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BINUCLEAR COMPLEXES OF TRANSITION METALS WITH A COMMON UNSATURATED LIGAND

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CONTENTS

I. INTRODUCTION

The rapid development of the chemistry of complex compounds has clearly demonstrated that an organic ligand coordinated to a transition metal atom behaves in a very different manner from the free ligand (see, for example refs. 1, 2). Thus, some reactions of coordinated ligands have been used as the basis for important industrial catalytic processes such as oxosynthesis etc. Coordination of an unsaturated ligand simultaneously to two transition metal atoms may have an even greater effect upon its properties and with this in mind the chemistry of such binuclear complexes is of considerable interest as it may lead to a number of unexpected discoveries.

Among binuclear complexes with a common organic ligand those containing metal-metal bonds (M–M) are of specific interest and will be discussed in this review. From the data available from the literature, it is obvious that a large variety of binuclear complexes with a common unsaturated ligand have been synthesized to date. However, since they have quite often been obtained purely by chance the data regarding their preparation are scattered and not easily available to chemists interested in this particular field. In this review the literature on this subject is discussed systematically and certain generalizations are made with respect to the effects of the geometry and character of the unsaturated ligand upon the length of the M–M bond. We have, however, confined the discussion to those complexes in which the bimetallic group is bound to an organic ligand via the carbon atom.

From the basis of the nature of the metal–ligand bond, bimetallic complexes with a common unsaturated organic ligand may be sub-divided into those in which the metals are combined to the ligand by σ- and π-bonds or by two π-bonds.

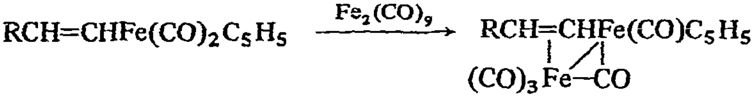
Thus, in order to simplify the discussion and to enable this to be done in a systematic manner, binuclear complexes have been broken down into two groups A and B depending upon whether the metal atoms are bound to the same or to different ligand fragments.

Literature up to the middle of 1971, as well as some later publications, have been included in this review.

II. σ,π-COMPLEXES

A. Complexes with a bimetallic group bound to the same structural ligand fragment (group A)

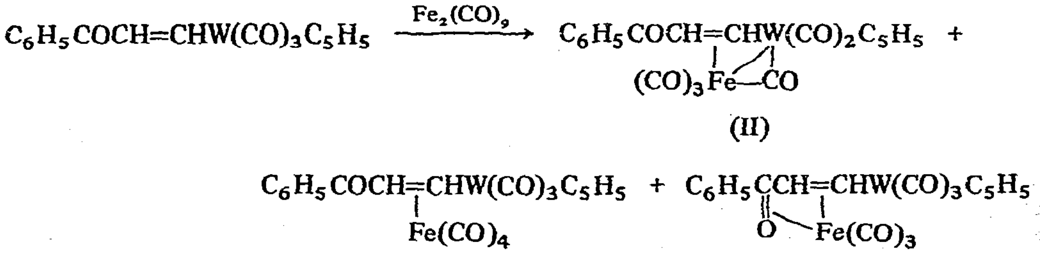
1. The olefin ligand complexes. In these complexes an olefin ligand is bound simultaneously by a σ-bond to one metal atom and by a π-bond to the other. In addition, in such compounds the metal atoms are usually linked to each other via bridging atoms or groups *e.g.* halogens, CO, SR, NR_2 etc. In most cases such complexes have been obtained purely by chance. The first systematic synthesis of σ,π-binuclear complexes involving monoolefin ligands used σ-vinyl transition metal compounds and $Fe_2(CO)_9$ as the starting materials. This method affords complexes with M–M bonding occurring not only between identical but also between different metal atoms. In this way the σ-vinyl iron complexes $RCH{=}CHFe(CO)_2C_5H_5$ ($R = CH_3CO$, C_6H_5CO, H, C_6H_5) led to the formation of binuclear complexes of type (I)[3-5].



(I)

The structure of complex (I), ($R = CH_3CO$), has been confirmed by X-ray data[6], the Fe–Fe bond length being 2.56 Å.

It was shown that the product composition in this reaction depends on the nature of the atom in the σ-complex since under the same conditions the compound $C_6H_5COCH{=}CHW(CO)_3C_5H_5$ gave three binuclear complexes only one of which contained an Fe–W bond[7]. The length of this bond was 2.81 Å[8].

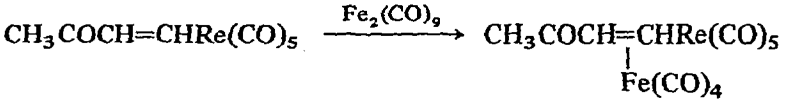


(II)

(III)

(IV)

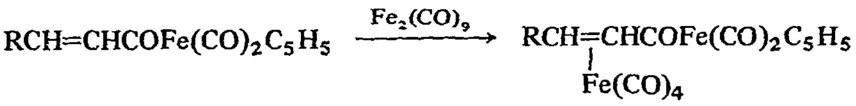
Using the same conditions, the σ-vinyl rhenium compound $CH_3COCH{=}CHRe(CO)_5$ produced only the binuclear complex (V) containing no M–M bonds[4].



$$CH_3COCH{=}CHRe(CO)_5 \xrightarrow{Fe_2(CO)_9} CH_3COCH\underset{\underset{Fe(CO)_4}{|}}{=}CHRe(CO)_5$$

(V)

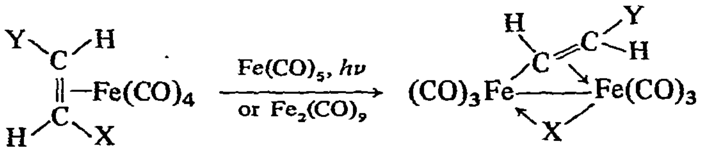
It is interesting to note that binuclear complexes containing Fe–Fe bonds were obtained only when the C=C bond of the initial σ-derivative was directly adjacent to the iron atom. The presence of even one carbon atom between the C=C group and the metal, as for example in the σ-acyl compounds $RCH{=}CHCOFe(CO)_2C_5H_5$ ($R = H, C_6H_5$), afforded with $Fe_2(CO)_9$ binuclear complexes (VI) not containing intermetallic bonds as the sole reaction product[4,5].



$$RCH{=}CHCOFe(CO)_2C_5H_5 \xrightarrow{Fe_2(CO)_9} RCH\underset{\underset{Fe(CO)_4}{|}}{=}CHCOFe(CO)_2C_5H_5$$

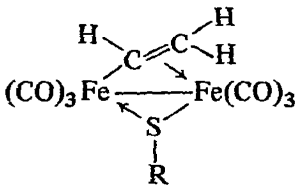
(VI)

The σ,π-binuclear complexes could also be obtained by oxidative addition reactions. As an example, the reaction of dihalogen-substituted ethylenes with iron carbonyls gave σ,π-binuclear complexes containing a halogen bridge[9] (X, Y = halogen atoms).



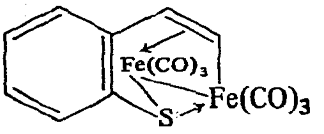
(VII)

Vinyl sulphides may also take part in the formation of σ,π-binuclear complexes from iron carbonyls. In this case the RS group behaves as a bridge. Alkylvinyl sulphides and $Fe_3(CO)_{12}$ yielded $[RSCH{=}CH_2]_2Fe_2(CO)_6$ where $R = CH_3$, C_2H_5, $CH_2{=}CH$ and $(CH_3)_2CH$[10] which are assumed (on the basis of chemical and spectral data) to possess structure (VIII).

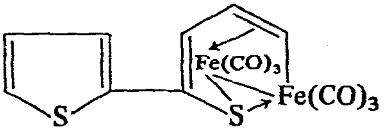


(VIII)

The cyclic analogue of vinyl sulphide, thianaphthene, reacts with $Fe_3(CO)_{12}$ to give complex (IX) with similar structure[10,11].



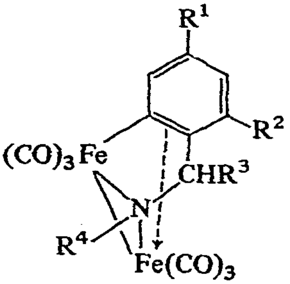
(IX)



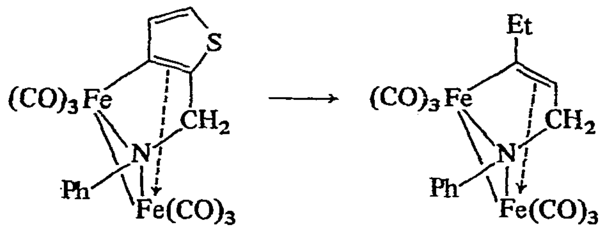
(X)

$Fe_3(CO)_{12}$ and 2,2′-dithienyl afforded crystalline $(C_8H_6S_2)Fe_2(CO)_6$[12]. A study of this compound by NMR spectroscopy has shown that only one thiophene ring is bound to the iron atoms. In a similar manner to the thianaphthene complex, structure (X) was assigned to the compound obtained.

Interesting complexes (XI) of the same type have been prepared from Schiff's bases and $Fe_2(CO)_9$[13,14]. The structure of (XI), ($R^1 = R^2 = R^3 = H$, $R^4 = CH_3C_6H_4$) was confirmed by X-ray data[15], the Fe–Fe bond length being 2.43 Å. Both Fe–N distances are approximately equal.



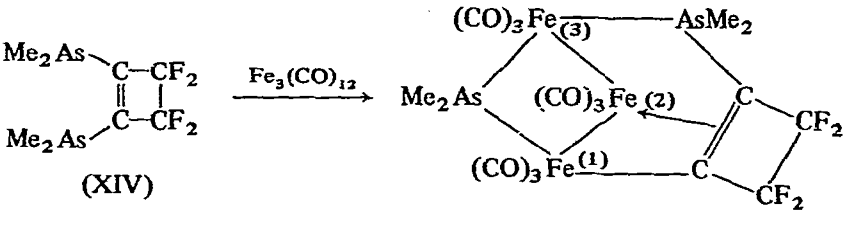
(XI)



(XII) (XIII)

Elimination of sulphur and simultaneous reduction of the thiophene derivative (XII) affords complex (XIII), the simplest representative of compounds of this type[16]. Unlike other σ,π-binuclear complexes, the bridging group in these compounds is bound to the common organic ligand and this obviously enhances their stability.

The dialkylarsino group may also act as a bridging group. Thus, refluxing $Fe_3(CO)_{12}$ with (XIV) in benzene[17] has led to the formation of a complex for which the X-ray analysis has revealed structure (XV)[18].

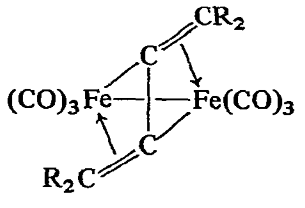


(XV)

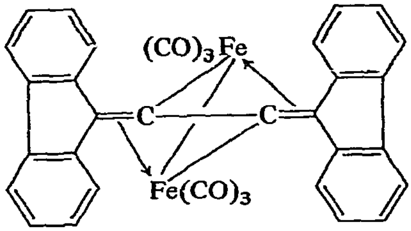
In this case the bridging group is the fragment $AsMe_2$-$Fe(CO)_3$. It is interesting that the Fe(1)–Fe(2) distance (2.67 Å) is considerably shorter than the Fe(2)–Fe(3) distance

(2.92 Å). This is apparently due to a "shrinking" effect of the olefin group. The C=C bond itself (1.44 Å) is considerably expanded relative to its standard value 1.34 Å[19] and is close in value to that in monoolefinic π-complexes.

In compounds with the olefin group σ,π-bonded with two transition metal atoms, other than a heteroatom with a lone p-electron pair, the π-bonded group (for example the vinyl group) may also act as a bridge. Thus the reaction of $R_2C{=}CBr_2$ and $XR_2C{-}C{\equiv}C{-}CR_2X$[20] or tetraphenylbutatriene[21] with iron carbonyls or their anions yields complexes of type (XVI).



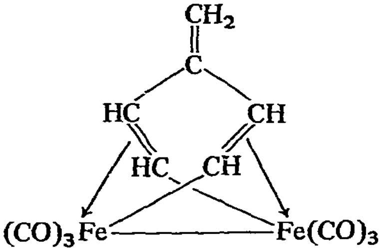
(XVI)



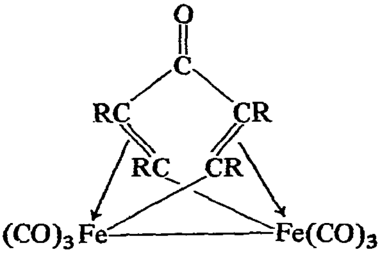
(XVII)

A similar structure (XVII) has been ascribed to a complex prepared from 9-dibromofluorene[20].

In addition to other compounds, acetylenes and iron carbonyls also produce σ,π-binuclear complexes (XVIII) and (XIX) containing a "cross" ligand[22-26]. From X-ray investigations, it has been established that the Fe–Fe distance in these complexes is 2.53 and 2.51 Å respectively.

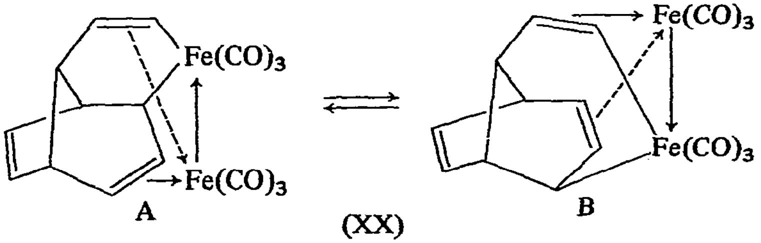


(XVIII)



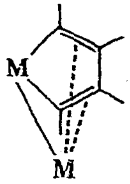
(XIX)

The binuclear complex (XX) obtained from $Fe_2(CO)_9$ and bulvalene[27] should also be regarded as of the σ,π-olefinic type. ^1H NMR spectroscopy of this complex indicates that enantiomers A and B rapidly rearrange with each other.



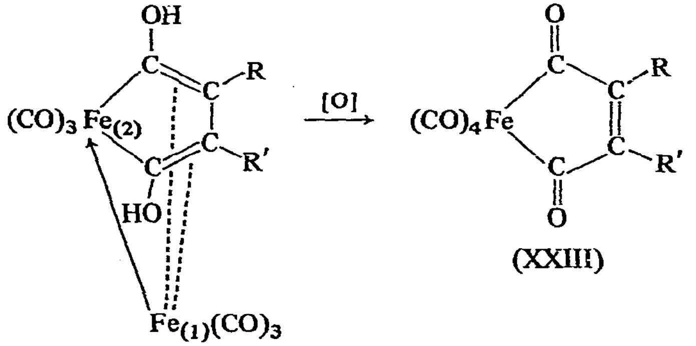
(XX)

2. *Complexes with a metallocyclic ligand.* Closely similar to the above-mentioned compounds are the binuclear complexes containing fragments of type (XXI) in which the diene group is combined via two σ-bonds to the same metal atom. The other metal atom is coordinated to the metallocycle via two π-bonds. At the same time it also takes part in the formation of the M–M bond (in many cases this bonding is of a donor–acceptor character as it is only in this way that both metal atoms with different oxidation states may attain an inert gas configuration).



(XXI)

Such complexes have been shown to be quite stable. Along with other products, they are formed in the reaction of metal carbonyls (or carbonylate anions) with acetylenes and other unsaturated compounds. The first representative of this class of complexes was prepared in 1958 by Reppe and Vetter[28] from acetylene and alkaline solutions of $Fe(CO)_5$ which contain the ions $[Fe_2(CO)_8]^{2-}$ [29]. Wender and Jones et al.[30-33] have extended this reaction to other acetylenes. As demonstrated by X-ray data[34-35], the reaction products have a structure similar to (XXII) with the metallocycle constructed from one acetylene and two CO molecules.



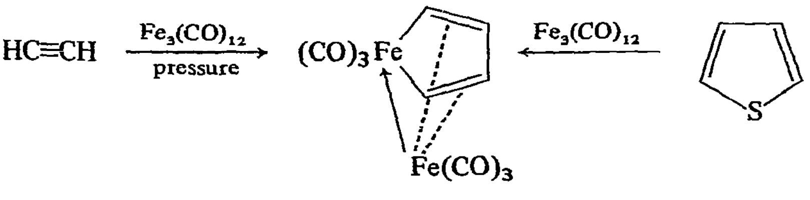
(XXII)

(XXIII)

The C–C bond lengths in the coordinated diene system of (XXII), ($R = R' = CH_3$) are virtually equal (1.42 Å). Thus bond levelling must occur in a similar manner to that in (butadiene)$Fe(CO)_3$ (1.45–1.46 Å)[36] which exhibits π-electron delocalization. The distance between the iron atoms (2.49 Å)[35] is close to that in $Fe_2(CO)_9$ (2.46 Å)[37] and $[C_5H_5Fe(CO)_2]_2$(2.49–2.53 Å)[38,39]. It should be pointed out that mild oxidation of (XXII) with aqueous $FeCl_3$ led to the formation of compound (XXIII)[33] which provides further evidence for the existence of a metallocycle.

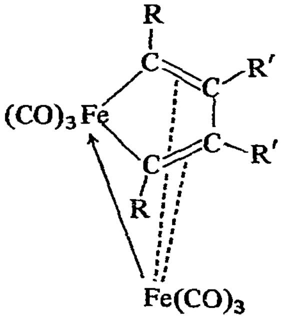
Qualitative analysis of the electronic structure of (XXII), $(R = R' = CH_3)$[40] using an MO approximation has led to the conclusion that the Fe(2) atom takes part in a certain amount of π-interaction with dienic structure although this is much weaker than that which occurs with the Fe(1) atom. The possible non-equivalence of the metal atoms in these complexes and their mutual transfer has been studied[41].

A thorough investigation of iron carbonyl reactions with acetylene has been carried out by Hübel et al.[42-46] and also independently by Schrauzer[47,48]. Depending upon the substituent in the acetylene molecule and the reaction conditions, it is possible to obtain a series of complexes including a binuclear species containing a metallocyclic ligand normally produced from two acetylene molecules. The simplest representative of compounds of this class containing an unsubstituted metallocycle has been synthesized from acetylene and $Fe_3(CO)_{12}$ using inert solvents under pressure[45,49] or alternatively Reppe-Vetter's reaction[50] (see above). The same complex (XXIV) was later unexpectedly found amongst the products of the reaction of $Fe_3(CO)_{12}$ with thiophene[51].

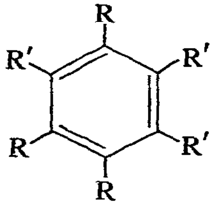


(XXIV)

Complexes of type (XXV) with substituted metallocyclic fragments have been prepared from different mono- and disubstituted acetylenes and iron carbonyls (R = Ph, R' = PhC≡C[52], R = R' = ferrocenyl[53], R = R' = C_6F_5[54] etc.).



(XXV)



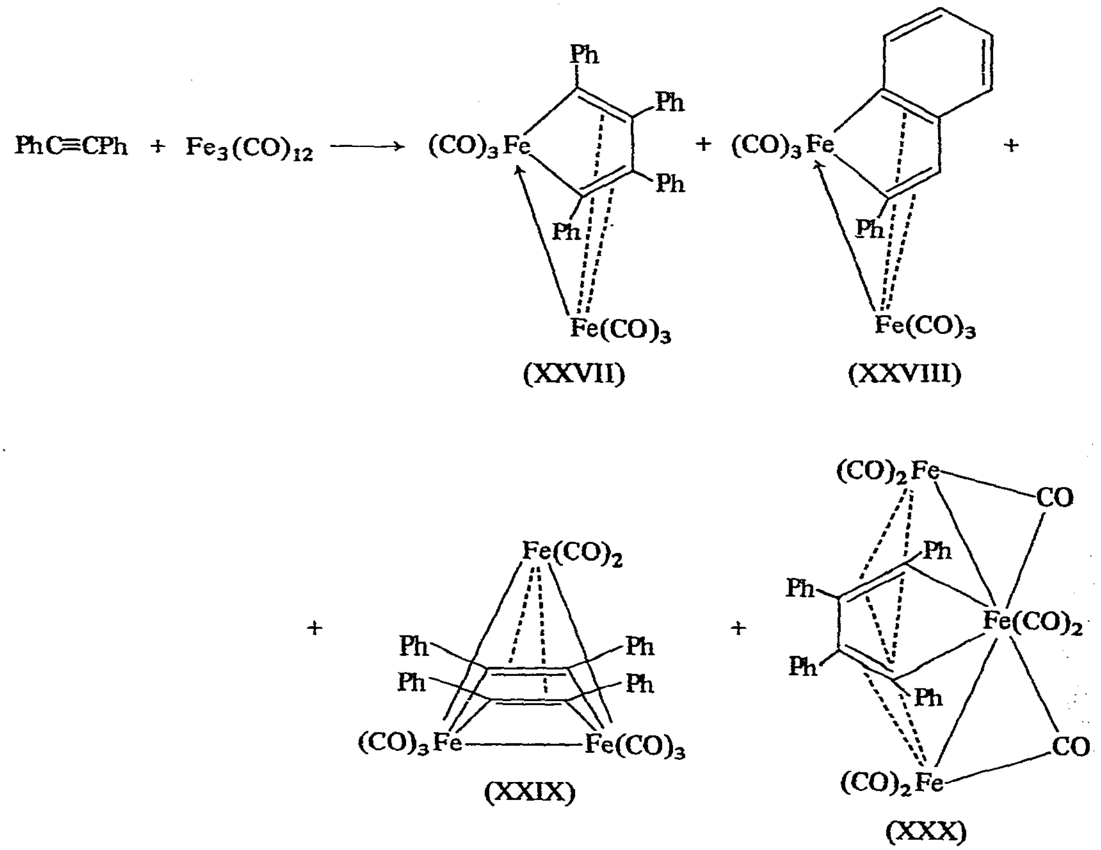
(XXVI)

It is interesting to note that the complexes formed from asymmetric acetylenes have a symmetric structure (XXV). The formation of these complexes has been suggested as a possible intermediate step in the trimerization of acetylene in the presence of metal carbonyls as catalysts[44]. The generation of asymmetrically-substituted benzenes (XXVI) in this reaction is in agreement with such an assumption.

The reaction of $Fe_3(CO)_{12}$ with tolane in inert non-polar solvents has been studied in greatest detail[42,43,47,48]. The reaction products were separated by chromatography or by the use of fractional crystallization. Several organometallic complexes including bi- and trinuclear ones were isolated.

Complex (XXVII) containing a tetraphenyl-substituted metallocycle was found to be the main product in this reaction.

In addition, a small quantity of (XXVIII) containing similar metal–ligand bonds was obtained, its structure being confirmed by X-ray analysis[22,55,56]. The specificity of the phenyl substituent was clearly exhibited in the formation of this complex.

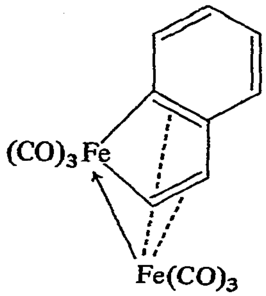


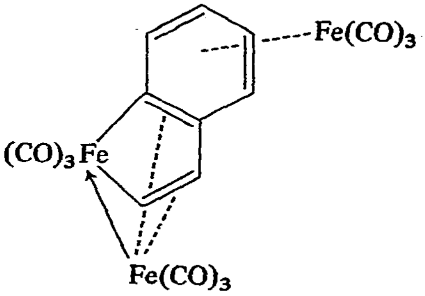
(XXVII) (XXVIII)

(XXIX) (XXX)

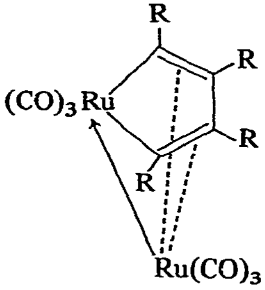
Besides complexes (XXVII) and (XXVIII), the reaction of $Fe_3(CO)_{12}$ with tolane afforded two isomeric trinuclear complexes (XXIX) and (XXX) whose ratio depended upon the solvent employed[42,48]. The structure of both compounds has been established by X-ray investigation[57].

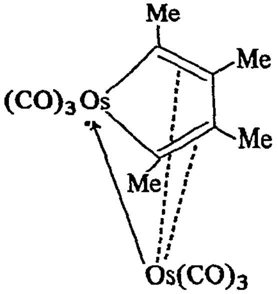
A binuclear complex (XXXI) similar to (XXVIII) and the complex (XXXII) with three iron atoms were obtained by the irradiation of *o*-bromostyrene in the presence of $Fe(CO)_5$[58].


(XXXI)


(XXXII)

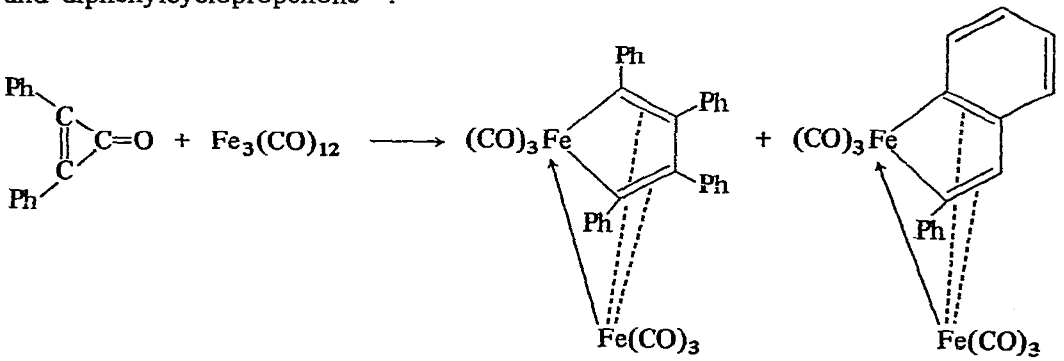
Complexes containing metallocyclic ligands have also been prepared for other iron group metals. The reaction of $Ru_3(CO)_{12}$ with tolane or *p,p'*-dichlorodiphenylacetylene[59-62] gives a number of organometallic complexes, including binuclear complexes of type (XXXIII) (R = C_6H_5, *p*-ClC_6H_4), which may be separated by thin-layer chromatography. The structures of many other complexes obtained in this reaction are similar to the analogous iron derivatives.


(XXXIII)

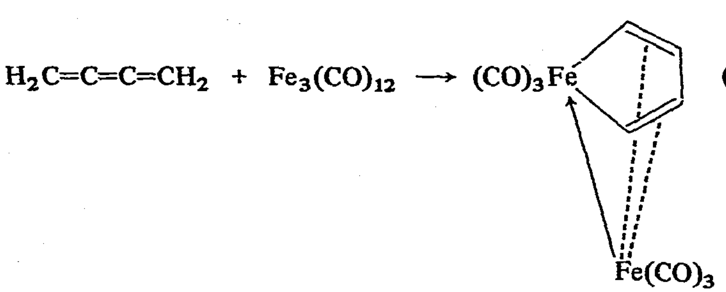

(XXXIV)

The reaction of $Os_3(CO)_{12}$ with 2-butyne yields complex (XXXIV) as one of the main products[63].

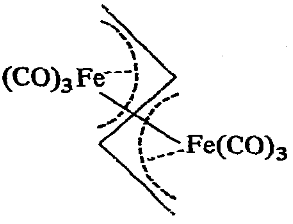
Binuclear complexes with metallocyclic rings are presumably quite stable as far as their energy is concerned as they are unexpectedly formed in many very different reactions. Thus, for example, these complexes have been synthesized from $Fe_3(CO)_{12}$ and diphenylcyclopropenone[64].


(XXVII) (XXVIII)

Similar products were isolated in the reaction of iron carbonyls with some cumulene systems[65-68], *e.g.*:



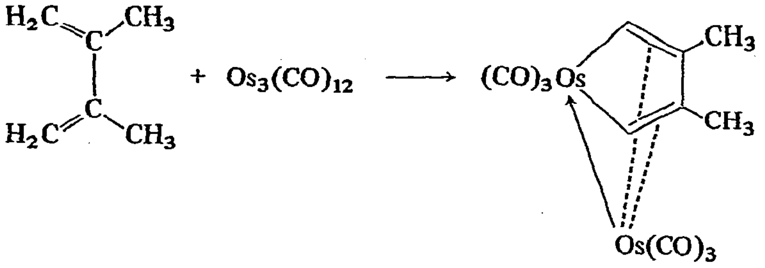
(XXIV)



(XXXV)

Although structure (XXXV) was assigned to the above compound in later studies[69,70], the grounds for this assignment are not particularly strong.

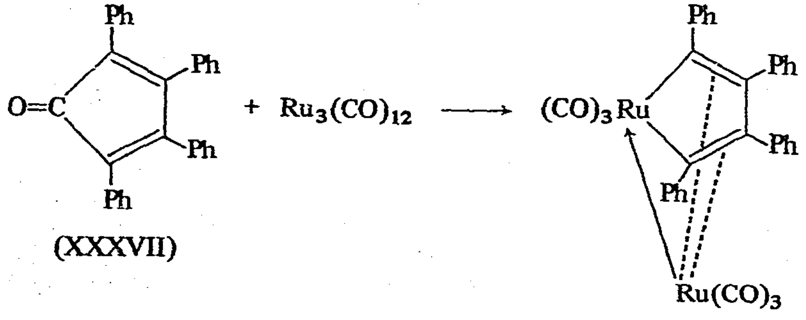
The first complex with an osmium-containing metallocycle was prepared from $Os_3(CO)_{12}$ and 2,3-dimethyl-1,3-butadiene[71]



(XXXVI)

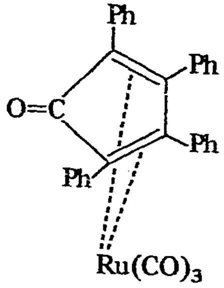
The structure of complex (XXXVI) has been confirmed by X-ray analysis[72] when it was found that the Os-Os bond (2.74 Å) is somewhat shorter than that in $Os_3(CO)_{12}$ (2.88 Å)[73] while the C-C bonds are equal as in the corresponding iron derivatives.

The ruthenium complex (XXXIII), (R = Ph) may be produced from $Ru_3(CO)_{12}$ and tetracyclone (XXXVII) in heptane or ligroin[60,74]

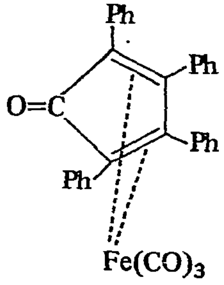


(XXXVII)

A similar reaction also occurs with osmium compounds[74]. It has been shown that the reaction of $Ru_3(CO)_{12}$ with tetracyclone is influenced by the solvent. Thus, in benzene a light-yellow complex (XXXVIII) was obtained[75].



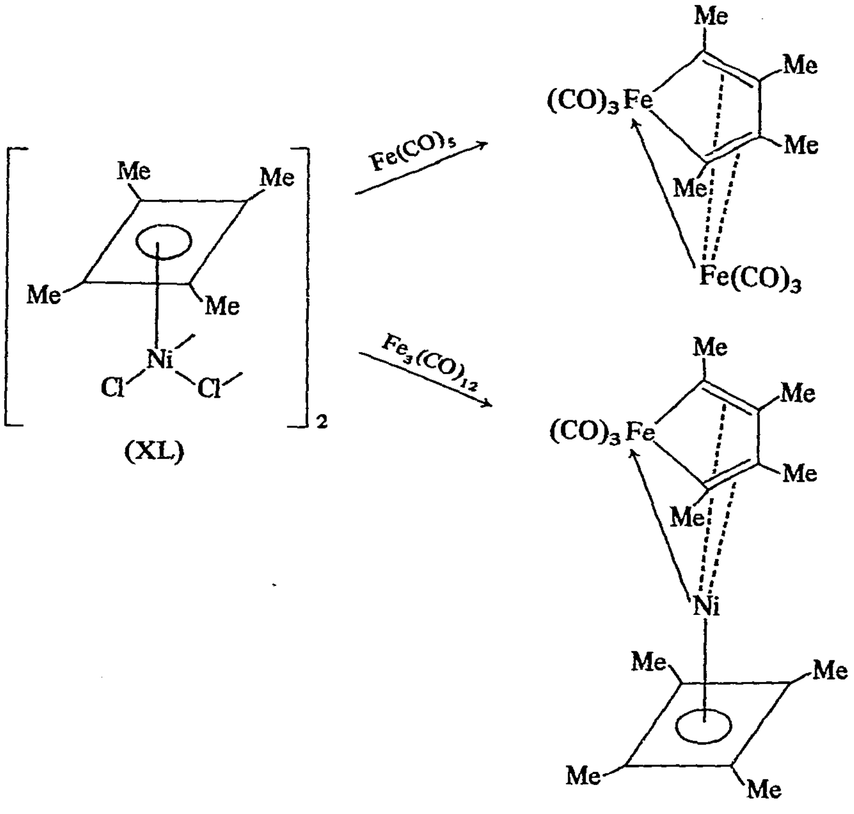
(XXXVIII)



(XXXIX)

It should be noted that the reaction of tetracyclone with iron carbonyls always leads to the formation of only one complex (XXXIX)[43,48].

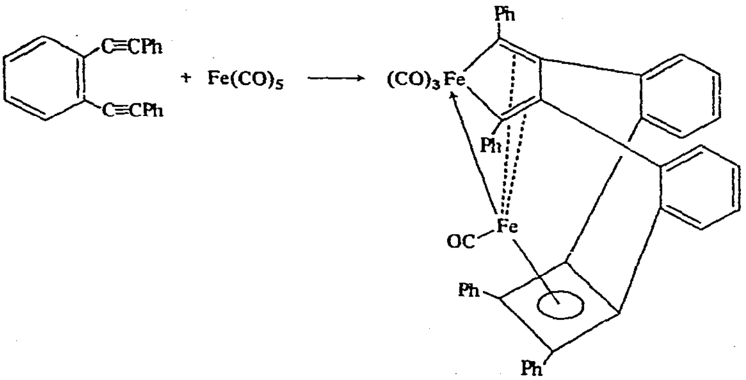
Coordinated cyclobutadienes were found to open the cycle to give binuclear complexes of Reppe-Vetter's type as in the reaction of the cyclobutadiene nickel complex (XL) with $Fe(CO)_5$[76].



(XL)

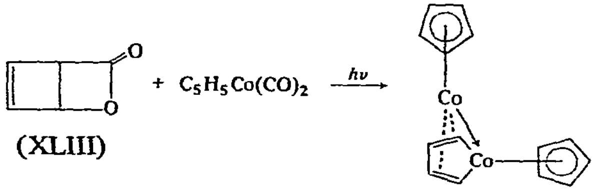
(XLI)

The related complexes (XLI) and (XLII), whose structures have been confirmed by X-ray analysis, were prepared from $[Me_4C_4NiCl_2]_2$ (XL) and $Fe_3(CO)_{12}$[77] and from *o*-bis(phenylethynyl)benzene and $Fe(CO)_5$ respectively[78,79].



(XLII)

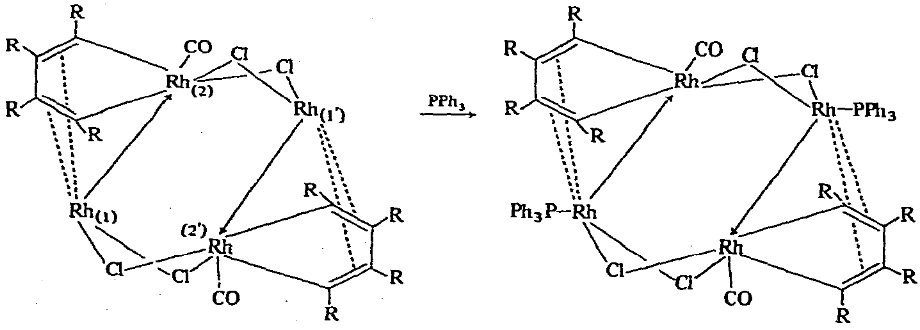
Similar binuclear complexes have also been synthesized for the cobalt group metals. Photolysis of an ethereal solution of photopyrene (XLIII) and $C_5H_5Co(CO)_2$ afforded a compound whose structure, (XLIV), has been confirmed by IR and NMR spectra[80,81].



(XLIII)

(XLIV)

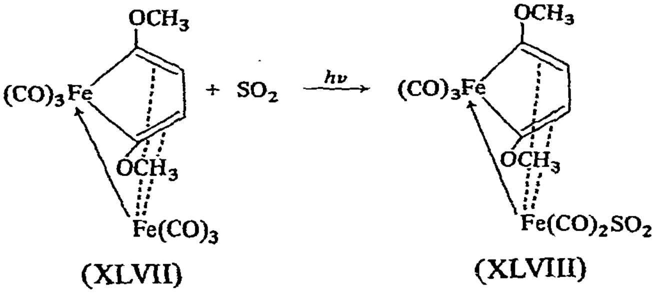
The dimeric rhodium complexes (XLV) were obtained from 3-hexyne[82] and tolane[83] respectively by reaction with $[Rh(CO)_2Cl]_2$, the structure of (XLV), (R = Et), being established by X-ray investigation[84].



(XLV) (XLVI)

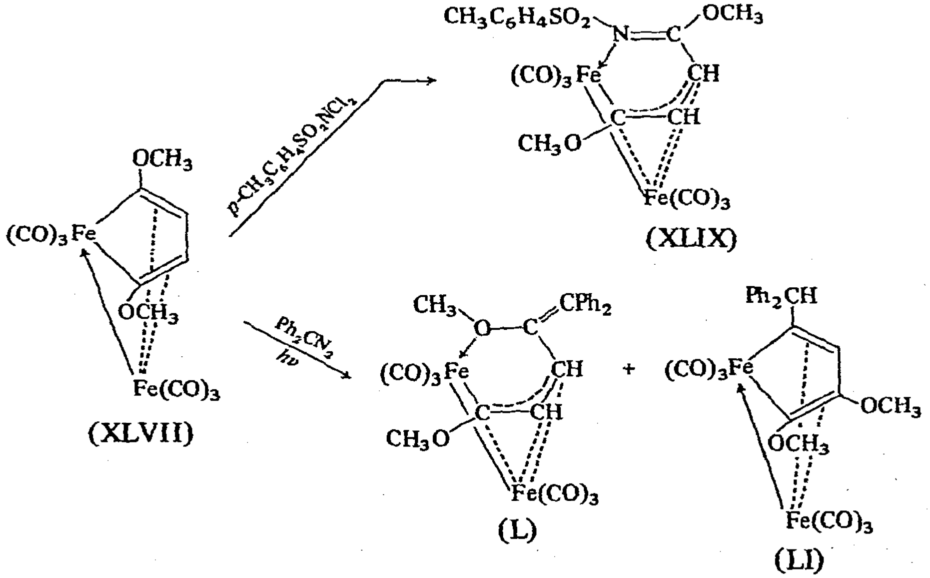
In the dimeric complex (XLV), the Rh(1) and Rh(1′) atoms do not acquire an inert-gas-like configuration and this enables complex (XLV) to readily combine with triphenylphosphine to give the new derivative (XLVI) which possesses a closed electron shell configuration for the rhodium atoms. The Rh–Rh distance in (XLV), (R = Et), is 2.70 Å, in agreement with a bond length of 2.68 Å in, for example, $Rh_2(C_5H_5)_2(CO)_3$[85].

The reactivity of binuclear complexes containing metallocyclic rings has as yet been little studied. However the few reactions known have shown that these compounds may react with the retention of their bimetallic structure. Thus, for example, the carbonyl group in these complexes may be replaced by other ligands, such as SO_2[86].



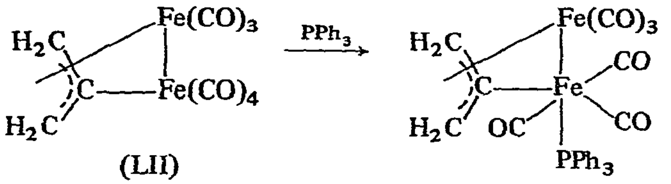
Some ruthenium complexes react with PPh_3 leading to the substitution of from one to three CO groups by triphenylphosphine[60].

Interesting reactions have been observed for (XLVII) when reacted with *p*-toluene-sulphonic acid dichloroamide[87] and diphenyldiazomethane[88]. Amongst others, products with an expanded metallocyclic ring have been found in these cases.



The structure of these complexes has been established on the basis of X-ray data[88,89], the Fe–Fe bond lengths in (XLIX) and (L) (2.64 and 2.62 Å, respectively) being greater than that in the initial reactant (~2.5 Å). In addition to a change in the geometry in the cyclic ring, this result probably is due to the fact that in this complex the Fe–Fe bond is not of the donor–acceptor variety. The iron atoms in complexes of type (XXV) may be replaced by various other heteroatoms to give heterocycles[46]. The electrochemical reduction of such complexes has been studied[90].

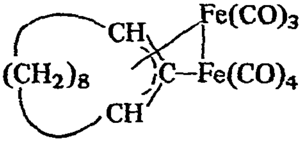
3. Complexes with an allyl ligand. A complex of group A with the allyl group linked via σ- and π-bonds to two iron atoms has been obtained from the reaction of allene and $Fe_2(CO)_9$[91]. On the basis of spectral data, this compound has been assigned structure (LII).



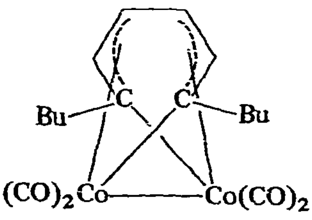
(LII)

(LIII)

When (LII) is reacted with triphenylphosphine substitution of one or two CO groups has been observed. The resulting $C_3H_4Fe_2(CO)_6PPh_3$ has been studied by X-ray methods[92] and has been shown to have structure (LIII). The Fe–Fe bond length in this compound is equal to 2.65 Å. According to X-ray analysis, this bond length is retained in compound (LIV) obtained from cyclic C_{11}-allene[93].



(LIV)

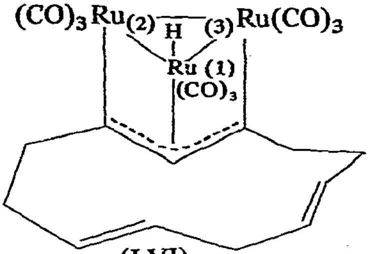


(LV)

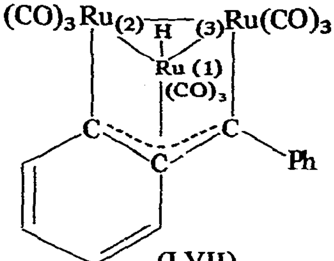
In other σ,π-allyl complexes of group A, which have been studied, the σ-bond involving one or two metal atoms is located through the terminal atoms of the allyl fragment. Such arrangements were obtained in complexes involving metallocyclic ligands (see above). A number of similar products have also been synthesized from different acetylenes and $Co_2(CO)_8$[94-98]. The structure of (LV) was established from X-ray analysis.

Similar complexes have also been prepared by the reaction of $Ru_3(CO)_{12}$ with some cycloolefins. In this case, however, as in many other cases involving the ruthenium atom, the latter displays its particular property of retaining its trinuclear cluster in the reaction products. The structure of (LVI) obtained from $Ru_3(CO)_{12}$ and 1,4,8-cyclododecatriene has been confirmed by X-ray data[99,100] the bonds between Ru(1) and Ru(2) as well as

Ru(3) (2.77–2.78 Å) being shorter than the Ru(2)–Ru(3) distance (2.93 Å). It has been found that the ruthenium atom π-bonded with the allylic fragment is linked to a hydride hydrogen which appears at τ = 30.24 in the ^{1}H NMR spectrum.



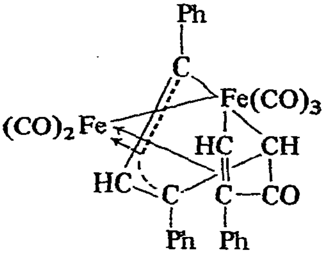
(LVI)



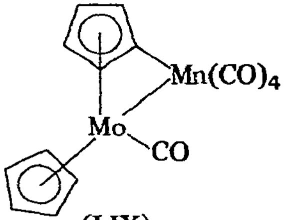
(LVII)

The ruthenium derivative of diphenylcarbene (LVII)[101] has a similar structure with the Ru(1)–Ru(2), and Ru(1)–Ru(3) bond lengths (2.77 Å) again being shorter than Ru(2)–Ru(3) (2.91 Å).

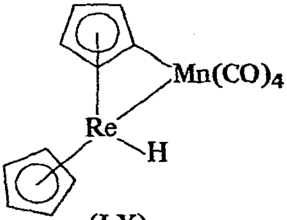
Phenylacetylene and iron carbonyls[102] react to produce a more complex compound (LVIII) in which a σ,π-bonded olefinic group exists in addition to the σ,π-bonded allylic fragment. Its structure has been confirmed by X-ray analysis, the Fe–Fe bond being 2.50 Å.



(LVIII)



(LIX)

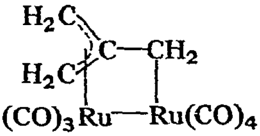


(LX)

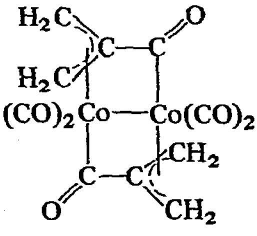
Recently the σ,π-binuclear complexes (LIX) and (LX) containing the common cyclopentadienyl ligand have been prepared[103].

B. Complexes with metal atoms coordinated to different structural ligand fragments (group B)

The simplest representative of such compounds exists in the ruthenium complex (LXI)[104]. A complex with a similar structure (LXII) has been obtained from allene and $Co_2(CO)_8$[105].

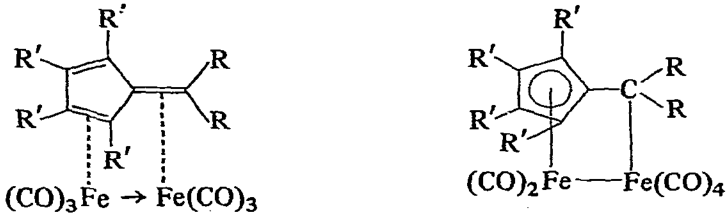


(LXI)



(LXII)

The fulvene complexes, which are known only for iron carbonyls, should also be assigned to this group of binuclear complexes. The synthetic procedures used were however quite different. Under mild conditions[106], some fulvenes react with $Fe_2(CO)_9$ to produce, alongside other compounds, complexes of the type (fulvene)$Fe_2(CO)_6$ (LXIII). Initially Hübel and Weiss[106] assigned structure (LXIIIa) to these compounds. After more detailed investigations of these reactions[107] however they suggested structure (LXIIIb).

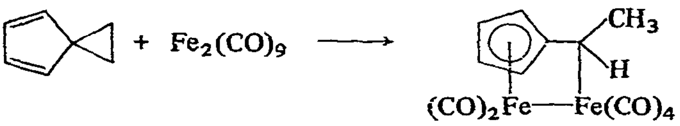


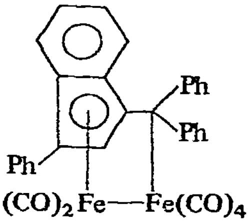
(a) (b)

(LXIII)

Complex $(C_2H_2)_3Fe_2(CO)_6$ (a dark-red isomer) resulting from acetylene and $Fe_3(CO)_{12}$ has a similar structure (LXIIIb, R = R' = H)[45,49]. This structure has been confirmed by X-ray studies[108], the Fe-Fe bond being 2.68 Å. Earlier, Van Meersche theoretically discussed the various possible structures for the iron fulvene complexes and suggested that structure (LXIIIb) was the most probable[109].

Formation of a complex cyclopentadienyl ring results in a gain in energy in the system and this takes place, for example, in the reaction of spiro[2,4]-4,6-heptadiene with $Fe_2(CO)_9$[110].



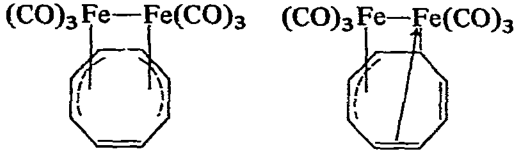


(LXIV)

Similar complexes, for example (LXIV), are produced together with other compounds in the reactions of $R_2C{=}CBr_2$ and $XR_2C{-}C{\equiv}C{-}CR_2X$ with iron carbonyls or carbonylate anions[20] as described above.

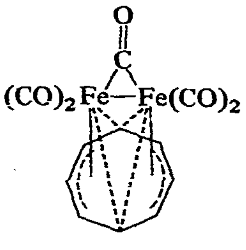
A large group of metal carbonyl complexes involving cyclopolyenes may be assigned to this class of σ,π-binuclear complexes. Some cyclopolyene complexes are known for iron and ruthenium including the binuclear σ,π-complexes.

The reaction of $Fe_2(CO)_9$ with cyclooctatetraene[111] affords several organometallic compounds but only one of them contains a metal-metal bond. It was initially assumed that this complex had a bis-π-allylic structure (LXVa). Later, after the analogous ruthenium complexes had been investigated, this structure was revised together with other similar ones and structure (LXVb) is now considered to be more likely.



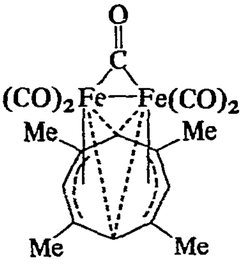
(a) (b)

(LXV)

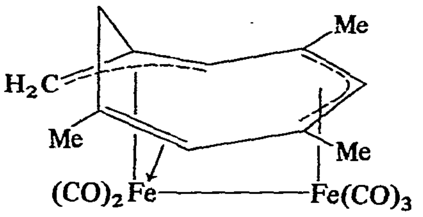


(LXVI)

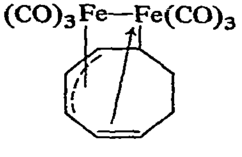
Complex (LXV) loses CO upon standing to produce (LXVI)[112]. The latter displays a single signal in the ^{1}H NMR spectrum, which can be explained by valence tautomerism involving fast rotation of the metal carbonyl fragment about the ring[112]. It has been shown by an X-ray study[113] that in addition to π-allyl bonds, three-centre bonds also exist in (LXVI). The Fe–Fe distance in this complex is 2.74 Å. In later studies, an analogue of (LXVI) was prepared using 1,3,5,7-tetramethylcyclooctatetraene as a ligand[114] and an X-ray study of this material was performed[115]. It was found that this complex has structure (LXVII), the Fe–Fe bond length being 2.72 Å. In addition, an isomer is also formed in the reaction, (LXVIII), containing π-allylic and π-olefinic bonds and with a somewhat greater Fe–Fe bond distance (2.77 Å)[116].



(LXVII)



(LXVIII)

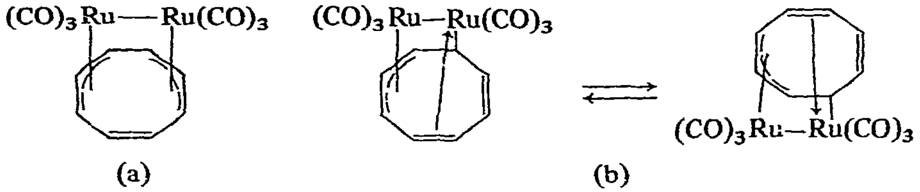


(LXIX)

Reaction of cyclooctatriene with $Fe_3(CO)_{12}$[117,118] results in the formation of a compound which according to X-ray data[119] has the structure (LXIX) similar to those of other Fe and Ru carbonyl complexes with cyclic polyolefins. The iron atoms in this structure are not equivalent, the Fe–Fe bond being 2.77 Å[119]. A study of the ^{1}H NMR spectrum at low temperatures has shown[120] that the same structure is retained in solution.

Complex (LXIX) may eliminate a hydride ion by reacting with $Ph_3C^+BF_4^-$ [118], and by interaction of the obtained salt, $[C_8H_9Fe_2(CO)_6]^+BF_4^-$, with various nucleophilic agents ligand-substituted complexes of type (LXIX) have been prepared[121].

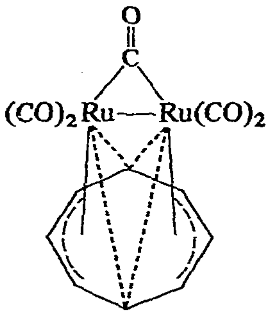
X-Ray *study of one such product*, $C_8H_8Ru_2(CO)_6$, carried *out by* Cotton *et al.*[illegible] *has* refuted the structure initially assumed (LXXa): this compound actually has the structure (LXXb), the Ru–Ru bond length being 2.86 Å. This work was of great importance, as it provided a stimulus to the revision of initially proposed structures for the iron analogues mentioned above.



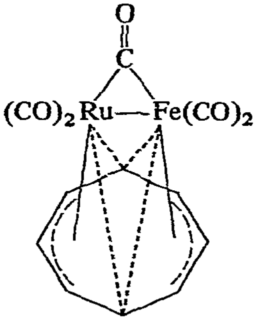
(LXX)

In solution, compound (LXX) undergoes rapid valence tautomerism in which two enantiomorphic structures rapidly transform with each other[125].

Another product of the reaction of $Ru_3(CO)_{12}$ with cyclooctatetraene is compound (LXXXI) which is similar to the iron complex (LXVI).



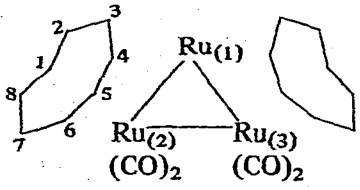
(LXXI)



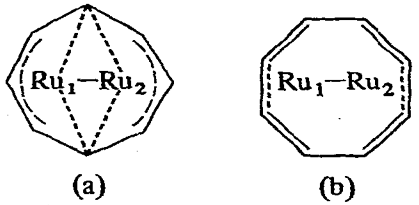
(LXXII)

Mixed complexes of similar type (LXXII) have been prepared from $C_8H_8Fe(CO)_3$ and $Ru_3(CO)_{12}$[126].

The main reaction product of $Ru_3(CO)_{12}$ with cyclooctatetraene is the trinuclear complex (LXXIII)[122], which may be attributed to the fact that ruthenium displays a greater tendency than iron towards retaining its trinuclear cluster structure.



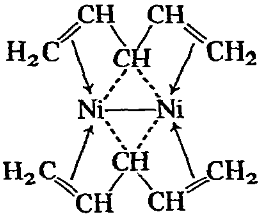
(LXXIII)



(LXXIV)

X-Ray data[127,128] has indicated that the Ru(1)-Ru(2) distance in this complex (2.94 Å) is greater than that between Ru(2) and Ru(3) (2.78 Å) which are not bound to the common organic ligand. It is quite obvious that in this case the ligand "expands" the Ru-Ru bond. The ruthenium atoms of each $C_8H_8Ru_2$ fragment are bound to two allylic systems (carbons 2, 3, 4 and 6, 7, 8) and to the atoms C(1) and C(5) of the cycle. The ^1H NMR spectrum of this complex in solution exhibits one signal which may be explained by a "fluxional" behaviour of the molecule, it being commonly accepted that a transition between structures of type (LXXIVa) may occur via structure (LXXIVb).

Reaction of a suspension of anhydrous $NiCl_2$ in 1,4-pentadiene with triethylaluminium[129] resulted in the formation of complex (LXXV) which contains three-centre bonds and may thus also be possibly assigned to the σ,π-binuclear complexes of group B. The structure of this compound was confirmed by X-ray analysis[130], the Ni-Ni distance (2.59 Å) being somewhat greater than that for example in $[C_5H_5NiCO]_2$ (2.36 Å)[131].



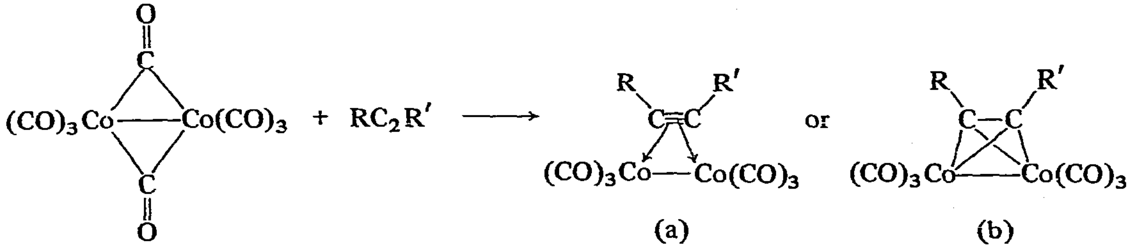
(LXXV)

III. π,π-COMPLEXES

A. Complexes of group A

Such compounds may include complexes of acetylenes with transition metal derivatives. These are most characteristic for cobalt and nickel.

Cobalt carbonyl reacts with a large number of acetylenes at room temperature giving compounds of formula $(RC_2R')Co_2(CO)_6$ (LXXVI)[53,54, 132-139].



(LXXVI)

In these complexes the acetylene molecule replaces two bridging CO groups. Structure (LXXVI), (R = R' = Ph), was confirmed for complex $(Ph_2C_2)Co_2(CO)_6$ on the basis of an X-ray study[140]. The cobalt-cobalt bond length was found to be 2.47 Å (*cf.* 2.52 Å in $Co_2(CO)_8$[141]) and the phenyl acetylene molecule has a different geometry from its unbound state (the C≡C bond is elongated from 1.20 to 1.37 Å and the angles between this bond and the Ph groups are about 140°). The tolane molecule is situated above the Co–Co bond and is almost perpendicular to it. The character of the bonds between the cobalt atoms and the acetylene ligand is rather ambiguous. Acetylene may use its doubly degenerate orthogonal p_x and p_y orbitals for bonding with two metal atoms (structure (LXXVIa), or the molecule $(RC_2R')Co_2(CO)_6$ could be regarded as being produced via σ-bonds (structure (LXXVIb)). The π-complex structure is, however, more convenient for describing the properties of these compounds.

The IR spectra of complexes (LXXVI) have been discussed[142]. Japanese authors have carried out a detailed spectroscopic study[143,144] and have assumed that the acetylene bond in these complexes is similar to that in acetylene in an excited state with the carbon hybridization changing from *sp* in acetylene to sp^2 in this complex.

The stability of the complexes $(RC_2R')Co_2(CO)_6$ and the nature of the bond in them depends considerably on the nature of the substituents R and R′ in the acetylene molecule[145]. When R and R′ are electron donors, the σ-character of the bond is enhanced, but when R and R′ are electron attractors back donation of electrons is favoured and the π-character of the bond between metal and ligand increases. In earlier studies it had been noted that when the π-character of the bond increases the stability of the complex also increases and the acetylene ligand is more difficult to replace. The behaviour of complexes (LXXVI) in mutual replacement reactions of acetylene ligands, *i.e.*

$$Co_2(CO)_6RC_2R' + R''C_2R''' \rightleftarrows Co_2(CO)_6R''C_2R''' + RC_2R'$$

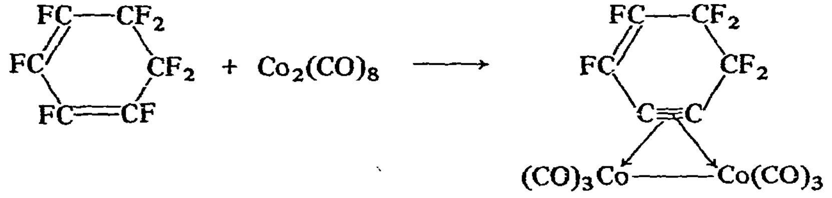
enabled the arrangement of the following series for acetylenes (each member of this series replaces ligands from the right-hand side) $C_2(CF_3)_2 > C_2(COOCH_3)_2 > C_2Ph_2 > CH_3C_2Ph > C_2(CH_3)_2 > HC_2Ph{=}HCH_2CH_3 > C_2H_2 > C_2(CH_2NEt_2)_2$. The observed replacement sequence enables the assumption that the π-character of the metal–ligand bond in complexes of type (LXXVI) is greater than its σ-character[145]. The nature of the bonding between two cobalt atoms in (LXXVI), ($R = R' = Ph$), has been discussed by Brown[146] in terms of MO theory. The exchange of CO groups in complexes of type (LXXVI) has been studied[147-149].

It is interesting to note that dicyanoacetylene reacts with $Co_2(CO)_8$[150] to give a product with the C≡C (rather than the CN) bond coordinated to the metal. Similar binuclear complexes have also been synthesized from acetylene derivatives of Si, Ge, Sn[151,152], As[153] and $Co_2(CO)_8$.

Compounds (LXXVI) could be prepared from acetylene and its numerous derivatives not only by reaction with cobalt carbonyl but also with the mercury salt of cobalt hydrocarbonyl, $Hg[Co(CO)_4]_2$[154-156].

Reaction of $Co_2(CO)_8$ with acetylenes is one of the few reactions of this type which have been studied kinetically[157]. The results obtained led to the conclusion that an active intermediate cobalt carbonyl form is involved in the reaction with acetylenes.

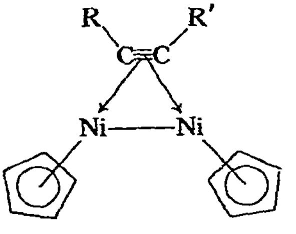
The binuclear π,π-acetylenic complexes are also produced in the dehalogenation of fluoroolefins under the action of cobalt carbonyl. In this way, an interesting binuclear complex (LXXVII) of the unstable hexafluorocyclo-3-hexene-1-yne has been obtained[158,159]. Its structure has been confirmed by X-ray analysis[160]. In the structure the cobalt atoms are separated by a distance of 2.47–2.49 Å[158,160] and are bound to the formal acetylene bond (1.29 Å) of the cyclic ligand.



(LXXVII)

Unlike free tolane, complex (LXXVI), (R = R′ = Ph), undergoes a Friedel-Crafts acylation to give *para*-acyl substituted complexes (LXXVI)[161]. This reaction again provides evidence that the properties of a ligand change during complex formation. Cleavage of the complexes thus obtained enables the synthesis of acylated tolanes which cannot be obtained by other methods. The reaction of $(C_2H_2)Co_2(CO)_6$ with PPh_3 gives the complex $(C_2H_2)Co_2(CO)_5PPh_3$. Acetylenic derivatives (LXXVI) may also be employed for the preparation of some aromatic compounds which are difficult to prepare by other methods, for example, tri- and tetra-t-butylbenzenes[94,162]. The latter were obtained when the complexes (LXXVI) were refluxed with the respective acetylenes in ligroin, compound (LV) (see above) being formed as an intermediate.

Nickel complexes of the general formula $(C_5H_5Ni)_2RC_2R'$, (LXXVIII), (R, R′ = Alk, Ph, CF_3, CN etc.), are similar to the acetylenic compounds of cobalt described above. They may be prepared by substituting the bridging carbonyl groups in $[C_5H_5NiCO]_2$ with an appropriate acetylene[134,135,163,164] or by the direct reaction of nickelocene with acetylene under pressure[165-167].

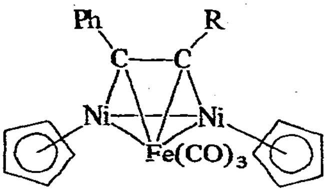


(LXXVIII)

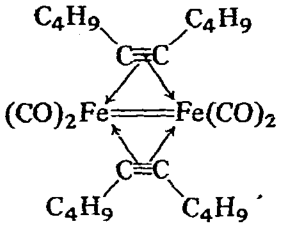
The structure of (LXXVIII), (R = R′ = Ph) was established from X-ray studies[131]. The Ni-Ni bond length in this compound (2.33 Å) is approximately equal to that in $[C_5H_5NiCO]_2$ (2.36 Å)[131], the acetylene bond length being 1.35 Å.

Reaction of $[C_5H_5NiCO]_2$ with diphenylbutadiyne affords two products, $[C_5H_5Ni]_2 . PhC_2C_2Ph$ (LXXIX) and $[C_5H_5Ni]_4 . PhC_2C_2Ph$ (LXXX), which correspond to coordination along one or two triple acetylenic bonds[63]. Employing the same diyne, one may obtain mixed metal complexes, for example, nickel and iron, nickel and cobalt from (LXXIX) and $Co_2(CO)_8$[163].

Complexes of type (LXXVIII) may react with $Fe(CO)_5$ producing a compound of structure similar to (LXXXI) (R = H, Ph, C≡CPh)[168,169] according to the authors.



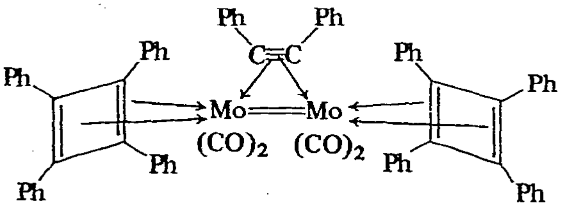
(LXXXI)



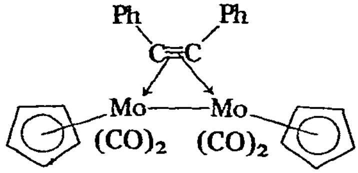
(LXXXII)

The first acetylenic iron complex (LXXII) was prepared from $Fe_3(CO)_{12}$ and di-t-butylacetylene[170]. X-Ray analysis revealed the presence of an Fe=Fe double bond (2.15 Å) which is in accord with the diamagnetic properties of the complex. The length of its acetylene bond is found to be 1.28 Å.

The acetylenic molybdenum complex (LXXXIII) was obtained by the reaction of $Mo(CO)_6$ with tolane[171]. The diamagnetic properties of the complex suggests the presence of an Mo=Mo double bond in this compound.



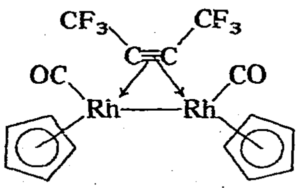
(LXXXIII)



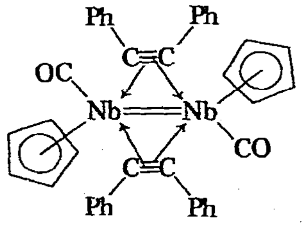
(LXXXIV)

In contrast to unsubstituted molybdenum hexacarbonyl, $CH_3Mo(CO)_3C_5H_5$ reacts with tolane to give a different acetylenic complex (LXXXIV)[172]. A similar complex was also prepared from phenylacetylene. It should be pointed out that it is possible to employ $C_5H_5Mo(CO)_3H$ or $[C_5H_5Mo(CO)_3]_2$ for the synthesis of these compounds, rather than $CH_3Mo(CO)_3C_5H_5$.

An acetylenic cyclopentadienyl rhodium carbonyl complex has recently been obtained. This complex has been assumed to have structure (LXXXV)[173] in which the rhodium atoms do not possess an inert-gas electron shell.



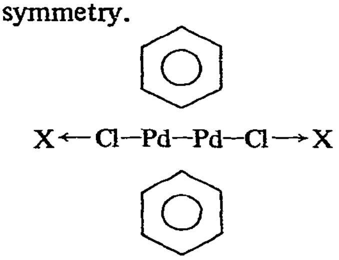
(LXXXV)



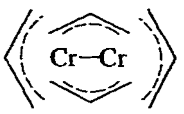
(LXXXVI)

An acetylenic binuclear niobium complex was prepared by heating a solution of $C_5H_5Nb(CO)_2Ph_2C_2$ in toluene[174]. From X-ray analysis this compound has been shown to have the structure (LXXXVI)[175,176]. The length of its coordinated triple bond (1.39 Å) is approximately equal to that in the related cobalt (LXXVI, R = R′ = Ph) and nickel derivatives (LXXVIII, R = R′ = Ph) (1.37 and 1.35 Å respectively). It is probable that the nature of the metal-acetylene bond in these complexes is similar (*cf.* page 20). The niobium-niobium bond (2.74 Å) is considerably shorter than that, for example, in crystalline α-NbI_4 (3.31 Å). For this reason, the authors have suggested the presence of a double bond, Nb=Nb, in (LXXXVI). Such an assumption is in agreement with the diamagnetic properties of this compound and also with the 18-electron shell rule. The structure of a similar complex with $CH_3OC(O)C{\equiv}CCOOCH_3$ has also been determined, the niobium-niobium bond being 2.73 Å and the C≡C coordinated bond length being 1.34 Å[177]. A similar tantalum derivative has been described but to date insufficient detail is available regarding its structure[175].

$PdCl_2$ reacts with benzene in the presence of $AlCl_3$ and aluminium powder[178-179] to yield a new type of sandwich compound (LXXXVII) (X = Al_2Cl_6, $AlCl_3$). X-Ray analysis shows that the bimetallic grouping Pd-Pd (2.57 Å) in this compound is simultaneously linked to both benzene nuclei, the latter exhibiting no deviations from hexagonal symmetry.



(LXXXVII)



(LXXXVIII)

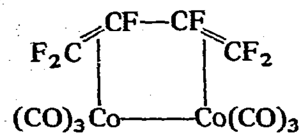
The grouping of the two chromium atoms in (LXXXVIII)[180] produces an entity possessing two common allylic ligands.

B. Complexes of group B

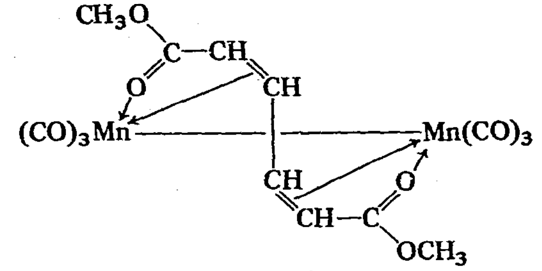
In complexes of this group the bimetallic grouping is coordinated to the unsaturated ligand fragments in a somewhat different manner. Among such complexes may be listed those containing π-olefin-π-olefin, π-allyl-π-allyl and π-allyl-π-cyclopentadienyl linkages as well as others.

The simplest example of π-olefin binuclear complexes, (LXXXIX), was prepared from $Co_2(CO)_8$ and perfluorobutadiene[181].

A similar manganese complex (XC) was obtained by heating the σ-derivative $CH_3OCOCH{=}C(COOCH_3)Mn(CO)_5$[182]. A new diene ligand is thus produced involving a change in the character of the metal-ligand bonding. Unfortunately, however, the structures of both olefin complexes have been assumed solely on the basis of spectral and chemical data without X-ray investigation.

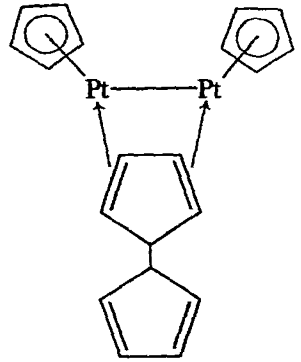


(LXXXIX)

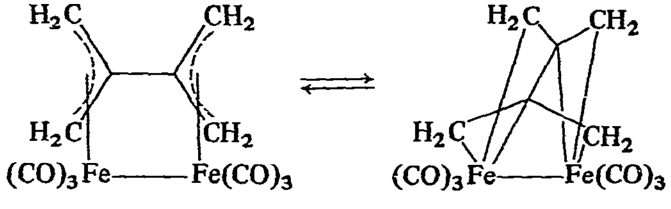


(XC)

Cyclopentadiene may act as a common ligand, for example in the binuclear platinum complex (XCI) whose structure has been elucidated by X-ray analysis[183], the Pt-Pt bond being 2.58 Å in length. This material is the only binuclear platinum complex with a common organic ligand known at present.



(XCI)

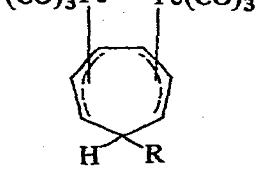


(a) (b)

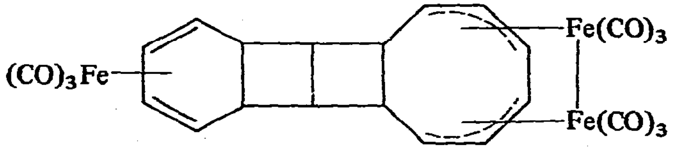
(XCII)

The simplest π-allyl-π-allyl complex, (XCII), has been synthesized together with other complexes from allene and $Fe_3(CO)_{12}$. Its structure has been investigated both by spectroscopic and chemical methods[105,184]. According to the authors, the presence of a singlet in the ^1H NMR spectrum may be explained by the existence of valence tautomerism involving (XCIIa and XCIIb). The complex generated from phenylallene and $Fe_2(CO)_9$[185] has a similar structure.

The bis-π-allylic structure (XCIII) has also been ascribed to the reaction products of $Fe_2(CO)_9$ with cycloheptatriene and the 7-methoxy derivative[118], and this has been confirmed by X-ray data, where it was shown that the Fe-Fe bond length is 2.87 Å (XCIII), (R = H)[186].

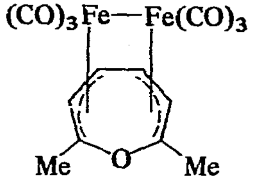


(XCIII)

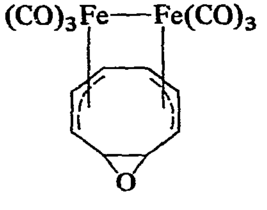


(XCIV)

The equivalence of two (out of three) iron atoms in the Mössbauer spectrum allows a similar structure to be assumed for the reaction product (XCIV) of the cyclooctatetraene dimer and iron carbonyls[187]. Similar complexes (XCV) and (XCVI) have been synthesized from dimethyloxepine and $Fe(CO)_5$ [188] as well as from $Fe_2(CO)_9$ and cyclooctatetraene oxide[189].

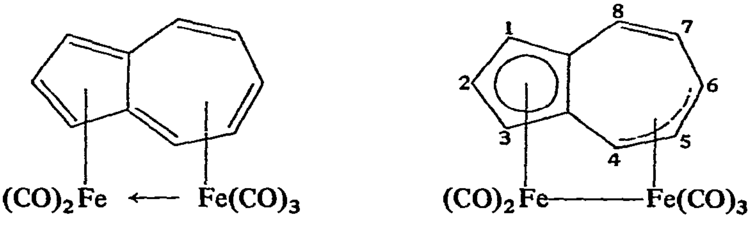


(XCV)



(XCVI)

π-Allyl-π-cyclopentadienyl complexes with bimetallic groupings have been obtained from azulenes. Thus prolonged interaction of an unsubstituted azulene with $Fe(CO)_5$ or $Fe_3(CO)_{12}$ in an inert solvent gave $C_{10}H_8Fe_2(CO)_5$ (XCVII)[190,191]. Initially the structure (XCVIIa) was assumed on the basis of the diamagnetic properties of the complex together with its high dipole moment (3.97 D)[190]. However, MO calculations[192] suggest that the $Fe(CO)_2$ group in (XCVII) should be bound to the five-membered azulene ring in such a way that the iron atoms assume a *trans* configuration with respect to the ligand. Further X-ray analysis[193,194] has finally established structure (XCVIIb) for this compound.



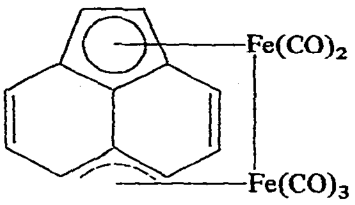
(a) (b)

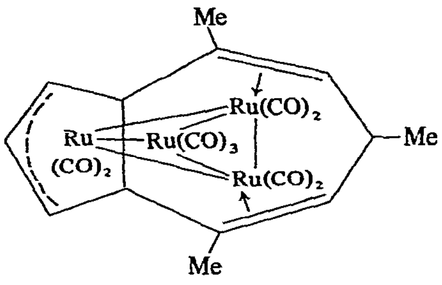
(XCVII)

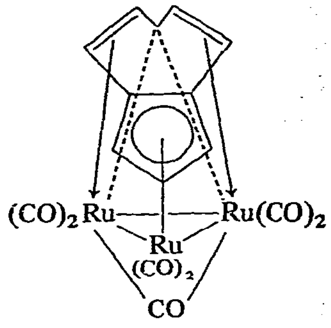
The azulene ligand in the complex is not exactly planar, the Fe–Fe bond length being 2.78 Å.

The high resolution ^1H NMR spectra of complex (XCVII) with azulene, 1,3-dideuteroazulene and 4,6,8-trimethylazulene indicate that, in contrast to the free hydrocarbons, the protons and groups at positions 1,8 and 7 in the complex are equivalent to those at positions 3,4 and 5, *i.e.* in the complex, the azulene molecule is asymmetric with respect to an axial plane passing through C_2-C_6 [190].

The acenaphthylene complex is related to the complexes formed between iron carbonyls and azulene[11,195]. The structure of this complex, (XCVIII), has been determined by means of X-ray analysis[196,197], the Fe–Fe distance (2.77 Å) being the same as in the azulene complexes.

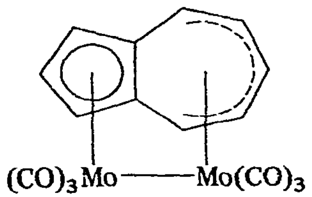

(XCVIII)

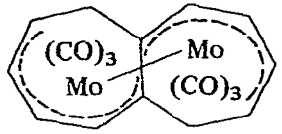

(XCIX)

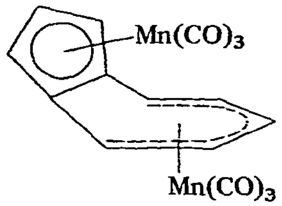

(C)

Unlike the iron carbonyls, ruthenium carbonyl $Ru_3(CO)_{12}$ reacts with 4,6,8-trimethylazulene after prolonged heating in ligroin to yield the tetraruthenium compound (XCIX)[198,199] whose structure has been established from X-ray data. As has been shown for unsubstituted azulene, this reaction may involve the formation of a trinuclear complex of type (C)[200] as an intermediate.

Burton and Wilkinson[201] have prepared the azulene molybdenum complex $C_{10}H_8Mo_2(CO)_6$ from $Mo(CO)_6$ and azulene. Complexes similar to the azulene derivatives were also synthesized[190,202]. X-Ray studies indicated structure (CI) for the unsubstituted complex[203-205]. The length of the Mo-Mo bond in this complex (3.24-3.26 Å) is comparable to that for example in $[C_5H_5Mo(CO)_3]_2$, 3.22 Å[206]. The complex with guaiazulene[207] has a similar structure, its Mo-Mo bond length being 3.27 Å. The respective azulenes could be regenerated in high yield upon thermal decomposition of these complexes. Due to their low solubility in organic solvents, complexes of type (CI) have not been studied in any detail by physical methods.


(CI)


(CII)


(CIII)

The dihydroheptalenic complex (CII) containing two $Mo(CO)_3$ fragments which was obtained later has a similar structure[208], its Mo-Mo bond distance being somewhat shorter (3.19 Å).

It is interesting that the nature of the bond in the manganese azulenic complex (CIII) is similar to that in the molybdenum compound (CI)[209] although the manganese atom attains a krypton-like electronic shell by avoiding the formation of a metal-metal bond. Both manganese atoms are *trans* with respect to the ligand.

IV. THE M–M BOND LENGTHS AND THE NATURE OF THE COMMON LIGAND FRAGMENT

When the available literature on binuclear transition metal complexes involving an intermetallic bond and a common organic ligand is reviewed, it is possible to arrive at certain generalizations regarding these systems. In one of the reviews which dealt in a general manner with inorganic binuclear complexes[210], it was noted that the strength of the M–M bond is not strictly related to its length. From this it follows that the M–M bond length may vary over quite a wide range from one complex to another. From the work reviewed here, it is evident that the length of the intermetallic bond in binuclear complexes with a common unsaturated ligand depends mainly on the type and geometry of the organic ligand and that for complexes of group B it may be considerably greater than that in group A complexes.

Thus, for example, the Fe–Fe distance in group A binuclear complexes ranges from 2.43 to 2.65 Å whereas in complexes of group B this distance ranges from 2.68 to 2.78 Å.

The M–M bond in complexes of group A is shorter than the standard intermetallic bond* and in this case it is possible to refer to the "shortening" effect of the common ligand.

The σ,π-olefinic group exhibits the greatest "shortening" effect of the common organic ligands. The Fe–Fe distance in such complexes is 2.43 Å in (XI), (R = $CH_3C_6H_4$)[15], 2.50 Å in (LVIII)[102], 2.51 Å in (XIX), (R = CH_3)[26], 2.53 Å in (XVIII)[25] and 2.56 Å in (I), (R = CH_3CO)[6]. A similar effect is exhibited by the σ,π-diene group: thus in Reppe–Vetter's complexes the Fe–Fe bond length is equal to 2.49 Å in (XXII), (R = R′ = CH_3)[35], 2.52 Å in (XXVIII)[56] and 2.54 Å in (LI)[88]. The σ,π-allylic group, on the other hand, exhibits only a very weak "shortening" effect, the Fe–Fe bond length being 2.62 Å in (L)[89], 2.64 Å in (XLIX)[88] and 2.65 Å in (LIII)[92] and (LIV)[93]. Similar dependences exist for the complexes of other metals.

The M–M separation in the group B complexes, on the other hand, are characterised by an increase relative to the standard. In such complexes the length of the Fe–Fe bond is only weakly dependent upon the nature of the metal–ligand bond. Thus, for example, the Fe–Fe distance is 2.68 Å in (LXIII), (R = R′ = H)[108], 2.77 Å in (LXIX)[119], (LXVIII)[116] and (XCVIII)[197], 2.78 Å in (XCVII)[194] and 2.87 Å in (XCIII), (R = H)[186].

It is interesting that in the ruthenium trinuclear complexes (LVI) and (LVII) the Ru–Ru bond distance between the atoms coordinated to a common structural ligand fragment (2.77–2.78 Å)[99-101] is shorter relative to that of the standard Ru–Ru bond in $Ru_3(CO)_{12}$ (2.85 Å)[212] while the Ru–Ru bond distance between atoms joined to different parts of a common ligand is increased (2.91–2.92 Å)[99-101]. In (LXXIII) the common ligand "expands" the Ru–Ru bond to 2.94 Å, while the bond length between ruthenium atoms having no common ligand is 2.78 Å[127,128].

Coordination of a bimetallic group to an olefin bond increases the length of this bond to the same extent as in mononuclear transition metal π-olefinic complexes. Thus, for example, in the complexes (XI), (R = $CH_3C_6H_4$), (XIX), (R = CH_3), (LVIII) and (LXIX)

---

[*] The Fe–Fe bond distance (~2.67 Å) in $Fe_3(CO)_{12}$, in a moiety containing no bridging CO groups, may be considered as the standard intermetallic bond length[211].

this bond length is in the range 1.38–1.44 Å[15,26,102,119]. In comparison, the C=C bond lengths in the iron tetracarbonyl complexes have the following values; acrylonitrile (1.40 Å)[213], fumaric acid (1.40–1.42 Å)[214-216], dibenzoylethylene (1.45 Å)[217].

As might be expected, the length of the acetylene bond in π,π-binuclear complexes is considerably greater (within the range 1.35–1.39 Å)[131,140,176] with respect to the standard value, 1.20 Å[19]. On the other hand, in the platinum mononuclear acetylenic complex $(Ph_3P)_2Pt\ (PhC_2Ph)$ it is equal to 1.32 Å[218].

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