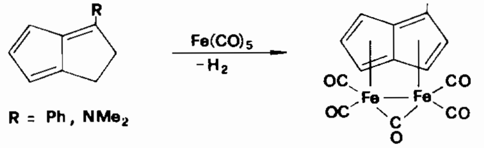
I



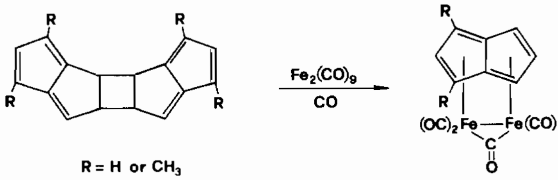
II

In contrast with its ten-π-electron derivative, the stable pentalenyl dianion (II)[155], all the attempts to prepare the eight-π-electron system pentalene have failed. There are, however, few cases of stable metal carbonyl complexes of pentalene.

Stabilisation of pentalenes by metal carbonyls has been obtained by reactions of hydrocarbons already containing the bicyclic ring system of pentalene with iron carbonyls or by dehydrogenative ring closure of systems containing a monocyclic C_8 ring with metal carbonyls (Fe, Ru). The first type of reactions involves: a) dehydrogenation of 3-R-1,2-dihydropentalenes (R = phenyl,[156] dimethylamino[157]) with $Fe(CO)_5$ in boiling methylcyclohexane; in the case of R = H dehydrogenation occurs with $Fe_2(CO)_9$ in refluxing ether:[157a]



b) fission of the corresponding pentalene dimers by $Fe_2(CO)_9$ under CO atmosphere:[158]



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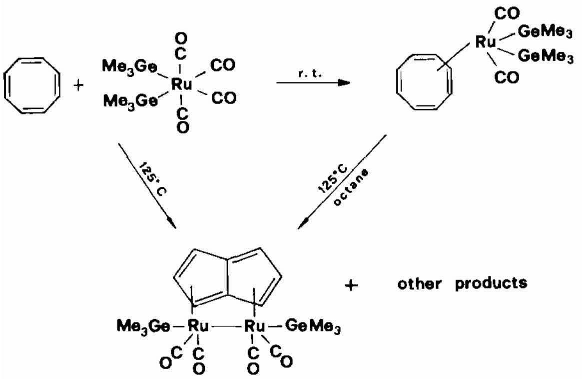
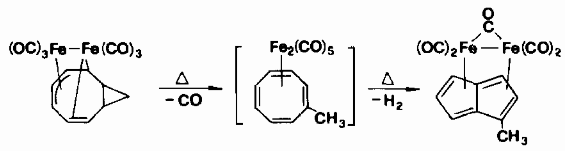
* A. Eisenstadt, *Tetrahedron Letters*, 2005 (1972); A.H.J. Wang, I.C. Paul and R. Aumann, *J. Organomet. Chem., 69*, 301 (1974).

** V. Heil, B.F.G. Johnson, J. Lewis, and D.J. Thompson, *J. C.S. Chem. Comm.*, 270 (1974).

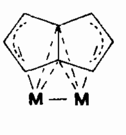
The pentalene metal carbonyl complexes obtained by dehydrogenative ring closure of a monocyclic C_8 ring system generally involve ruthenium carbonyl derivatives. One example, however, has been reported for the iron case, *i.e.*, the formation of η-(1-methyl pentalene)μ-carbonyl–tetracarbonyldiiron (Fe–Fe)[159] from (η^6-bicyclo[6.1.0]nonatriene)hexacarbonyldiiron (Fe–Fe). Structurally related is (η-pentalene)$Ru_2(CO)_4(GeMe_3)_2$[160], obtained from high temperature reaction of cyclooctatetraene with $Ru(CO)_4(GeMe_3)_2$. The mechanism of formation is not clear but the isolation of a cyclooctatetraene–$Ru(CO)_2(GeMe_3)_2$ complex at low temperature suggests that, at least in this case, the formation of the pentalene complex is due to a dehydrogenation and ring closure of the above metal complex rather than to a promotion by the metal carbonyl of the rearrangement of cyclooctatetraene, followed by metal coordination of the labile pentalene moiety.

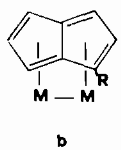


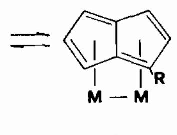
It is also possible that an intermediate of the type $(Me\text{-}C_8H_7)Fe_2(CO)_5$ is formed in the rearrangement of (*cis*-bicyclo[6.1.0]nonatriene)hexacarbonyldiiron (Fe–Fe)[159]:



The X-ray crystal and molecular structure of the ruthenium pentalene complex has been resolved and the data are consistent with configuration *a*, rather than *b* or *c*:


a


b


c

The two rings of the organic unit are individually planar but hinged to one another at an angle of 173° away from the molecular center.[160] The Ru–Ge bonds are also directed away from the molecular center (Figure 29):

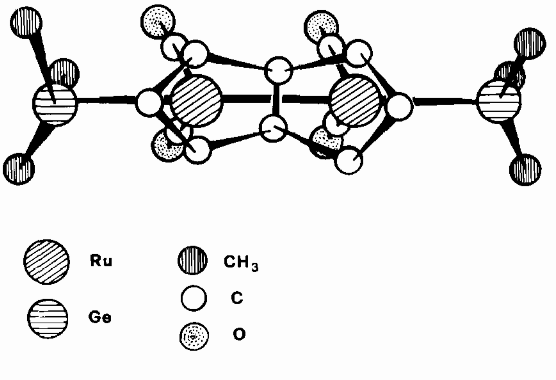
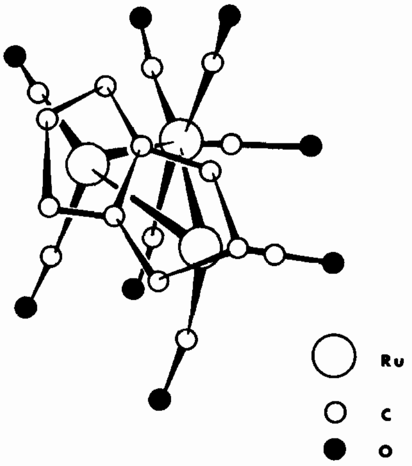
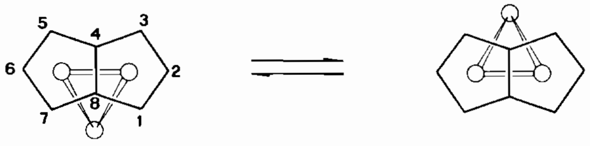


Figure 29. Molecular structure of $(C_8H_6)Ru_2(CO)_4(GeMe_3)_2$.

It is likely that a similar configuration is pertinent to the other pentalene metal carbonyl complexes. Their spectroscopic features are indeed comparable. The pmr spectra show triplets for the internal allylic proton coupled to doublets for the external allylic protons (J = 2.5 Hz). Another series of pentalene complexes of ruthenium containing the $Ru_3(CO)_8$ group has been obtained by reaction of cyclooctatetraenes ($R\text{-}C_8H_7$; R = H, Me, Ph)[160a] or trimethylsilyl-substituted cycloocta-1,3,6-trienes[160b] with $Ru_3(CO)_{12}$ or $[Ru(SiMe_3)(CO)_4]_2$. In these complexes, of which $(C_8H_6)Ru_3(CO)_8$ is typical, the pentalene moiety is symmetrically coordinated to the two ruthenium atoms of the *triangulo* Ru_3 group, bearing two carbonyls. The other Ru atom is in the apical position of the *triangulo* and bears the other four carbonyls:



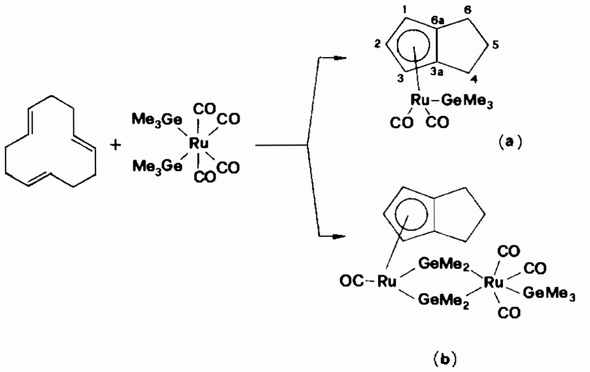
The angle between the main plane of the pentalene and that of the three ruthenium atoms is 50°. Consequently, the fluxional behaviour of these complexes having an unsubstituted or 2-substituted pentalene moiety can be easily explained by the rapid interconversion of the two enantiomeric forms:[160a]



This explains also the non-fluxional character of the 1-substituted pentalene complexes: in that case the two limiting forms are not equal in energy. Accordingly, (2,5-trimethylsilylpentalene)$Ru_3(CO)_8$ does not show fluxional behaviour while the similar symmetric 1,3,6-trimethylsilyl-subsituted pentaleneruthenium complex does.[160b]

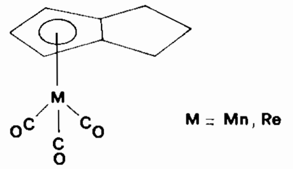
B. Tetrahydropentalenyl Complexes

All-*trans*-cyclododeca-1,5,9-triene undergoes ring closure with loss of a C_4 unit when heated with *cis*-$Ru(CO)_4(GeMe_3)_2$[161]. The mechanism of this reaction is not clear:

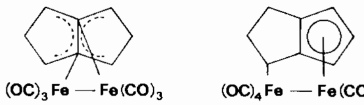


The presence of the 1,4,5,6-tetrahydropentalenyl ligand follows from mass and ^1H nmr spectra of the compounds. The bridging $GeMe_2$ groups are distinguishable in the pmr spectrum and therefore are not equivalent.

The compounds *a* and *b* were also obtained when 1,5-cyclooctadiene or mixtures of cycloocta-1,3,5- and -1,3,6-trienes[50a] were used in the place of cyclododecatriene. Intermediate formation of a ruthenium complex of COD (which has been isolated in the reaction of COD) in the rearrangement of CDT is quite possible[161]. The high stability of the tetrahydropentalenyl configuration is supported also by the isolation of the corresponding $M(CO)_3$ complexes when cyclooctatetraene is reacted with $Mn_2(CO)_{10}$[162] and cyclooctadiene with $Re_2(CO)_{10}$[163]:



In the reaction between dihydropentalene and $Fe_2(CO)_9$ in boiling ether the following complexes are formed:[157a]



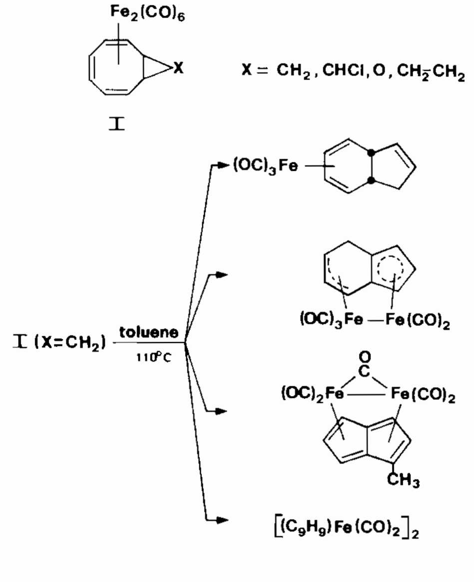
Further heating leads to formation of the already described (pentalene)$Fe_2(CO)_5$ complex.

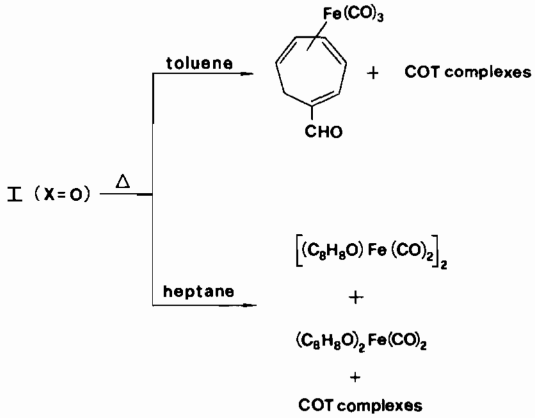
C. Rearranged Products from Cis-bicyclo[6.n.0] triene Complexes

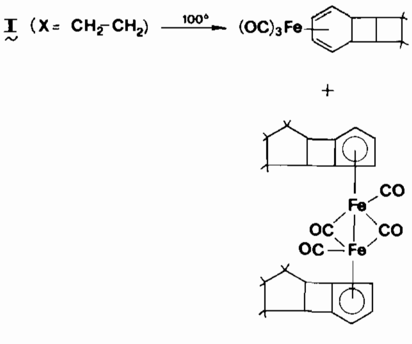
In the reaction of bicyclotrienes with $Fe_2(CO)_9$ at room temperature an $Fe_2(CO)_6$ complex of the starting polyolefin can be isolated. Its yield, however, is progressively reduced and eventually no trace of it can be found upon increasing the temperature of the reaction up to 100° C.

Consequently some new compounds are obtained whereas the yield of others increases. It is sometime difficult, however, to interprete these results which can be due to the thermolysis of (bicyclotriene)$Fe_2(CO)_6$ and to further reactions of already rearranged complexes with the excess of $Fe_2(CO)_9$.

Although this cannot be ruled out in the thermolysis of the pure $Fe_2(CO)_6$ complex, the occurrence of secondary reactions appear more unlikely since the extra $Fe(CO)_3$ groups are only due to the decomposition of the starting material (breaking of Fe–Fe bond). Thermolysis of I gives respectively:[101, 104, 159]







A

From the results of the above scheme it appears that thermolysis of (COTOX)$Fe_2(CO)_6$ is a particular one since it depends on whether the solvent is aromatic or not. The deoxygenation of the ligand is however solvent independent. For the formation of (carboxaldehyde)$Fe(CO)_3$ the assistance of the solvent has been suggested:[101]

No data, except mass spectra, are available for the COTOX dimeric complexes.

In the other two cases considered[164], some common features can be envisaged: the formation of the same $Fe(CO)_3$ complex obtained when the ligands are reacted at room temperature with $Fe_2(CO)_9$ and the series of (substituted cyclopentadienyl)$Fe(CO)_2$ dimers. It must be recalled that the $Fe(CO)_3$ complexes described are now the only $Fe(CO)_3$ complexes obtained in the thermolysis whereas other isomers were isolated in the original reactions.

The X-ray crystal structure of A has been determined (Figure 30):[154]

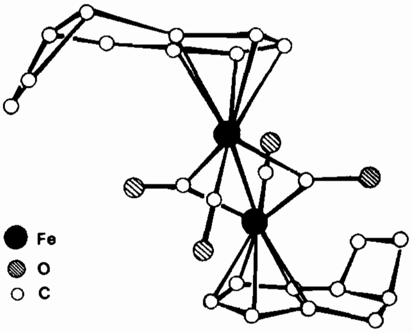
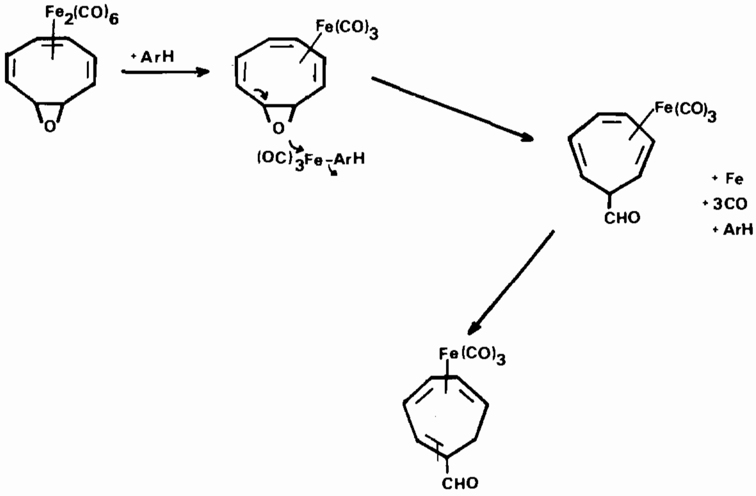


Figure 30. Molecular structure of $[(C_{10}H_{11})Fe(CO)_2]_2$.

Whatever the mechanism, the last two steps are very likely

$$(\text{polyolefin})Fe(CO)_2 \xrightarrow{\text{abstraction of H}} (\text{polyolefin–H})Fe(CO)_2H \xrightarrow{-H_2} [(\text{substituted Cp})Fe(CO)_2]_2$$

(Cp = cyclopentadienyl)



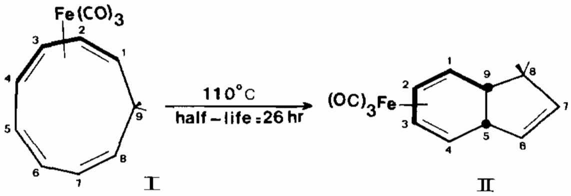
The $Fe(CO)_2$–$Fe(CO)_3$ complex is probably similar to the (azulene)$Fe_2(CO)_5$ complex.

$(C_9H_9)Fe_2(CO)_5$ is formed in much higher yield together with other complexes in the high temperature (boiling xylene) reaction of 8,9-dihydroindene with $Fe_2(CO)_9$.[159] Thus, the possibility that these complexes arise from reaction of the 8,9-dihydroindene complexes, primarily formed in the thermolysis, with excess of $Fe(CO)_3$ groups, finds strong support.

The (methylpentalene)$Fe_2(CO)_5$ complex has been described in the "Pentalene" section.

D. Other Rearrangements of Polyolefin Complexes

(η^4-1,2,3,4-*cis*^{4}-cyclonona-1,3,5,7-tetraene)irontricarbonyl has been shown to be quite stable. It rearranges cleanly to (*cis*-η^4-1,2,3,4-*cis*-8,9-dihydroindene) irontricarbonyl only at 100° C. The reaction has been followed by three different techniques and results, within experimental errors, are quite comparable:



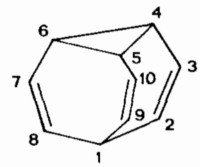
Thus, the rearrangement has been followed in deuteriotoluene by the disappearance of the multiplet corresponding to protons $H_{2,3}$ in the pmr of I and the appearance of the multiplet corresponding to the three protons $H_{1,4,5}$ of II. Integration of the spectrum in the region of the above peaks allows the progress of the reaction to be followed.[96] This reaction was followed also by gas-chromatography of the mixture of $Fe(CO)_3$ complexes or of the free ligands after oxidation with Ce(IV) solution.[146] The activation energy is 28.4 Kcal/mol. It should be noticed that the same rearrangement of the free ligand occurs with $\Delta F =$ 23.0 Kcal/mol. The increase of the activation energy in the case of the metal derivative can be accounted for, at least partially, by considering the 1,2 shift of the $Fe(CO)_3$ group which must occur to obtain the *cis*-8,9-dihydroindene complex in the electrocyclic ring closure.

The dihydroindene configuration appears the most stable one since the other complexes containing an iron carbonyl group obtained in the room temperature reaction of *cis*-bicyclonona[6.1.0]triene with $Fe_2(CO)_9$ undergo formation of II upon heating for several hours at 100° C.[96,146]

6. Rearrangements of Bullvalene and Semibullvalene Complexes

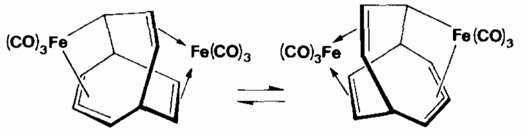
A. Bullvalene

Tricyclo[3.3.2.0^{4,6}]deca-2,7,9-triene (Bullvalene, I) contains two functions which are in principle suitable for bonding to a metal: two 1,4 diene units ($C_3C_2C_9C_{10}$ and $C_7C_8C_9C_{10}$) and the cyclopropane ring ($C_4C_5C_6$):



I

Reaction of I with $Fe_2(CO)_9$ yields six isomers $(C_{10}H_{10})Fe_2(CO)_6$ and a $(C_4H_4)Fe_2(CO)_6$ complex.[165] Of these some were fully characterized: η^4(2,3,4,6)η^4(7,8,9,10)bicyclo[3.3.2]decatrienediironhexacarbonyl (II),



II

was obtained as racemate of the two possible enantiomers. The i.r. spectrum shows six bands for terminal CO at 2054(a), 2024(b), 1996(a), 1992(a), 1980(b), 1964(b), cm^{-1}, where (a) = 2,3,4,6-*tetrahapto*Fe$(CO)_3$ and (b) = 7,8,9,10-*tetrahapto*$Fe(CO)_3$. The pmr spectrum supports the above configuration.

An X-ray crystal and molecular structure determination confirms the proposed structure[166] (Figure 31):

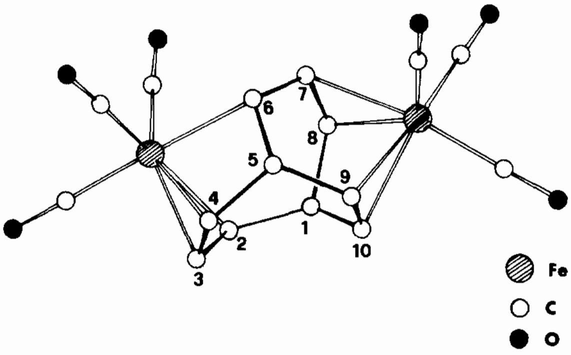
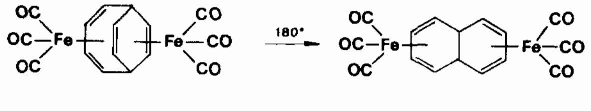


Figure 31. Molecular structure of $(C_{10}H_{10})Fe_2(CO)_6$ (II).

No change in the pmr spectrum was noticeable upon variation of the temperature.

η^4(2,3,4,5)η^4(7,8,9,10)bicyclo[4.2.2]decatetraenediironhexacarbonyl (III)[141] undergoes further rearrangement to *octahapto*-9,10-dihydronaphthalene (IV):



III IV

The structure of III was confirmed by X-ray investigation (Figure 32):[167]

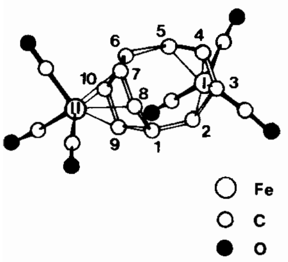
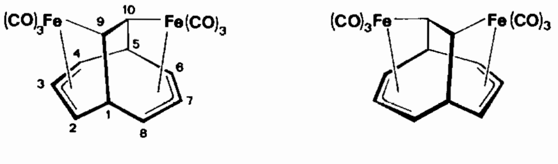


Figure 32. Molecular structure of $(C_{10}H_{10})Fe_2(CO)_6$ (III).

The Fe(II)–C distances are much longer (2.122–2.175 Å) than Fe(I)–C (2.038–2.100 Å) supporting a weaker bond of the iron attached to the 1,4 diene unit, as suggested by simple Hückel theory.[168]

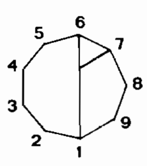
Two enantiomers which rapidly interconvert at −45° C are also obtained.[169] The limiting pmr spectrum of η^4(2,3,4,9)η^4(6,7,8,10)bicyclo[3.3.2]decatetraene (V) represents the mixture of the two enantiomers.



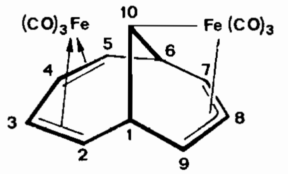
V

On warming the signals corresponding to protons H_2H_4 and H_6H_8 broaden and at 45° C the spectrum is averaged. The minimum change in the relative position of atoms should be obtained if the process involves an inversion at C_9 and C_{10}. This is supported by the invariance of the signals relative to $H_{1,5}$ and $H_{3,7}$ which remain in the same magnetic environments.

Thermolysis of V gives a derivative of isobullvalene (VI), η^4(2,3,4,5)η^4(7,8,9,10)bicyclo[4.3.1]decatetraenediironhexacarbonyl (VII):



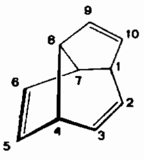
VI



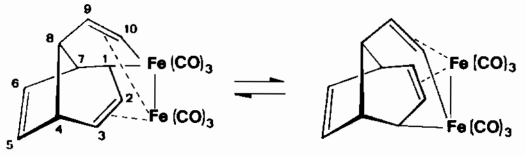
VII

No further rearrangement to (*octahapto*-9,10-dihydronaphthalene)diironhexacarbonyl (IV) was found even at 180° C.[125]

In the reaction between bullvalene (I) and $Fe_2(CO)_9$ another complex was obtained, which could be considered a derivative of tricyclo[5.3.0.0^{4,8}]deca-2,5,9-triene (VIII) upon breaking the C_1–C_{10} bond (IX). IX (two enantiomers) can be represented in a diagrammatic form as follows:[170]



VIII



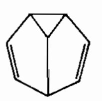
IX

The pmr changes with the temperature. Since protons H_2, H_8, H_9, H_{10} remain unchanged they must have the same magnetic environment in both forms. Protons $H_{5,6}$, $H_{4,7}$ and $H_{1,3}$ should give a rapid equilibration: decomposition of the complex at −90° C does not allow the coalescence of $H_{4,7}$ and $H_{1,3}$ to be reached.

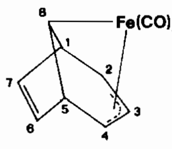
The exchange of the magnetic environments around the above couple of protons was however demonstrated by double resonance relaxation experiments.

B. Semibullvalene

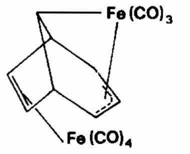
A green oil* was prepared in the reaction of tricyclo [3.3.0.0^{2,8}]octa-3,6-diene (semibullvalene, X) and $Fe_2(CO)_9$[172] in boiling benzene. Its i.r. spectrum (ν(CO) at 2070, 2035, 1975 cm^{-1}) and pmr spectrum are in agreement with the proposed structure[172, 173a]:



X



XI



XII

When the above reaction is carried out at lower temperature, XII is isolated. Thus, since XI can be easily obtained on heating XII, the $Fe(CO)_4$ group which is eliminated can produce $Fe_3(CO)_{12}$, responsible for the green colour of XI.[171]

When semibullvalene is reacted with $Fe(CO)_5$ under UV irradiation, an $Fe(CO)_4$ complex with an intact

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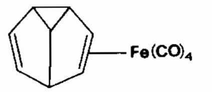
* The green colour is very likely due to the presence of traces of $Fe_3(CO)_{12}$. The pure compound is yellow.[171]

semibullvalene skeleton is obtained together with XI:[173b]



IV. Reactivity

1. Hydride or Proton Abstraction

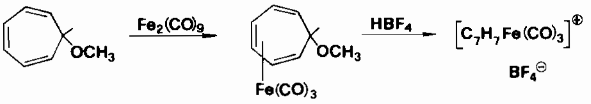
A. Cycloheptatrienyl Complexes

As noted earlier, cycloheptatrienyl ($C_7H_7^+$) is usually denoted as tropylium and its complexes are referred to as tropylium complexes, independent of the number of π-electrons involved in the bond to the metal. There are in fact four types of tropylium complexes which contain respectively:

a) seven carbons symmetrically bonded to the metal. The ring is planar; b) five carbons bonded to the metal. A double bond remains uncoordinated; c) three carbons bonded to the metal as a π-allylic moiety. A diene-type unit remains uncoordinated; d) a σ-bond involved in the bond to the metal. A system of three conjugated double bonds remains uncoordinated.

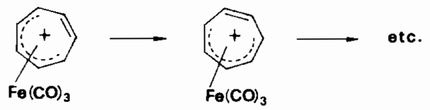
Most of the tropilium complexes are prepared by hydride abstraction from the corresponding cycloheptatriene complexes but there are few cases in which the above abstraction occurs spontaneously.

Attempts to prepare $[C_7H_7Fe(CO)_3]^+$ by hydride abstraction from the corresponding cycloheptatriene complex gave, in contrast, addition of the trityl cation to the C_7H_8 moiety.[7] The synthesis of (tropilium) irontricarbonyl was carried out by the following series of reactions:[16]



An intense absorption band at 731 cm^{-1} suggests the presence of a *cis* uncoordinated double bond.

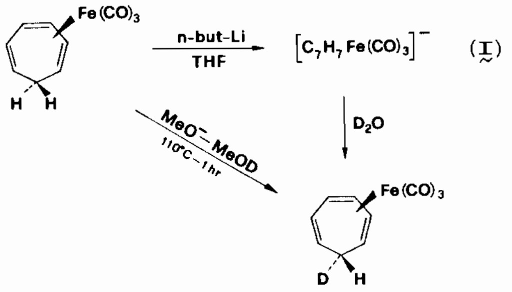
To account for the single line of its pmr spectrum ($\tau = 4.2$) a rapid valence tautomerism was postulated:



This fluxional behaviour was later confirmed for this and a similar complex, $(C_7H_7)Mn(CO)_3$.[174]

At least in the manganese complex the ring is still partially aromatic as suggested by the greater shift found in respect to the isoelectronic $[C_7H_7Fe(CO)_3]^+$ in comparison with the corresponding manganese[175,176] and iron[4,7,177,178] complexes of cycloheptadienyl and cyclohexadienyl ligands. Accordingly, the rate of rotation is 3–8 kcal mol^{-1} higher in the $Mn(CO)_3$ complex since a weaker back-bond is expected for a neutral complex in comparison to a positive one (the $Fe(CO)_3$ complex).[174]

Reaction of $(C_7H_8)Fe(CO)_3$ with butyllithium in THF gives a complex of the cycloheptatrienyl anion:[179]



The configuration of I is not yet established. The pmr spectrum in THF (only one singlet ($\tau = 5.35$) down to −65° C) and the i.r. spectrum (ν(CO) = 1942 and 1868 cm^{-1}) suggest that I is a fluxional complex of heptatrienyl anion,[179,180] isoelectronic with the (tropylium)Co(CO)$_3$ complex.

Further corroboration that I is $[(C_7H_7)Fe(CO)_3]^-$ comes from the facility of the exchange of the exo-hydrogen in 10% MeONa–MeOD with deuterium. The same conditions for 24 hr do not affect cycloheptatriene itself. The same deuterated complex is obtained by quenching the solution of I with D_2O.[179]

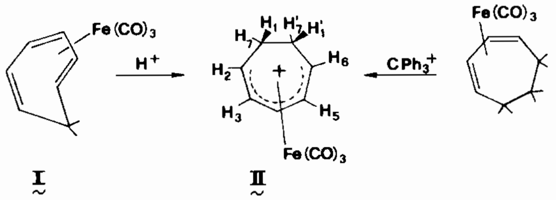
2. Protonation

Addition of a proton to a polyolefin metal complex stabilizes carbonium ion metal complexes. Their configuration, however, depends on the metal, the electronic requirements of which may give rearrangements of the organic cation.

Protonation is quite easy and usually is obtained by treatment of the corresponding neutral complex with acids.

A. Cycloheptatriene Iron Tricarbonyl

In principle complexes of metals which require four or less π-electrons to achieve their stable configuration can be protonated. Thus, $(C_7H_8)Fe(CO)_3$ reacts with HX (X = Cl, Br, BF$_4$) to give the cationic cycloheptadienyl iron tricarbonyl:[4,7]

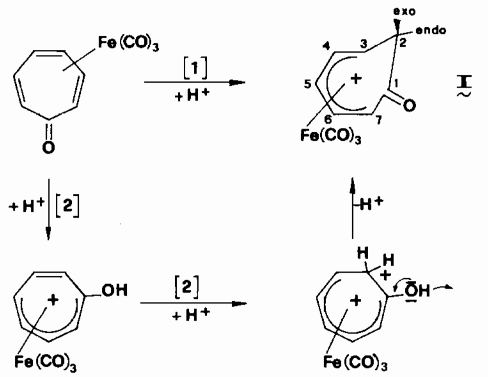


Protonation appears to be stereospecific[181,182] since the pmr spectrum of II and of the complex obtained by deuteration with D_2SO_4 differ only by the intensity of the signal at higher field. The protonation is very likely in the *exo*-position as suggested by the above modification (higher field protons usually are *exo*[183]).

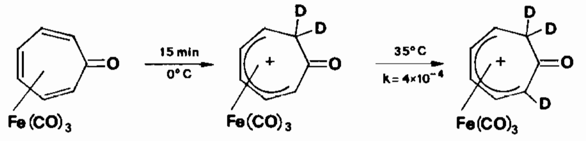
The same complex, $(C_7H_9)Fe(CO)_3^+$ can be prepared by hydride abstraction from (cycloheptadiene) irontricarbonyl.[7]

B. Tropone Iron Tricarbonyl

Extraction of $(C_7H_6O)Fe(CO)_3$ in CH_2Cl_2 with H_2SO_4 at 0° C gives protonation on the carbon adjacent to the keto group.[21,184] This type of protonation is rather surprising since one might expect it to occur on the keto group [1]. However, I might be the final product of a very rapid reaction through pathway [2]:[21]



Deuteration (D_2SO_4) is also more interesting since the first product formed is II which then more slowly is converted to III:

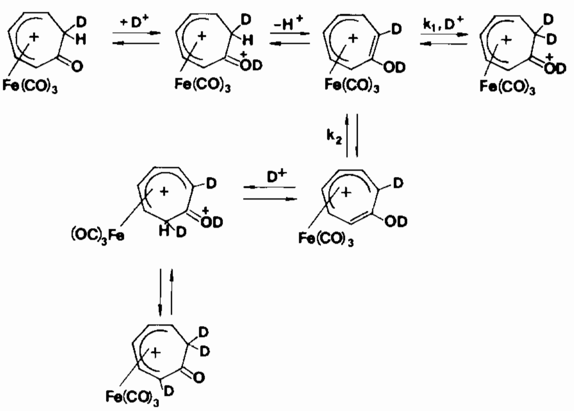


II III

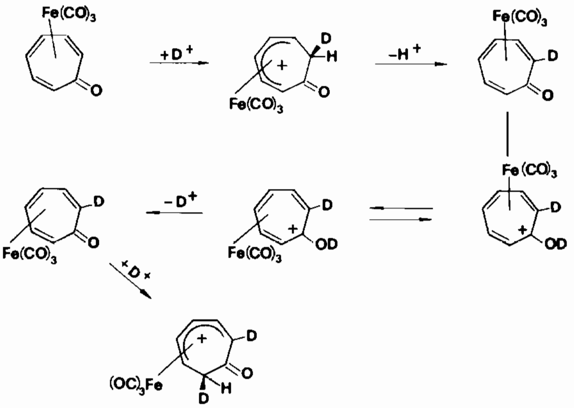
When the protonation is carried out in trifluoroacetic acid the process is also stereoselective and occurs at the coordinated double bond from the *exo* position.[184] Since electronic density after coordination to a transition metal should be decreased on the *exo* position, the stereoselective protonation at this position suggests that some other factors may be of importance.

Stereoselectivity is not found if the reaction is carried out in H_2SO_4. When SO_2–FSO_3D is used as deuterating agent the whole process is slower.

A tentative explanation of this process (especially the deuteration in C_7) is a 1,2 shift of the pentadienyl tricarbonyl system around the ring:



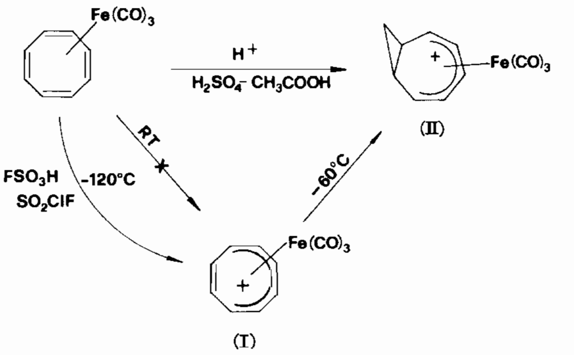
in which k_2 (rate of isomerization of the enolic double bond) is much slower than k_1 (rate of deuteration of such double bond). This mechanism involves protonation of both the carbon atoms of the coordinated double bond as well as of the keto oxygen to give an intermediate di-cation.[21] Another mechanism has been proposed to account for the stereoselective protonation in trifluoroacetic acid:[184]



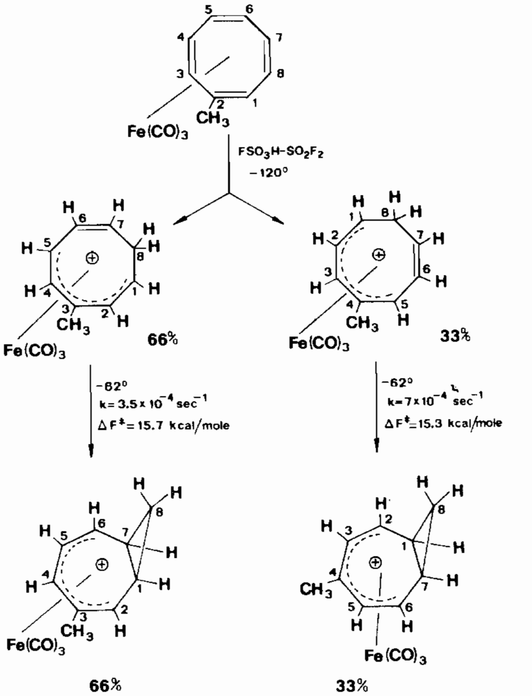
C. Cyclooctatetraene Metal Carbonyls

Protonation of $(C_8H_8)M(CO)_3$ (M = Fe, Ru, Os, Mo, W) is very interesting since many types of complexes have been obtained depending on the electronic requirements of the metal group. However, even in electronically equivalent groups protonation occurs in different ways.

Room temperature protonation of $(\eta^4\text{-}C_8H_8)Fe(CO)_3$ in H_2SO_4–CH_3COOH does not afford (η^5-cyclooctatrienyl)irontricarbonyl cation (I) as was reported[185] but (η^5-bicyclo[5.1.0]octadienyl)irontricarbonyl cation (II)[181, 182]:



The formation of (I) was however achieved by low temperature protonation of (η^4-C_8H_8)$Fe(CO)_3$.[186, 187] At –60° C (I) undergoes electrocyclic ring closure to (II) by a clean first-order reaction ($k = 3 \times 10^{-4}$ sec^{-1}, $\Delta F^{+} = 15.7$ Kcal/mol; Figure 33):*



The pmr spectrum of the mixture of the substituted bicyclo[5.1.0]trienyl complexes is fully in accord with the proposed mechanism.

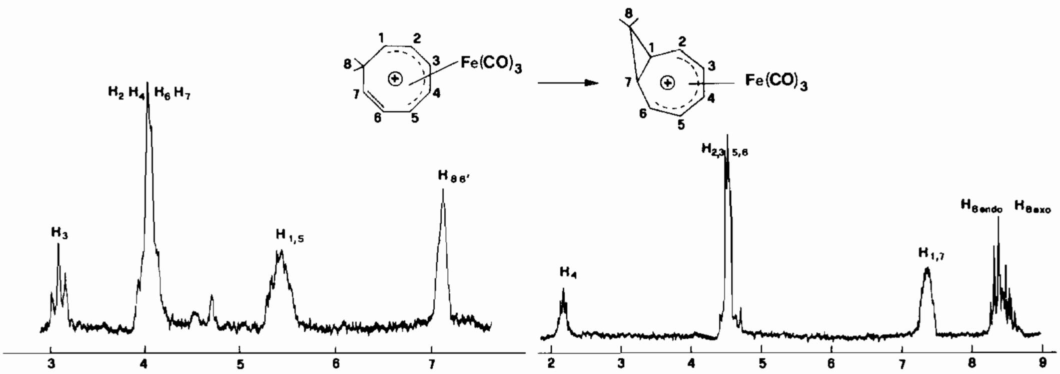


Figure 33. Electrocyclic ring closure in $(C_8H_9)Fe(CO)_3^+$.

The site of protonation of (η^4-C_8H_8)$Fe(CO)_3$ is at C-6 and C-7, as proven by analogy with protonation of (η^4-CH_3-C_8H_7)$Fe(CO)_3$ which is suitable for differentiation of the sites of protonation. The occurrence of the only isomers I and II is in agreement with the equivalence of the C-6 and C-7 positions in cyclooctatetraeneirontricarbonyl. Protonation of the methylcyclooctatetraene-$Fe(CO)_3$ complex is reported in the following scheme:

When $(C_8H_8)Ru(CO)_3$ is protonated in H_2SO_4 the first product which is formed is tricarbonyl(bicyclo [5.1.0]octadienium)ruthenium (I).[188] Isomerization to II takes then place slowly in H_2SO_4, rapidly if HPF_6 in Et_2O/H_2O is the protonating agent. I can be isolated by immediate precipitation with ether as fluoroborate salt if HBF_4/Ac_2O is used for the protonation.

The pmr spectrum of II is consistent either with a η^5-1,4,5,6,7(IIa) or η^5-1,2,5,6,7(IIb) cyclic structure:

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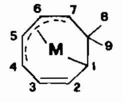
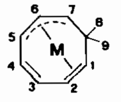
* (Bicyclo[5.1.0]octadienyl)$Fe(CO)_3$ undergoes a series of regio- and stereospecific additions at C_1, C_2, or C_3 depending on the type of nucleophile; R. Aumann, *J. Organomet. Chem.*, *78*, C31 (1974), and references therein.



IIa



IIb

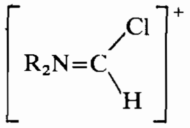
$M=Ru(CO)_3^+$

The similar $(C_8H_8)Os(CO)_3$ complex displays the same behaviour as the ruthenium analog upon protonation. In this case, however, no separation of the two types of products has been obtained.

3. *Formylation*

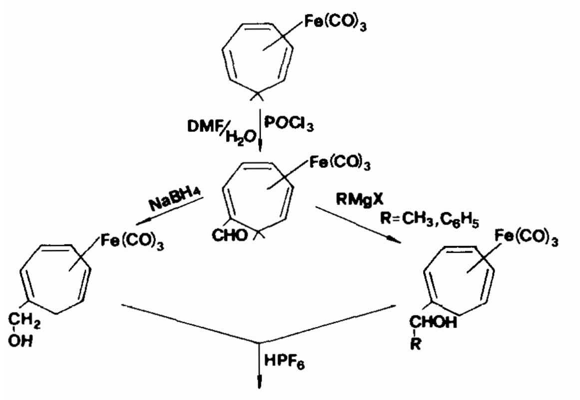
A series of reactions have been carried out on the organic unit of cyclic polyolefin complexes of metal carbonyls. The reactivity of cyclic polyolefins towards electrophilic substitution is usually markedly affected by coordination of a metal carbonyl group and this fact can be used as a simple way to synthesize substituted polyolefins. The free organic derivative is usually obtained easily by reaction with $(NH_4)_2Ce(NO_3)_6$.[189]

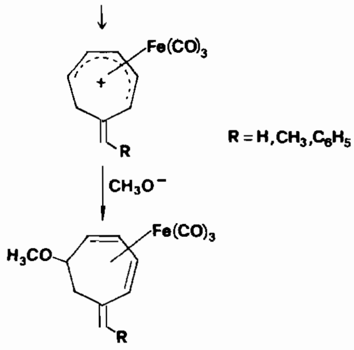
Both (cyclooctatetraene)- and (cycloheptatriene) irontricarbonyl can be formylated by $POCl_3$ in DMF/H_2O.[17, 190–192] The reaction must occur with the same mechanism with both complexes: it involves a primary attack by a carbonium ion



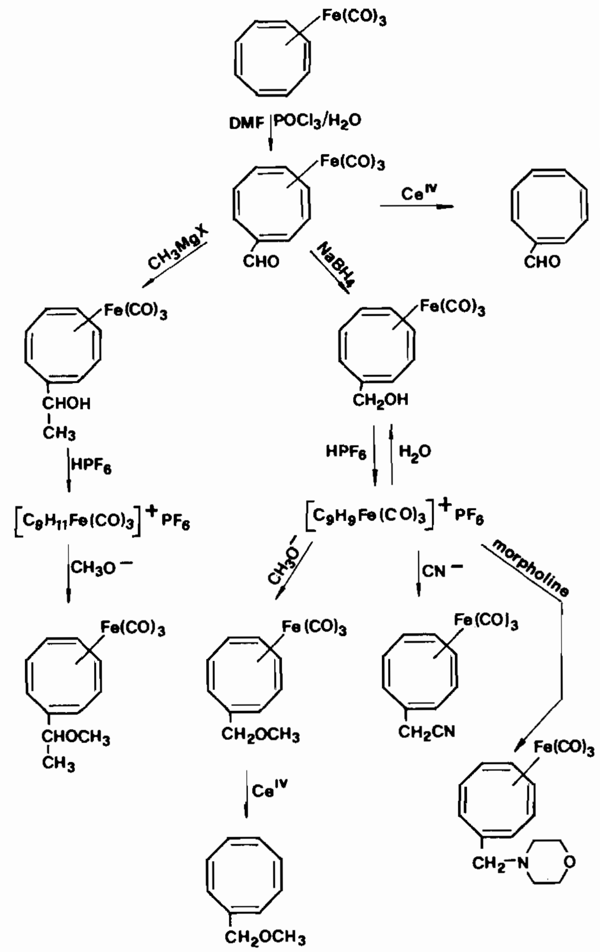
$$\left[R_2N{=}C\begin{matrix}Cl\\H\end{matrix}\right]^+$$

followed by hydrolysis of the Vilsmeyer-type salt.[192] The same (formyl-cycloheptatriene)$Fe(CO)_3$ complex has been obtained in the thermal rearrangement of $(COTOX)Fe_2(CO)_6$[101]. The rate of the reaction is however much faster in the case of the cyclooctatetraene complex.[192] The reactivity of the aldehydo group is as expected and is reported in the following scheme:[17]



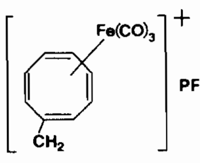


The substituted cycloheptatriene organic unit cannot be obtained by Ce^{IV} oxidation of the corresponding $Fe(CO)_3$ complex. This is very likely due to the instability of the cycloheptatriene compounds in the reaction medium:

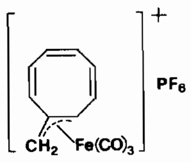


The formyl-cyclooctatetraene complex is fluxional as other monosubstituted COT complexes.[192] Its pmr spectrum at room temperature is indeed very simple and inconsistent with its instantaneous structure.

The cationic complex $[(C_9H_9)Fe(CO)_3]^+$ deserves further comments since its reaction with nucleophiles such as CH_3O^- leads to formation of the ether, suggesting a higher reactivity of the *exo*cyclic methylene group with respect to the ring.[192] The impossibility of obtaining the pmr spectrum of this salt allows only speculations about its configuration:



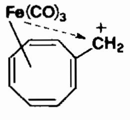
A



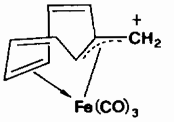
B

Structure A can be stabilized by coordination of the metal carbonyl unit to the carbonium ion (2A). The allyl configuration in which the metal is two electrons short of the noble gas configuration can be explained less easily.

Further coordination (2B) to a double bond of COT could explain the stability of the complex but not its reactivity at the *exo*cyclic methylene.



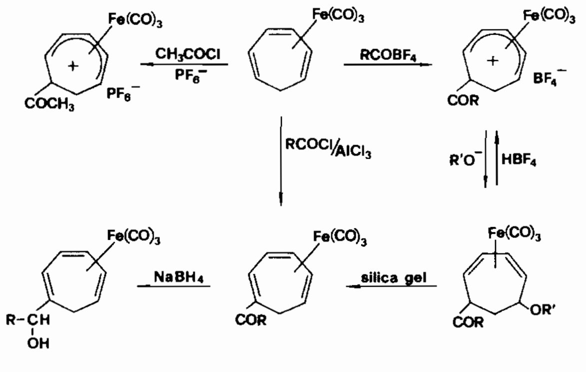
2A



2B

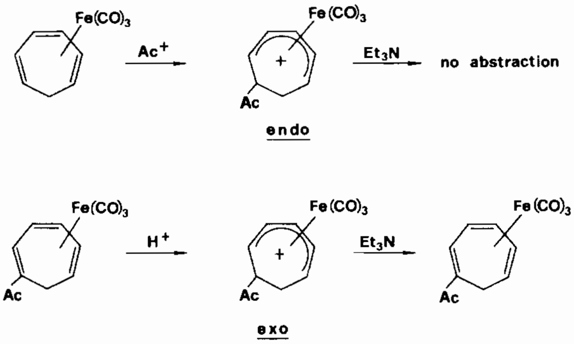
4. *Acetylation*

Acetyl chloride in the presence of $AlCl_3$ has been found to promote acetylation of cycloheptatriene-[17,190] and cyclooctatetraene-$Fe(CO)_3$ complexes.[191,192] In both cases the acetylation occurs with electrophilic addition to give cationic complexes and substitution reactions to give neutral substituted complexes:



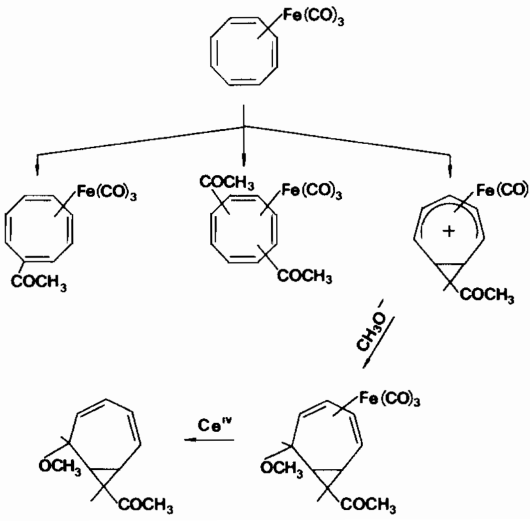
R = CH_3 or C_6H_5
R' = H or CH_3

Only cationic complexes, however, have been isolated in the reaction of (cycloheptatriene)$Fe(CO)_3$ with acyl tetrafluoroborates.[17] Further reaction with methoxide ion gives neutral complexes from which the CH_3O^- group can be easily eliminated. Thus, high yields of the substituted acyl derivatives can be achieved. As for the stereochemistry of the reaction it is important to notice that the cationic complex obtained with both reagents is in the *endo* configuration with respect to proton and it is not an intermediate to the acyl complex. The *endo* proton, in fact, is not abstracted by reaction with Et_3N whereas the elimination is easily achieved from the *exo* isomer obtained in the protonation of the acyl derivative:



The fact that both neutral and cationic complexes have been obtained in the acetylation in the presence of $AlCl_3$ can be related to the high degree of covalent character of the $AlCl_3$ adduct which allows substitution to take place.

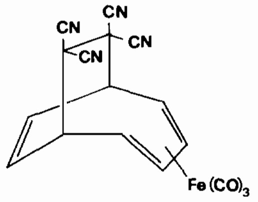
Similar products are obtained on acetylation of (COT)$Fe(CO)_3$ with $AlCl_3$–CH_3COCl. Three products are obtained:[192]

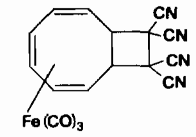


The bicyclic configuration of the cationic complex has been confirmed by double irradiation experiments of its pmr spectrum and by further reaction with OCH_3^-.

5. Addition of Dienophiles

The reaction of (η^4-cyclooctatetraene)irontricarbonyl with a very strong dienophile such as tetracyanoethylene (TCNE)[53, 140, 181, 182] has been known for a long time and two structures had been proposed:[182, 193]





The X-ray structure determination of the similar adduct (η^4-cycloheptatriene)Fe(CO)$_3$ with TCNE has, however, re-opened the question of the bonding of TCNE to coordinated cyclic polyolefins[194, 195] (Figure 34):

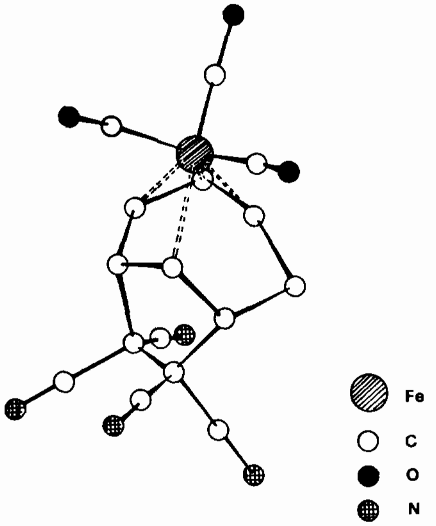
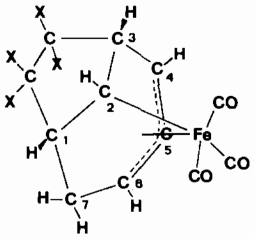


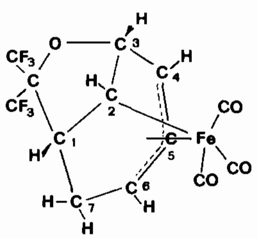
Figure 34. Molecular structure of $(C_7H_8)Fe(CO)_3 \cdot TCNE$.

The complex has a novel (η^4-1,2,3,5)-bonded system. This statement is based on the similar distance of the iron atom from C_1, C_2, C_3, C_5 than on the lengths of C_1–C_2 and C_2–C_3 bonds (0.02 Å standard deviation). It must be pointed out that TCNE attacks $(C_7H_8)Fe(CO)_3$ in the *exo*-position.*

Similar reaction of (η^4-C_7H_8)Fe(CO)$_3$ with other dienophiles including hexafluoroacetone, 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene, and 1,2-dicyano-1,2-bis(trifluoromethyl)ethylene gives adducts which can be safely formulated as the above TCNE adduct on the basis of the similarity of pmr spectra:[198]



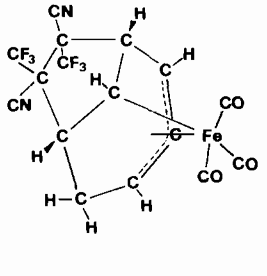
I: X = CN
II: X = CF_3



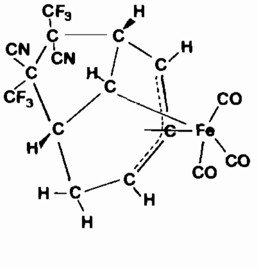
III

The reaction of $(C_7H_8)Fe(CO)_3$ with *trans*-1,2-dicyano-1,2-bis(trifluoromethyl)ethylene yields a mixture of two compounds (1:1.5 ratio, A, B) corresponding to a *cis* or trans position of a cyano group to the methylene group.

In addition to these isomers a mixture of *cis* and *trans* (1:3) 1,2-dicyano-1,2-bis(trifluoromethyl)ethylene gives a third isomer (C). The ratio of A, B to C remains 3:1 suggesting no change in the stereochemistry of the reacting olefin:



A



B

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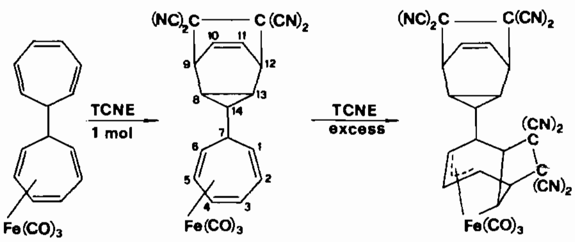
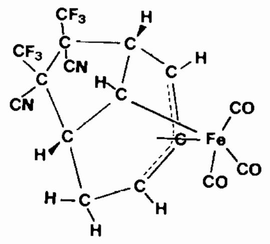
* A comparative study on the reactivity of TCNE with cycloheptatriene coordinated and non-coordinated to iron tricarbonyl shows that the presence of Fe(CO)$_3$ disactivates the ring.[196] The first attack of TCNE is on the uncoordinated cycloheptatriene unit of ditropylirontricarbonyl, whereas excess of TCNE undergoes reaction on the coordinated ring:

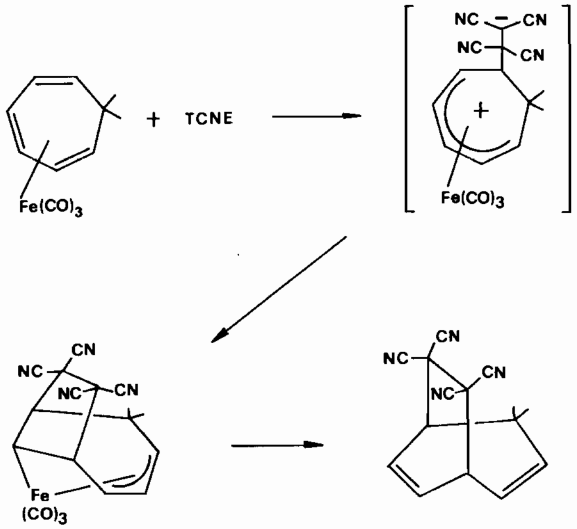


Both additions occur in the position which has been found in the reaction of TCNE with cycloheptatriene (1–4 addition)[197] and with its iron tricarbonyl complex (1–3 addition).[194]

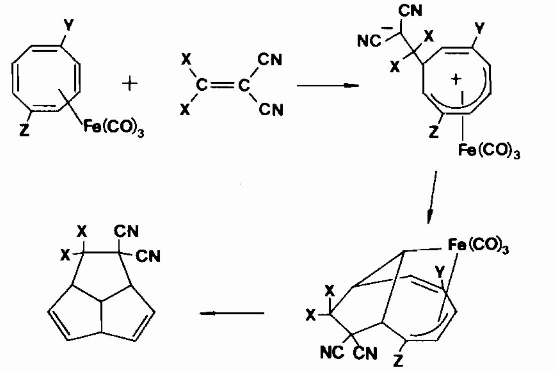


C

Thus, it appears that the presence of the metal carbonyl allows isolation of compounds containing novel types of coordination. The same conclusion was reached on the basis of the oxidative degradation of the (C_7H_8) Fe$(CO)_3$TCNE adduct with Ce(IV) salts.[199] The isolation of 8,8,9,9-tetracyanobicyclo[3.2.2]nona-2,5-diene is consistent with the above formulation of the TCNE adduct and suggests the formation of a zwitterionic intermediate:[198, 199]



A similar mechanism can be proposed for the reaction of (η^4-COT)Fe$(CO)_3$ with TCNE and other electronegative olefins:

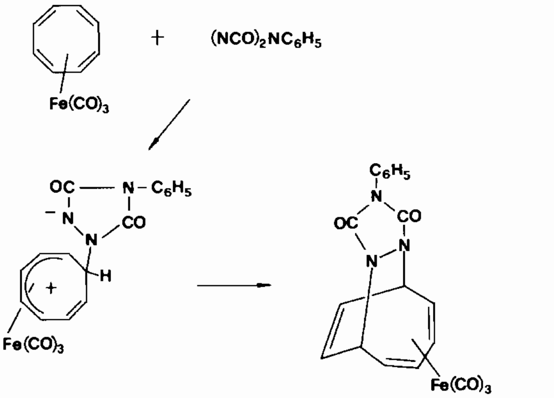


X	Y	Z
CF_3 or CN	H	H
	H	CH_3
	Br	H
	C_6H_5	H

The results are consistent with the substitution described in the scheme[198] and with the oxidative degradation of the TCNE adduct which affords 8,8,9,9-tetracyanotricyclo[5.2.1$0^{4,10}$]deca-2,5-diene.

The X-ray crystal and molecular structure[200] of the (methyl-COT)Fe$(CO)_3$TCNE adduct confirms the proposed configuration.

Another strong dienophile has been used in the reaction with (η^4-cyclooctatetraene)irontricarbonyl, *i.e.* 4-phenyl-1,2,4-pirazoline-3,5-dione.[193, 198] If also in this case a dipolar intermediate is assumed, ring closure must occur in such a way as to form an 1–4 adduct in contrast with the 1–3 adduct which occurs with the electronegatively substituted olefins:



6. Reactions on Coordinated Metals

A. Substitution Reactions

In the series of polyolefin metal carbonyl complexes, reactions with neutral ligand like phosphines, phosphites or phosphine oxide, involve substitution of the polyolefin. These reactions have been used to prepare mixed complexes of the type *cis*-M$(CO)_3L_3$ (M = Cr, Mo, W; L = PR_3, $P(OR)_3$ or R_3PO) or complexes of the type *trans*-M$(CO)_3L_2$ or M$(CO)_3$(L–L) (M = Fe, Ru, L = PR_3 or $P(OR)_3$, L–L = chelating diphosphine):[201–203]

$$1)\ (C_7H_8)M(CO)_3 + 3L \xrightarrow[M\,=\,Cr,\ Mo,\ W]{-C_7H_8} cis\text{-}M(CO)_3L_3 + C_7H_8$$

$$2)\ (C_8H_{10})Fe(CO)_3 + 3L \xrightarrow[M\,=\,Fe]{-C_8H_{10}} trans\text{-}M(CO)_3L_2$$

$$3)\ (C_8H_8)M(CO)_3 + 2L \xrightarrow[M = Fe, Ru]{-C_8H_8} trans\text{-}M(CO)_3L_2$$

$$4)\ (C_8H_8)M(CO)_3 + L\text{–}L \xrightarrow[M = Fe, Ru]{-C_8H_8} cis\text{-}M(CO)_3(L\text{–}L)$$

Some of the above reactions have been investigated in details. The rate determining step of reaction 1 with M = Cr, Mo and W and L = $(CH_3O)_3P$ appears to be a bimolecular S_N2 process involving the complex and the phosphite.[204]

Kinetic measurements on the reaction of $(C_8H_8)M(CO)_3$ (M = Fe, Ru[205,206]) with monodentate and bidentate phosphines suggest again a S_N2 process, leading to a labile intermediate *A*, and followed by rapid elimination of the polyolefin:

$$\begin{array}{c}(C_8H_8)M(CO)_3 + L \xrightarrow{k_2} (C_8H_8)M(CO)_3L \\ \phantom{(C_8H_8)M(CO)_3 + L \xrightarrow{k_2}} A \\ {\scriptstyle +L}\big\downarrow{\scriptstyle \text{fast}} \\ trans\text{-}M(CO)_3L_2 + C_8H_8\end{array}$$

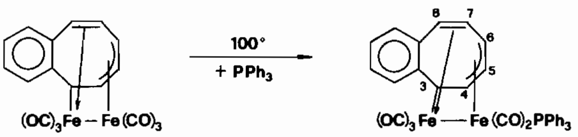
This mechanism is favoured in respect to a fast pre-equilibrium step between L and the substrate followed by the rate-determining release of C_8H_8 since the highly negative values of activation entropy (see table III) imply a decrease of some degrees of freedom in the formation of the transition state.

The higher reactivity for the ruthenium derivative as compared to the iron analog originates from a less negative activation entropy which offsets the slightly higher activation enthalpy. When L = $E(C_6H_5)_3$ (E = As or Sb), substitution of one carbonyl group instead of the polyolefin readily occurs.[3] Thus, the following pathway has been verified, at least for (cyclooctatetraene)$Fe(CO)_3$:

$$(C_8H_8)Fe(CO)_3 \xrightarrow{+L} \left\{\begin{array}{l} \xrightarrow{L = PPh_3} Fe(CO)_3(PPh_3)_2 + C_8H_8 \\ \\ \xrightarrow[E = As, Sb]{L = EPh_3} (C_8H_8)Fe(CO)_2(EPh_3) + CO \end{array}\right.$$

The ruthenium analog gives a similar complex $Ru(CO)_3[P(OCH_2)_3CEt]_2$ with $P(OCH_2)_3CEt$[70] whereas dimeric species of the type $[Ru(CO)_3I_2]_2$ or $[Ru(CO)_3(HgX)X]_2$ have been obtained by reaction with I_2 and HgX_2 (X = Cl, Br or SCN) respectively.

Particularly interesting is the reaction of (benzocyclooctatetraene)$Fe_2(CO)_6$ with PPh_3:[91]



The phosphine enters the iron farthest from the benzene ring since P–H coupling is evident with $H_{5,6}$ but not with $H_{3,8}$. The equivalence of these two protons in the room temperature pmr suggests that also this molecule contains a time-averaged simmetry plane. However, the low solubility of the complex prevented low temperature studies.

$(C_8H_{10})Fe(CO)_3$ undergoes breaking of the metal–carbon bonds when reacted with phosphine; the already discussed $Fe(CO)_3(PPh_3)_2$ is obtained.[20]

B. Absorption or Release of CO

We have already described that some complexes which contain $M_2(CO)_6$ (M = Fe or Ru) easily lose one mol of CO to give the more stable complexes of the type $(COT)M_2(CO)_5$:[71,78]

$$cis\text{-}(COT)M_2(CO)_6 \rightarrow (COT)M_2(CO)_5 + CO$$

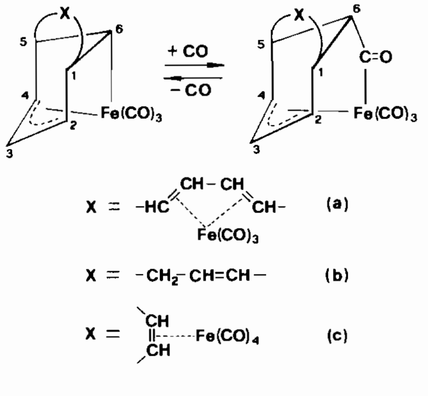
Other examples of release of CO are well documented but since they involve also rearrangement of the polyolefin they have been discussed in the relative section.

Complexes of iron carbonyls bonded to the vinyl-

TABLE III. Activation Parameters for Reactions of $(C_8H_8)M(CO)_3$ with Phosphorus(III) Ligands.

Compound	Ligand	$\Delta H^{\neq}$ (Kcal/mol)	$\Delta S^{\neq}$ (e.u.)	Ref.
$(C_8H_8)Fe(CO)_3$	$P(n\text{-}C_4H_9)_3$	11.4	–38.1	205
$(C_8H_8)Ru(CO)_3$	$P(n\text{-}C_4H_9)_3$	14.5	–23.7	206
$(C_8H_8)Fe(CO)_3$	$(C_6H_5)_2PC_2H_4P(C_6H_5)_2$	14.3	–30.3	205
$(C_8H_8)Ru(CO)_3$	$(C_6H_5)_2PC_2H_4P(C_6H_5)_2$	17.1	–18.2	206

cyclopropane ring of cyclic polyolefins undergo CO insertion reversibly.[173, 207] Thus:



In the of case x = a or b the above reaction occurs at room temperature, whereas when X = c only at 70° C does the reaction occur but then it involves release of $Fe(CO)_4$ group. The insertion of CO shifts downfield the signal of H_6 and reduces the coupling constants $J_{1,6}$, $J_{5,6}$ and $J_{1,2}$ suggesting an increase of the angle $2\ \hat{1}\ 6$ and $4\ \hat{5}\ 6$.

The above reactions (a and b systems) can be reversed by heating the product in hexane.

V. References

1 E.O. Fischer and H. Werner, *Angew. Chem. Int. Ed., 2,* 80 (1963).

2 R. Burton, M.L.H. Green, E.W. Abel and G. Wilkinson, *Chem. Ind.* (London), 1592 (1958).

3 T.A. Manuel and F.G.A. Stone, *J. Am. Chem. Soc., 82,* 366 (1960).

4 R. Burton, L. Pratt and G. Wilkinson, *J. Chem. Soc.,* 594 (1961).

5 L. Kruczynski and J. Takats, *J. Am. Chem. Soc., 96,* 932 (1974).

6 F.A. Cotton, V.W. Day, B.A. Frenz, K.I. Hardcastle and J.M. Troup, *J. Am. Chem. Soc., 95,* 4522 (1973) and references therein.

7 H.J. Dauben, Jr. and D.J. Bertelli, *J. Am. Chem. Soc., 83,* 497 (1961).

8 G.F. Emerson, J.E. Mahler, R. Pettit and R. Collins, *J. Am. Chem. Soc., 86,* 3590 (1964).

9 F.A. Cotton, B.G. De Boer, and T.J. Marks, *J. Am. Chem. Soc., 93,* 5069 (1971).

10 For a review on fluxional behaviour see: F.A. Cotton, *Accounts Chem. Res., 1,* 283 (1968).

11 G. Deganello, *J. Organomet. Chem., 59,* 329 (1973).

12 A.J.P. Domingos, B.F.G. Johnson and J. Lewis, *J. Organomet. Chem., 49,* C33 (1973).

13 R. Bau, J.C. Burt, S.A.R. Knox, R.M. Laine, R.P. Phillips and F.G.A. Stone, *Chem. Comm.,* 726 (1973).

14 T.H. Whitesides and R.A. Budnik, *Chem. Comm.,* 302 (1974).

15 A. Brookes, J. Howard, S.A.R. Knox, V. Riera and F.G.A. Stone, *Chem. Comm.,* 727 (1973).

16 J.E. Mahler, D.A.K. Jones and R. Pettit, *J. Am. Chem. Soc., 86,* 3589 (1964).

17 B.F.G. Johnson, J. Lewis, P. McArdle and G.L.P. Randall, *J.C.S. Dalton,* 456 (1972).

18 D.J. Bertelli and J.M. Viedrock, *Inorg. Chem., 7,* 1240 (1968).

19 W. Hübel and E. Weiss, *Ber., 95,* 1179 (1962).

20 R.B. King, *Inorg. Chem., 2,* 807 (1963).

21 A. Eisenstadt and S. Winstein, *Tetrahedron Letters,* 613 (1971).

22 W. Hübel and E. Weiss, *Chem. and Ind.,* 703 (1959).

23 D.L. Smith and L.F. Dahl, *J. Am. Chem. Soc., 84,* 1744 (1962).

24 R.P. Dodge, *J. Am. Chem. Soc., 86,* 5429 (1964).

25 D.J. Ehntholt, G.F. Emerson and R.C. Kerber, *J. Am. Chem. Soc., 91,* 7547 (1969).

26 R.C. Kerber and D.J. Ehntholt, *J. Am. Chem. Soc., 95,* 2927 (1973).

27 M.R. Churchill and J.P. Fennesey, *Chem. Comm.,* 1056 (1970).

28 E.O. Fischer and K. Fichtel, *Ber., 94,* 1200 (1961).

29 M.R. Churchill and B.G. DeBoer, *Inorg. Chem., 12,* 525 (1973).

30 a) G.T. Rodeheaver, G.C. Farrant and D.F. Hunt, *J. Organomet. Chem., 30,* C22 (1971);
b) B.F.G. Johnson, J. Lewis, P. McArdle and G.L.P. Randall, *J.C.S. Dalton,* 2076 (1972); *Chem. Comm.,* 177 (1971).

31 R. Mason, Special Lecture presented at XXIII I.U.P.A.C., Boston, 26–30 July 1971, Vol 6, pag. 31.

32 J.A.S. Howell, B.F.G. Johnson, P.L. Josty and J. Lewis, *J. Organomet. Chem., 42,* 329 (1972).

33 R. Burton, L. Pratt and G. Wilkinson, *J. Chem. Soc.,* 4290 (1960).

34 M.R. Churchill, *Progr. Inorg. Chem., 11,* 53 (1970).

35 R.B. King, *J. Am. Chem. Soc., 88,* 2075 (1966).

36 M.R. Churchill and P.H. Bird, *J. Am. Chem. Soc., 90,* 3241 (1968).

37 M.R. Churchill, *Inorg. Chem., 6,* 190 (1967); *Chem. Comm.,* 450 (1966).

38 M.R. Churchill and P.H. Bird, *Inorg. Chem., 8,* 1941 (1969).

39 M.R. Churchill and P.H. Bird, *J. Am. Chem. Soc., 90,* 800 (1968).

40 M.R. Churchill, K. Gold and P.H. Bird, *Inorg. Chem., 8,* 1956 (1969).

41 M.R. Churchill and F.R. Sholer, unpublished results quoted in ref. 42 and 43.

42 M.R. Churchill, F.R. Sholer and J. Wormald, *J. Organomet. Chem., 28,* C21 (1971).

43 M.R. Churchill and J. Wormald, *Inorg. Chem., 12,* 191 (1973).

44 J.L. Rosemberg, J.E. Mahler and R. Pettit, *J. Am. Chem. Soc., 84,* 2842 (1962).

45 T.A. Manuel and F.G.A. Stone, *J. Am. Chem. Soc., 82,* 6240 (1960).

46 A. Nakamura and N. Hagihara, *J. Chem. Soc. Japan, 82,* 1389 (1961).

47 W. McFarlane, L. Pratt and G. Wilkinson, *J. Chem. Soc.,* 2162 (1963).

48 G. Deganello, unpublished data.

49 F.A. Cotton and W.T. Edwards, *J. Am. Chem. Soc., 91,* 843 (1969).

50 F.A. Cotton and T.J. Marks, *J. Organomet. Chem., 19,* 237 (1969).

50a A.C. Szary, S.A.R. Knox and F.G.A. Stone, *J.C.S. Dalton,* 662 (1974).

51 A. Nakamura and N. Hagihara, *Bull. Chem. Soc. Japan, 32,* 881 (1959).

52 T.A. Manuel and F.G.A. Stone, *Proc. Chem. Soc.,* 90 (1959).

53 M.D. Rausch and G.N. Schrauzer, *Chem. and Ind.,* 957 (1959).

54 R. Grubbs, R. Breslow, R. Herber and S.J. Lippard, *J. Am. Chem. Soc., 89,* 6864 (1967).

55 F.A. Cotton, *J. Chem. Soc.,* 400 (1960).

56 D.A. Brown, *J. Inorg. Nucl. Chem., 10,* 39 (1959).

57 B. Dickens and W.N. Lipscomb, *J. Am. Chem. Soc., 83,* 4062 (1961).

58 B. Dickens and W.N. Lipscomb, *J. Chem. Phys., 37,* 2084 (1962).

59 R.T. Bailey, E.R. Lippincott and D. Steele, *J. Am. Chem. Soc., 87,* 5346 (1965).

60 A. Davison, W. McFarlane, L. Pratt and G. Wilkinson, *Chem. and Ind.,* 553 (1961).

61 H.P. Fritz and H. Keller, *Ber., 95,* 158 (1962).

62 H.P. Fritz, *Ber., 95,* 820 (1962).

63 C.G. Kreiter, A. Maasbol, F.A.L. Anet, H.D. Kaesz and S. Winstein, *J. Am. Chem. Soc., 88,* 3444 (1966).

64 F.A. Cotton, A. Davison and J.W. Faller, *J. Am. Chem. Soc., 88,* 4507 (1966).

65 C.E. Keller, B.A. Shoulders and R. Pettit, *J. Am. Chem. Soc., 88,* 4760 (1966).

66 F.A.L. Anet, H.D. Kaesz, A. Maasbol and S. Winstein, *J. Am. Chem. Soc., 89,* 2489 (1967).

67 F.A.L. Anet, *J. Am. Chem. Soc., 89,* 2491 (1967).

68 G. Rigatti, G. Boccalon, A. Ceccon and G. Giacometti, *Chem. Comm.,* 1165 (1972).

69 M.I. Bruce, M. Cooke, M. Green and F.G.A. Stone, *Chem. Comm.,* 523 (1967).

70 M.I. Bruce, M. Cooke and M. Green, *J. Organomet. Chem., 13,* 227 (1968).

71 F.A. Cotton, A. Davison and A. Musco, *J. Am. Chem. Soc., 89,* 6796 (1967).

72 W.K. Bratton, F.A. Cotton, A. Davison, A. Musco and J.W. Faller, *Proc. Natl. Acad. Sci. U.S., 58,* 1324 (1967).

73 F.A. Cotton and R. Eiss, *J. Am. Chem. Soc., 91,* 6593 (1969).

74 F.A. Cotton, A. Davison, T.J. Marks and A. Musco, *J. Am. Chem. Soc., 91,* 6598 (1969).

75 M.I. Bruce, M. Cooke, M. Green and D.L. Westlake, *J. Chem. Soc. (A),* 987 (1969).

76 M.I. Bruce, M. Cooke and M. Green, *Angew. Chem. Int. Ed., 7,* 639 (1968).

77 M. Cooke, R.J. Goodfellow, M. Green, J.P. Maher and J.R. Yandle, *Chem. Comm.,* 565 (1970).

78 C.E. Keller, C.F. Emerson and R. Pettit, *J. Am. Chem. Soc., 87,* 1388 (1965).

79 E.B. Fleischer, A.L. Stone, R.B.K. Dewar, J.D. Wright, C.E. Keller, and R. Pettit, *J. Am. Chem. Soc., 88,* 3158 (1966).

80 E.W. Abel and S. Moorhouse, *Inorg. Nucl. Chem. Letters, 6,* 621 (1970).

81 B. Dickens and W.N. Lipscomb, *J. Am. Chem. Soc., 83,* 489 (1961).

82 G.K. Wertheim and R.H. Herber, *J. Am. Chem. Soc., 84,* 2274 (1962).

83 F.A. Cotton and W.T. Edwards, *J. Am. Chem. Soc., 90,* 5412 (1968).

84 M.J. Bennett, F.A. Cotton and P. Legzdins, *J. Am. Chem. Soc., 90,* 6335 (1968); *89,* 6797 (1967).

85 A.J. Campbell, C.A. Fyfe and E. Maslowsky, Jr., *J. Am. Chem. Soc., 94,* 2690 (1972); *Chem. Comm.,* 1032 (1971).

86 C.A. Fyfe, "Advances in Molecular Complexes", Vol. 1, R. Foster Ed., Logos Press, London.

87 C.E. Cottrell, C.A. Fyfe and C.V. Senoff, *J. Organomet. Chem., 43,* 203 (1972).

88 A. Carbonaro and A. Greco, *J. Organomet. Chem., 25,* 477 (1970).

89 I.W. Bassi and R. Scordamaglia, *J. Organomet. Chem., 37,* 353 (1972).

89a R.R. Schrock and J. Lewis, *J. Am. Chem. Soc., 95,* 4102 (1973).

90 J.A. Elix and M.W. Sargent, *J. Am. Chem. Soc., 91,* 4734 (1969).

91 H.W. Withlock, Jr. and H. Stucki, *J. Am. Chem. Soc., 94,* 8594 (1972).

92 F.A. Cotton and A. Musco, *J. Am. Chem. Soc., 90,* 1444 (1968).

93 F.A. Cotton, J.W. Faller and A. Musco, *J. Am. Chem. Soc., 88,* 4506 (1966).

94 F.A. Cotton, J.W. Faller and A. Musco, *J. Am. Chem. Soc., 90,* 1438 (1968).

95 F.A. Cotton and M.D. La Prade, *J. Am. Chem. Soc., 90,* 2026 (1968).

96 G. Deganello, A. Maltz and J. Kozarich, *J. Organomet. Chem., 60,* 323 (1973).

97 G. Deganello,·unpublished data.

98 G. Deganello, G. Carturan and P. Uguagliati, unpublished results.

99 G. Deganello and G. Carturan, unpublished results.

100 J. Takats, personal communication.

101 H. Maltz and G. Deganello, *J. Organomet. Chem., 27,* 383 (1971).

102 F.A. Cotton and G. Deganello, *J. Am. Chem. Soc., 94,* 2142 (1972).

103 F.A. Cotton and G. Deganello, *J. Am. Chem. Soc., 95,* 396 (1973).

104 F.A. Cotton and G. Deganello, *J. Organomet. Chem., 38,* 147 (1972).

105 F.A. Cotton, H. Frenz, G. Deganello and A. Shaver, *J. Organomet. Chem., 50,* 227 (1973).

106 O.A. Gansow, A.R. Burke and W.D. Vernon, *J. Am. Chem. Soc., 94,* 2550 (1972).

107 a) F.A. Cotton *et al.,* personal communication, in press.

107 b) J. Takats, G. Deganello, *et al.,* manuscript in preparation.

108 G. Wilke, *Angew. Chem. Int. Ed., 2,* 105 (1963).

109 H. Breil, P. Heimbach, M. Kröner, H. Müller and G. Wilke, *Makromol. Chem., 69,* 18 (1963).

110 R.G. Solomon and J.K. Kochi, *Chem. Comm.,* 559 (1972).

111 G. Paiaro, N. Neto, A. Musco and R. Palumbo, *Ric. Sci., Rend. Sez. A, 8* (6), 1441 (1965).

112 L.I. Zakharkin and V.V. Korneva, *Doklady Akad. Nauk. SSSR, 132,* 1078 (1960).

113 S. Kuribayashi, N. Yasuoka, T. Mitsui, N. Takahashi and M. Yamaguchi, *Bull. Chem. Soc. Japan, 37,* 1242 (1964).

114 K.C. Untch and D.J. Martin, *J. Am. Chem. Soc., 87,* 3518 (1965).

115 R. Hüttel, H. Reinheimer and H. Dietl, *Ber., 99,* 462 (1966).

116 H.L. Haight, J.R. Doyle, N.C. Baenziger and G.F. Richards, *Inorg. Chem., 2,* 1301 (1963).

117 B. Bogdanovic, M. Kröner and G. Wilke, *Ann., 699,* 1 (1966).

118 H. Dietrich and H. Schmidt, *Naturwiss., 52,* 301 (1965).

119 D.I. Brauer and K. Krüger, *J. Organomet. Chem., 44,* 397 (1972).

120 K. Jonas, P. Heimbach and G. Wilke, *Angew. Chem. Int. Ed., 7,* 949 (1968).

121 E. Kuljian and H. Frye, *Z. Naturforsch., 19b,* 651 (1965).

122 G. McCauley and H. Frye, *Inorg. Nucl. Chem. Letters, 4,* 21 (1968).

123 H. Weber, W. Ring, U. Hochmuth and W. Franke, *Ann., 681,* 10 (1965).

123a W. Fröhlic, *Thesis,* Univ. München, 1961.

124 a) M.I. Bruce, M.A. Cairns and M. Green, *J. C. S. Dalton,* 1293 (1972); b) M.I. Bruce, M.A. Cairns, A. Cox, M. Green, M.D.H. Smith and P. Woodward, *Chem. Comm.,* 735 (1970); c) A. Cox and P. Woodward, *J. Chem. Soc. (A),* 3599 (1971); d) R. Belford, M.I. Bruce, M.A. Cairns, M. Green, H.P. Taylor and P. Woodward, *Chem. Comm.,* 1159 (1970).

125 R. Aumann, *Angew. Chem. Intern. Ed., 10,* 190 (1971) and references therein.

126 E.P. Woo and K. Stockel, unpublished experiments quoted in ref. 127.

127 K. Stockel, F. Sondheimer, T.A. Clarke, M. Guss and R. Mason, *J. Am. Chem. Soc., 93,* 2571 (1971).

128 M. Avram, E. Sliam and C.D. Nenitzescu, *Ann., 636,* 184 (1960).

129 Y. Menachem and A. Eisenstadt, *J. Organomet. Chem., 33,* C29 (1971).

130 A. Eisenstadt, *J. Organomet. Chem., 38,* C32 (1972).

131 J.S. Ward and R. Pettit, *J. Am. Chem. Soc., 93,* 262 (1971).

132 R.B. King, *J. Am. Chem. Soc., 84,* 4705 (1962).

133 M. Brookhart, N.M. Lippman and E.J. Reardon, Jr., *J. Organomet. Chem., 54,* 247 (1973).

134 R. Huisgen, F. Mietzsch, G. Böche and H. Seidl, *Chem. Soc., Sp. Publ., 19* (1965), pp. 3–20.

135 M. Cais and N. Maoz, *J. Chem. Soc. (A),* 1811 (1971).

136 H.W. Whitlock, Jr. and R.L. Markezich, *J. Am. Chem. Soc., 93,* 5290 (1971).

137 F.A. Cotton and J. Takats, *J. Am. Chem. Soc., 90,* 2031 (1968).

138 J. Schwartz, *Chem. Comm.,* 814 (1972).

139 W. Strohmeier, *Angew. Chem. Int. Ed., 3,* 730 (1964).

140 G.N. Schrauzer and S. Eichler, *Angew. Chem. Int. Ed., 1,* 454 (1962).

141 G.N. Schrauzer, P.W. Glockner and R. Merenyi, *Angew. Chem. Int. Ed., 3,* 509 (1964).

142 G.N. Schrauzer and P.W. Glockner, *J. Am. Chem. Soc., 90,* 2800 (1968).

143 M.R. Truter, ref. 20 in ref. 142.

144 A. Robson and M.R. Truter, *Tetrahedron Letters,* 3079 (1964). *J. Chem. Soc. (A),* 794 (1968).

145 A.H.J. Wang, I.C. Paul and G.N. Schrauzer, *Chem. Comm.,* 736 (1972).

146 E.J. Reardon, Jr. and M. Brookhart, *J. Am. Chem. Soc., 95,* 4311 (1973).

147 W. Grimme, *Ber., 100,* 113 (1967).

148 G. Deganello, to be published.

149 G. Büchi and E.M. Burgess, *J. Am. Chem. Soc., 84,* 3104 (1962).

150 S.W. Staley and T.J. Henry, *J. Am. Chem. Soc., 93,* 1292 (1971).

151 F.A. Cotton, *et al.,* personal communication.

152 F.A. Cotton, B.A. Frenz and J.M. Troup, *J. Organomet. Chem., 61,* 337 (1974).

153 F.A. Cotton and J.M. Troup, *J. Am. Chem. Soc., 95,* 3798 (1973); *J. Organomet. Chem., 76,* 81, *77,* 83 (1974).

154 F.A. Cotton, B.A. Frenz, J.M. Troup and G. Deganello, *J. Organomet. Chem., 59,* 317 (1973).

155 T.J. Katz and M. Rosemberg, *J. Am. Chem. Soc., 84,* 865 (1962); T.J. Katz, M. Rosemberg and R.K. O'Hara, *J. Am. Chem. Soc., 86,* 249 (1964).

156 D.F. Hunt and J.W. Russel, *J. Organomet. Chem., 46,* C22 (1972).

157 D.F. Hunt and J.W. Russel, *J. Am. Chem. Soc., 94,* 7198 (1972).

157a D.F. Hunt and J.W. Russel, *VI ICOMC, Amherst, Comm. 13,* 1973.

158 W. Weidemüller and K. Haffner, *Angew. Chem. Int. Ed., 12,* 925 (1973).

159 G. Deganello and L. Toniolo, *J. Organomet. Chem., 74,* 255 (1974).

160 A. Brookes, J. Howard, S.A.R. Knox, F.G.A. Stone, and P. Woodward, *J. C. S., Chem. Comm.,* 587 (1973).

160a J.A.K. Howard, S.A.R. Knox, V. Riera, F.G.A. Stone, and P. Woodward, *J.C.S., Chem. Comm.,* 452 (1974).

160b J.A.K. Howard, S.A.R. Knox, F.G.A. Stone, A.C. Szary and P. Woodward, *J.C.S., Chem. Comm.,* 788 (1974).

161 S.A.R. Knox, R.P. Phillips and F.G.A. Stone, *J. C. S., Chem. Comm.,* 1227 (1972); *J.C.S. Dalton,* 658 (1974).

162 T.H. Coffield, K.G. Ihrman and W. Burns, *J. Am. Chem. Soc., 82,* 4209 (1960).

163 K.K. Joshi, R.H.B. Mais, F. Nyman, P.G. Owston and A.M. Wood, *J. Chem. Soc. (A),* 318 (1968).

164 G. Deganello, *Chim. e Ind. (Milan), 56,* 303 (1974).

165 R. Aumann, *Angew. Chem. Int. Ed., 10,* 188 (1971).

166 G. Huttner and D. Regler, *Ber., 105,* 3936 (1972).

167 G.N. Schrauzer, P. Glockner, K.I.G. Reid and I.C. Paul, *J. Am. Chem. Soc., 92,* 4479 (1970).

168 M.R. Churchill and R. Mason, *Adv. Organomet. Chem., 5,* 93 (1967).

169 R. Aumann, *Angew. Chem. Int. Ed., 10,* 189 (1971).

170 R. Aumann, *Angew. Chem. Int. Ed., 10,* 560 (1971).

171 R. Aumann, private communication (1972).

172 R.M. Moriarty, Chin-Lung Yeh and K.C. Ramey, *J. Am. Chem. Soc., 93,* 6709 (1971).

173 R. Aumann, *Angew. Chem. Int. Ed., 11,* 522 (1972).

173a D. Ehntholt, A. Rosan and M. Rosenblum, *J. Organomet. Chem., 56,* 315 (1973).

173b R. Aumann, *J. Organomet. Chem., 66,* C6 (1974).

174 T.H. Whitesides and R.A. Budnik, *Chem. Comm.,* 1514 (1971).

175 G. Winkhaus, L. Pratt and G. Wilkinson, *J. Chem. Soc.,* 2021 (1961).

176 F. Haque, J. Moller, P.L. Pauson and J.B.Pd. Tripathi, *J. Chem. Soc. (C)*, 743 (1971).
177 E.O. Fischer and R.D. Fischer, *Angew. Chem., 72,* 919 (1960).
178 D. Jones, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, 4458 (1962).
179 H. Maltz and B.A. Kelly, *Chem. Comm.,* 1390 (1971).
180 L. Kruczynski, L. Shing Man and J. Takats, *VI ICOMC, Amherst, Comm. 6,* 1973.
181 A. Davison, W. McFarlane and G. Wilkinson, *Chem. and Ind.,* 820 (1962).
182 A. Davison, W. McFarlane, L. Pratt and G. Wilkinson, *J. Chem. Soc.,* 4821 (1962).
183 M.R. Churchill and F.R. Scholer, *Inorg. Chem., 9,* 1950 (1969).
184 D.F. Hunt, G.C. Farrant and G.T. Rodeheaver, *J. Organomet. Chem., 38,* 349 (1972).
185 G.N. Schrauzer, *J. Am. Chem. Soc., 83,* 2966 (1961).
186 M. Brookhart and E.R. Davis, *J. Am. Chem. Soc., 92,* 7622 (1970).
187 M. Brookhart, E.R. Davis and D.L. Harris, *ibid., 94,* 7853 (1972).
188 M. Cooke, P.T. Draggett, M. Green, B.F.G. Johnson, J. Lewis and D.J. Yarrow, *Chem. Comm.,* 621 (1971).
189 L.A. Paquette and L.D. Wise, *J. Am. Chem. Soc., 89,* 6659 (1967).
190 B.F.G. Johnson, J. Lewis and G.L.P. Randall, *Chem. Comm.,* 1273 (1969).
191 B.F.G. Johnson, J. Lewis, A.W. Parkins and G.L.P. Randall, *ibid.,* 595 (1969).
192 B.F.G. Johnson, J. Lewis and G.L.P. Randall, *J. Chem. Soc. (A),* 422 (1971).
193 M. Green and D.C. Wood, *ibid.,* 1172 (1969).
194 M. Green, S. Tolson, J. Weaver, D.C. Wood and P. Woodward, *Chem. Comm.,* 222 (1971).
195 J. Weaver and P. Woodward, *J. Chem. Soc. (A).,* 3521, (1971).
196 P. McArdle, *J.C.S., Chem. Comm.*, 482 (1973).
197 G.H. Wahl, *J. Org. Chem., 33,* 2158 (1968).
198 M. Green, S. Heathcock and D.C. Wood, *J. Chem. Soc. (Dalton),* 1564 (1973).
199 D.J. Ehntholt and R.C. Kerber, *J. Organomet. Chem., 38,* 139 (1972).
200 J. Weaver and P. Woodward, ref. 15 in ref. 198.
201 E.W. Abel, M.A. Bennett and G. Wilkinson, *J. Chem. Soc.,* 2323 (1959).
202 F.A. Cotton and F. Zingales, *Chem. and Ind.,* 1219 (1960).
203 L. Chandrasegaran and G.A. Rodley, *Inorg. Chem., 4,* 1360 (1965).
204 A. Pidcock and B.W. Taylor, *J. Chem. Soc. (A),* 877 (1967).
205 F. Faraone, F. Zingales, P. Uguagliati and U. Belluco, *Inorg. Chem., 7,* 2362 (1968).
206 F. Faraone, F. Cusmano and R. Pietropaolo, *J. Organomet. Chem., 26,* 147 (1971).
207 R. Aumann, *ibid., 47,* C29 (1973) and references therein.