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Oligomerisation of Acetylenes in the Presence of Transition Metal Compounds

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The literature data on acetylene cyclo-oligomerisation and polymerisation reactions in the presence of transition metal compounds are reviewed. Both catalytic reactions leading to the synthesis of benzene and cyclo-octatetraene derivatives and linear polymers and cyclo-oligomerisation reactions leading to the formation of organometallic compounds are considered. Modern ideas on the mechanism of acetylene cyclo-oligomerisation and polymerisation reactions are discussed in detail.
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I. INTRODUCTION

A wide variety of inorganic and organometallic compounds (OMC) of transition metals give rise to the cyclo-oligomerisation and polymerisation of acetylenes. Catalytic reactions result in the formation of benzene and cyclo-octatetraene derivatives and also linear polymers. In many cases the cyclo-oligomerisation products are formed as π-complexes with the transition metal. Arene and cyclobutadiene complexes are produced in this way. The reaction of acetylenes with metal carbonyls is frequently accompanied by the insertion of the carbonyl group, which leads to the formation of cyclopentadienones, tropones, quinones, and their π-complexes. When acetylenes react with σ-derivatives of transition metals, the formation of simple cyclotrimerisation products may be accompanied by the formation of products involving the σ-group. The metal atom can also participate in the formation of a heterocycle with M–C bonds.

II. CATALYTIC OLIGOMERISATION REACTIONS OF ACETYLENES

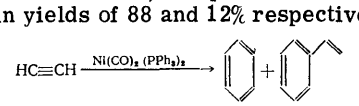
Since the discovery of the cyclo-oligomerisation of acetylenes in the presence of nickel compounds by Reppe in 1940, this reaction has become a convenient method for the synthesis of organic compounds which are otherwise difficult to obtain, such as cyclo-octatetraene, trivinylbenzene, and other benzene derivatives. An enormous number of original studies have been made on the cyclo-oligomerisation and polymerisation of acetylenes under the influence of transition metal compounds and many reviews have been written of which several may be recommended[1-6]. In the present review most attention has been devoted to studies in recent years.

The cyclotrimerisation of acetylenes is catalysed by transition metal compounds of various types, among which homogeneous and mixed metal carbonyls and catalysts of the Ziegler–Natta type are most frequently used. Certain organometallic compounds, salts, etc. also exhibit catalytic activity. The cyclotrimerisation of acetylenes is accompanied by linear polymerisation which becomes the main reaction under certain conditions.

The cyclotetramerisation of acetylenes takes place almost exclusively in the presence of nickel catalysts. Copper(I) salts catalyse the linear oligomerisation of acetylenes.

1. Catalysis by Metal Carbonyls

The first catalysts used in the cyclotrimerisation of acetylenes were carbonylphosphinenickel complexes[7-9]. When acetylene reacts with dicarbonyldi(triphenylphosphine)nickel in acetonitrile, the products are benzene and styrene (in yields of 88 and 12% respectively):



Detailed studies showed that monosubstituted acetylenes form a mixture of 1,2,4- and 1,3,5-trisubstituted benzenes[10-15]. The majority of disubstituted acetylenes (with the exception of but-2-yne-1,4-diol and its ethers[16] as well as monosubstituted acetylenes containing substituents such as t-butyl, COOH, CN, and halogens do not react.

Linear polymerisation of acetylenes occurs together with cyclotrimerisation. The preferential formation of benzene derivatives or linear polymers depends mainly on the nature of the substituent at the triple bond. More reactive monomers give rise mainly to aromatic products, while the yield of linear polymer increases for less reactive acetylenes.

The catalytic activity of the nickel atom and the nature of the product also depend on the nature of the ligand linked to the metal. For example, $Ni(CO)_3PPh_3$ is an effective catalyst of the polymerisation and cyclotrimerisation of acetylenes, while $Ni(CO)(PPh_3)_3$ and $Ni(PPh_3)_4$ are inactive in these reactions[7,17,18]. Reports have been published on catalysis by nickel tetracarbonyl[19-21]. $Ni(CO)_2[P(OPh)_3]_2$ promotes the aromatisation of acetylenes, while linear polymerisation takes place preferentially[17] in the presence of $Ni(CO)_2[P(CH_2CH_2CN)_3]_2$.

The cyclotrimerisation of tolane under the influence of iron, cobalt, manganese, nickel, molybdenum, and tungsten carbonyls has been investigated[20]. As shown below (see Section III), these metal carbonyls react with acetylenes, forming organometallic compounds of various types. Organic products are formed under more severe conditions. For example, tolane reacts with $Fe_3(CO)_{12}$ at 260–280°C with formation of hexaphenylbenzene (yield up to 75%);[20] at lower temperatures a number of organoiron compounds have been isolated[22,23]. Cyclo-octyne cyclotrimerises in the presence of $Fe(CO)_5$ even at room temperature[24].

Carbonyl derivatives of cobalt—$Co_2(CO)_8$, $MgCo_2(CO)_8$, $Hg[Co(CO)_4]_2$, and $RC_2R'Co_2(CO)_6$—exhibit a very high catalytic activity in the aromatisation of acetylenes. Both mono- and di-substituted acetylenes react. Acetylenes with various substituents give rise preferentially or exclusively to asymmetrically substituted benzenes[20,25]. When acted upon by $Hg[Co(CO)_4]_2$, substituted butadiynes are converted into a mixture of 1,2,4- and 1,3,5-trialkylnylbenzenes[26]. Non-conjugated terminal diacetylenes form, together with polymers, also dimers containing one aromatic ring and one triple bond[27]. The cyclotrimerisation of ferrocenylacetylenes in the presence of $Co_2(CO)_8$ has been described[28–30]. $[Co(CO)_3NO]$ has also been suggested as a catalyst[18,31].

Cobalt carbonyl and $RhM_4(CO)_{12}$ have been compared in the cyclotrimerisation of phenyl acetylene[32]. In catalysis by cobalt carbonyl 1,2,4-triphenylbenzene is formed 7–9 times faster than the symmetrical isomer; in catalysis by the rhodium compound the isomer ratio is 2:1.

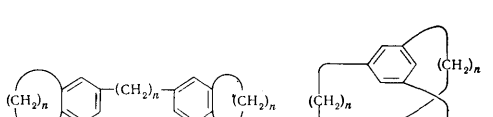
$[RhCl(CO)_2]_2$ has been used for the cyclotrimerisation of tolane[33].

Cyclotrimerisation also takes place in the presence of molybdenum and tungsten hexacarbonyls[20] and triacetonitriletricarbonyl[34] and arenetricarbonyl complexes of chromium and molybdenum[35].

2. Ziegler–Natta Catalysts

Acetylenes undergo linear polymerisation[36–38] and cyclotrimerisation[39–47] in the presence of a catalytic system comprising titanium halides or alkoxides and alkylaluminium derivatives. The R_3Al–$TiCl_4$ systems (R = ethyl or t-butyl) are usually employed to synthesise benzenes. The yields of the corresponding benzene derivatives and linear polymers depends markedly on the Ti:Al ratio[48,49]. Monosubstituted acetylenes do not decompose the catalyst but cyclotrimerise with formation of a mixture of 1,2,4- and 1,3,5-trisubstituted benzenes[28,50].

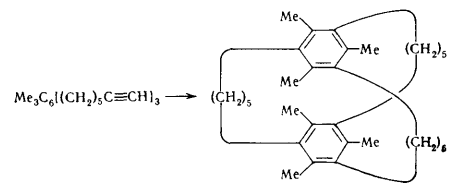
The reactions of conjugated and non-conjugated diacetylenes and triacetylenes have been investigated[27,51–55]. Hexa-2,4-diyne forms trimethyltripropynylbenzene (5%) together with polymers. Non-conjugated alkadiynes $HC{\equiv}C(CH_2)_nC{\equiv}CH$ produce, together with polymers, two types of trimers: (I) (in yields up to 13% for $n = 2$) and traces (less than 1%) of compound (II) containing two benzene rings linked by three polymethylene chains:



(I)

(II)

Cage compounds have been obtained in yields up to 50% from aromatic triynes[51]:



Acetylenes trimerise and polymerise in the presence of trialkylaluminium and vanadium[39,56–60] or cobalt[61,62] derivatives. The $i\text{-}Bu_3Al$–NiX_2[63–65] and $i\text{-}Bu_3Al$–iron(III) naphthenate[66] systems polymerise acetylene. Et_2Zn–$Cr(OBu\text{-}t)_3$ induces the dimerisation of monosubstituted acetylenes to vinylacetylene derivatives[67]. The replacement of diethylzinc by triethylaluminium leads to the formation of alkylbenzenes.

It has been shown for the R_3Al–$VOCl_3$ and $i\text{-}Bu_3Al$–$TiCl_4$ catalytic systems that the activity of the catalyst is related to the formation of a reduced form of the metal[56,68].

3. Catalysis by Organometallic Compounds

Dicyclopentadienyl derivatives of titanium[69] and vanadium[70] polymerise acetylene. Many monosubstituted acetylenes give rise to the corresponding benzene derivatives in the presence of vanadocene and phenylacetylene produces a linear oligomer. A catalytic effect of tricyclopentadienyllanthanides in the cyclotrimerisation of certain acetylenes has been mentioned[71].

Acetylenes cyclotrimerise and copolymerise with olefins in the presence of di(cyclo-octatetraene)iron[72,73]. The linear polymerisation and cyclotrimerisation of acetylenes is catalysed by cyclo-octa-1,5-dienenickel halides[75] and π-allyl complexes of palladium and nickel[76–79].

Both catalytic and stoichiometric cyclisation and polymerisation reactions of acetylenes take place in the presence of diacrylonitrilenickel. Thus acetylene produces cyanoheptatriene, benzene, and cyclo-octatetraene (COT)[80,81]. Triphenylphosphine suppresses the formation of COT and the synthesis of benzene becomes a catalytic process. In the presence of an excess of acrylonitrile, the main reaction product is cyanoheptatriene (see also Cairns et al.[82]). Disubstituted acetylenes give rise to tetrasubstituted benzonitriles together with hexasubstituted benzenes[80,83]. Similarly hexaphenylbenzene and tetraphenylbenzaldehyde have been obtained from tolane and diacroleinnickel.

When acted upon by diacrylonitrilenickel, but-2-yne[20] and hexafluorobut-2-yne (HFB)[84] undergo linear polymerisation together with cyclotrimerisation. Propargyl alcohol, phenylpropiolaldehyde, propiolic and acetylenedicarboxylic acid esters, and phenylacetylene form polymers[80].

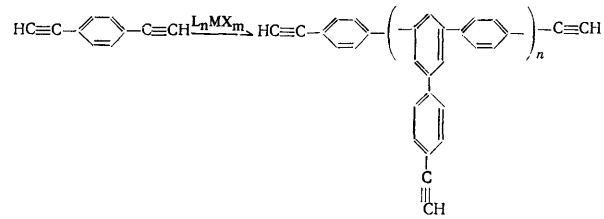
Dimesitylcobalt catalyses the trimerisation of but-2-yne[85]. The cyclisation of acetylenes in the presence of σ-aryl and σ-alkyl derivatives of other metals is a stoichiometric reaction and will be considered below (see Section III). Platinum and nickel σ-acetylides $(Ph_3P)_2M(C{\equiv}CPh)_2$ polymerise phenylacetylene[86,87].

2. Catalysis by Phosphine and Phosphite Complexes of Cobalt Subgroup Metals

Certain rhodium and iridium complexes catalyse the cyclotrimerisation and polymerisation of acetylenes[88].

Thus $RhCl(PPh_3)_3$ causes the polymerisation of HFB [89]. Dimers have been obtained from dialkylethynylmethanols [90]. Phenylacetylene produces a polymer together with the dimer [90-92]. Certain disubstituted acetylenes give rise to the corresponding benzene derivatives [93]. Rhodium and iridium complexes $RhH(CO)(PPh_3)_3$, $IrH(CO)_2(PPh_3)_2$, [94] and certain others [89,90] catalyse the cyclotrimerisation of alk-1-ynes.

Cobalt complexes, for example $CoBr[P(OEt)_3]_4$, have been used for the polycyclotrimerisation of aromatic diacetylenes [95-98]:



Complexes of zerovalent nickel with phosphines and certain other ligands of a similar type are active in the copolymerisation of acetylenes with butadiene [99].

5. Catalysis by Salts of Transition Metals and Their Complexes

Palladium(II) chloride and its benzonitrile complex $(PhCN)_2PdCl_2$ (BNP) [100-103], nickel compounds $(R_3P)_2NiX_2$ [60, 87,104], and $K_4Ni_2(CN)_6$ [105], and rhenium, niobium, and tantalum pentahalides and their adducts with NaX, KX, $POCl_3$, and amines [106-108] catalyse the cyclotrimerisation of disubstituted acetylenes.

Copper(I) salts catalyse the linear polymerisation of acetylenes. When acetylene is passed into an acid solution of CuCl in the presence of NH_4Cl, vinylacetylene, divinylacetylene, and polymers are formed [109,110]. These reactions have been reviewed in detail in monographs [111-113].

6. Other Catalysts

A number of catalytic systems comprising Group VIII transition metal salts and a hydride reducing agent, for example $(Ph_3P)_2NiCl_2$–$NaBH_4$), have been suggested for acetylene cyclotrimerisation and linear polymerisation reactions [18,92,114-118]. Acetylenes cyclotrimerise in the presence of metal oxide catalysts (chromoaluminosilicate, alumina–nickel oxide–molybdenum oxide, and others [119]). Various acetylenes are converted into dimers, benzene derivatives, and higher polymers in the presence of palladium on charcoal [120].

7. Cyclotetramerisation of Acetylenes

The cyclotetramerisation of acetylenes is catalysed almost exclusively by nickel compounds. Among compounds with other metals, $Zn[Co(CO)_4]_2$ is known; acetylene gives rise to about 3% of COT together with benzene [121].

The interaction of acetylene with bivalent nickel compounds (cyanide, acetylacetonate) takes place at temperatures in the range 80–120°C and pressures between 15 and 25 atm. [8,122] The yields of COT amount to 70 to 90%, in addition up to 15% of benzene is obtained as well as polymers and a nickel-containing product resembling cuprene. Insignificant amounts of styrene, 1-phenylbuta-1,3-diene, and vinylcyclo-octatetraene as well as traces of azulene and naphthalene are produced [123-128]. Under analogous conditions, substituted acetylenes form linear polymers and benzene derivatives [129]. In the mixed cyclotetramerisation of acetylene with mono- and di-substituted acetylenes, a number of mono- and di-substituted cyclo-octatetraenes were obtained [130-134].

Acetylenic alcohols, for examples 2-methylbut-2-yn-3-ol, form the corresponding isomeric tetrasubstituted cyclo-octatetraenes in the presence of the following catalytic systems: nickel tetracarbonyl and di(cyclo-octa-diene) nickel; nickel cyanide, acetylacetonate, and ethoxide; $NiCl_2$ – $NaBH_4$. [135] When acted upon by di-(π-allyl)- nickel propargyl alcohol and 2-methylbut-3-yn-2-ol are converted into linear dimers and cyclo-octatetraene derivatives [136]. The addition of phosphine suppresses the formation of the latter. The formation of small amounts of tetrasubstituted cyclo-octatetranes was observed also when $Ni(PX_3)_4$ (X = = Cl or F) were allowed to act on propiolic acid esters [137]; in this case the main reaction products are benzene derivatives.

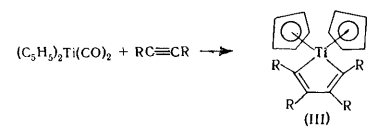
III. SYNTHESIS OF ORGANOMETALLIC COMPLEXES BY THE CYCLO-OLIGOMERISATION OF ACETYLENES

When acetylenes were allowed to react with various transition metal compounds, cyclo-oligomerisation resulted in the formation of all types of π-complexes known at present as well as compounds with an M–C σ-bond. The synthesis of organometallic compounds from acetylenes has been described in a number of reviews (see, for example, Refs. 2, 4, 5, and 138–142).

1. Reactions of Acetylenes with Metal Carbonyls

The reactions of acetylenes with the carbonyls of certain metals (iron, nickel) were investigated for the first time by Reppe [8,143], who isolated a number of organometallic compounds and organic cyclo-oligomerisation and carbonylation products.

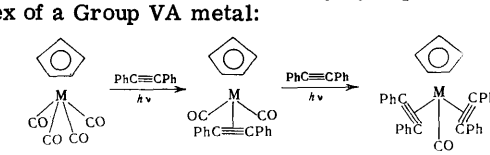
Acetylenes cyclo-oligomerise in the presence of carbonyl-cyclopentadienyl complexes of Group IVA and VA metals. The two carbonyl groups of dicarbonyldicyclopentadienyltitanium are displaced by phenylacetylene and tolane with dimerisation of acetylene and the inclusion of the metal atom in the ring [144]:



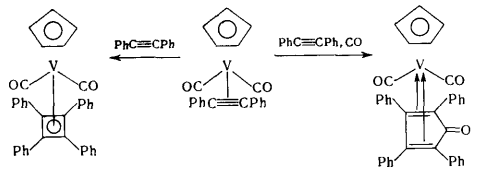
(III)

Acetylenic π-complexes and also π-complexes with other organic ligands and benzene and cyclopentadienone derivatives have been obtained from tolane and tetracarbonylcyclopentadienyl complexes of vanadium [145], niobium [146], and tantalum [147]. It was possible to trace the formation of cyclobutadiene, cyclopentadienone, and benzene structures in these reactions.

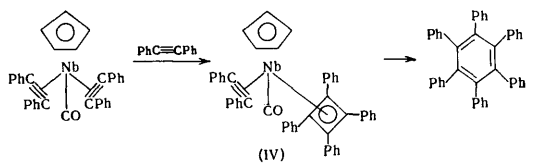
Two acetylene molecules can be introduced successfully into the molecule of the tetracarbonylcyclopentadienyl complex of a Group VA metal:



The ditolane complex of vanadium decomposes fairly readily with formation of tetracyclone. On heating, the monotolane complex combines with another tolane molecule with formation of a cyclobutadiene complex. In the presence of carbon monoxide, a tetracyclone complex is formed together with the cyclobutadiene complex[148]:



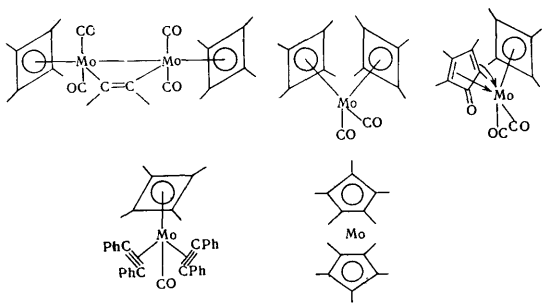
The ditolane complex of niobium combines with a third tolane molecule to form a mixed diphenylacetylene–tetraphenylcyclobutadiene complex (IV).[149] On heating, the complex decomposes with formation of hexaphenylbenzene:



The ditolane complex of tantalum undergoes similar reactions[147]. The structures of the niobium[149–153] and vanadium[154] complexes have been confirmed by X-ray diffraction.

Thus the formation of cyclic structures is preceded by the incorporation in the acetylene complex of a second and third acetylene molecule. The formation of the cyclopentadienone fragment is due to the insertion of a carbonyl group linked to the metal or of the carbon monoxide introduced into the system, which probably is also first coordinated to the metal. Hexaphenylbenzene is presumably formed as a result of an intramolecular interaction of the coordinated acetylene and cyclobutadiene. The parallel orientation of the triple bond of the acetylene ligand in relation to one of the sides of the cyclobutadiene ligand in complex (IV), which was established by X-ray diffraction analysis, suggested that the formation of hexaphenylbenzene proceeds via an intermediate complex with Dewar benzene.

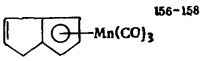
The following complexes have been obtained from tolane and molybdenum carbonyls [$Mo(CO)_6$ and (diglyme)$Mo(CO)_3$]:



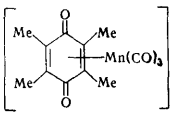
as well as tetracyclone and hexaphenylbenzene[155].

The reaction of triacetonitriletricarbonylchromium with tolane gives rise to a cyclopentadienone complex of chromium, which rapidly decomposes with formation of tetracyclone[34].

Carbonyl derivatives of manganese, $Mn_2(CO)_{10}$ or $CH_3Mn(CO)_5$, react with acetylene at an elevated pressure and temperature to form[156–158]



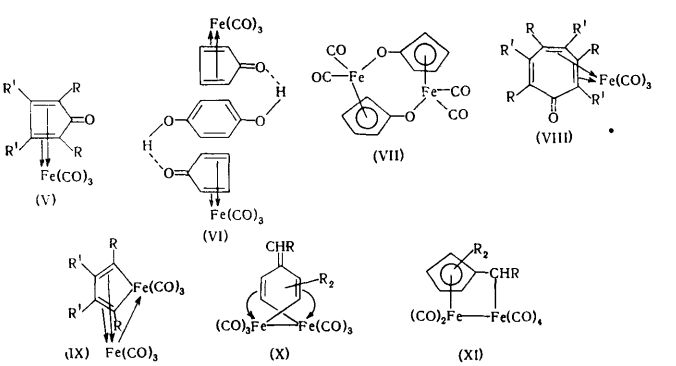
The reaction of but-2-yne with $[Mn(CO)_5]^-$ in sunlight leads to the formation of a mixture of products, one of which is duroquinone[159]. It is presumably formed from the intermediate duroquinone complex



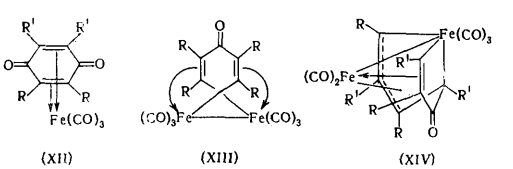
The most typical products of the reactions of acetylenes with iron carbonyls are organometallic complexes with new ligands formed as a result of the cyclo-oligomerisation of acetylenes with participation of the carbonyl group and/or the iron atom. Complexes of certain types are produced only from acetylene or its monosubstituted derivatives, while others are formed from disubstituted acetylenes.

The reaction of acetylene with $Fe(CO)_5$[8,143] or $Fe_3(CO)_{12}$ and $Fe_2(CO)_9$[138,160–164] yielded complexes (see Scheme 1) with cyclopentadienone [(V)–(VII)] and tropone (VIII) as ligands as well as metal-containing cyclic products [(IX)–XI) (R and R′ = H)].

Scheme 1



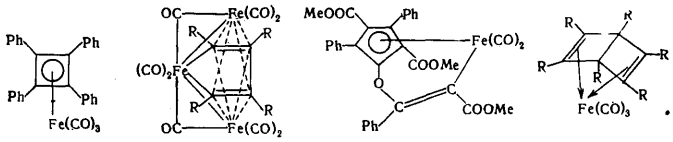
The formation of quinone complexes (XII)[24,165] and also complexes of types (XIII)[22,166] and (XIV)[138] is characteristic of dialkylacetylenes:



Cyclobutadiene (XV) and cyclopentadienone (V) complexes as well as di- and tri-nuclear metal-containing cyclic complexes (IX), (XIII), and (XVI) have been obtained from diarylacetylenes[22,23,167–173]. Complexes of types (V), (IX), (XIII), and (XVI) have been synthesised from diferrocenylacetylene[30].

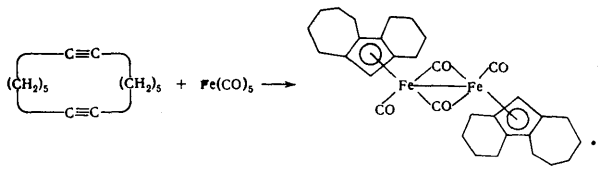
The complex (XVII) has been synthesised from ethyl phenylpropiolate and iron nonacarbonyl[174]. The structure of a complex (XVIII) with a hexasubstituted Dewar benzene as the ligand has been attributed to the product of the

reaction of the dimethyl ester of acetylenedicarboxylic acid with $Fe_2(CO)_9$ (Avram et al.[175]):

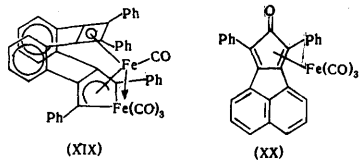


(XV) (XVI) (XVII) (XVIII)

Fluoroacetylenes form complexes analogous to (V) and (IX).[84,176-178] Only one of the two triple bonds is involved in the reaction of diphenylbutadiyne with iron carbonyls and the products are isomeric complexes of types (V), (IX), etc. with phenyl- and phenylethynyl-substituted ligands[26]. Both triple bonds of non-conjugated diacetylenes are involved in the reaction, for example[179]:



The reaction of *o*-di(phenylethynyl)benzene with $Fe(CO)_5$ and $Fe_3(CO)_{12}$ gives rise to a number of complexes[180], one of which has the structure (XIX)[181]. Acecycloneiron tricarbonyl (XX) has been obtained from 1,8-di(phenylethynyl)naphthalene and $Fe(CO)_5$ (Bossenbrock and Shechter[182]):



(XIX) (XX)

Many of the organoiron products described can be obtained by the reaction of acetylenic π-complexes of iron $RC_2RFe(CO)_4$ and $RC_2RFe_2(CO)_7$ with acetylenes[138].

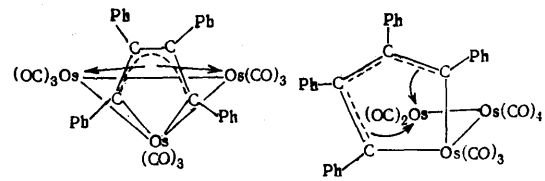
The structures of iron complexes were established on the basis of infrared and NMR spectroscopic data and chemical properties and in many cases also by specific synthesis. X-Ray diffraction structural studies have been made on the following complexes: (V),[183] (VIII),[184,185] (IX),[186] (X),[187,188] (XI),[188,189] (XIII),[190,191] (XIV),[192] (XV),[193] (XVI),[194] (XVII),[174], and (XIX).[181]

The formation of the ferracyclopentadiene structure was traced in the reaction of tolane with tri-iron dodecacarbonyl. Low yields of polynuclear complexes containing one[195] and two[22,194] acetylenic ligands were isolated from the reaction products under mild conditions. Determination of the structures of these intermediates by X-ray diffraction made it possible to deduce the mode of the gradual transformation of the acetylenic ligand into a metal-containing ring (see Scheme 2). In the first reaction stage carbonyl groups in $Fe_3(CO)_{12}$ are replaced by an acetylene molecule as in compound (XXI). Further substitution of CO results in the formation of a violet complex (XXII) which contains two independently coordinated acetylenic ligands. The violet complex then rearranges to the black isomer (XVI) containing the ferracyclopentadiene fragment. In the last stage one of the iron atoms is eliminated with formation of the stable dinuclear complex (XIX) with a metal-containing ring.

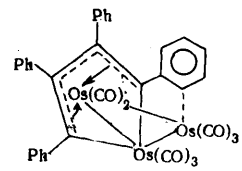
When phenylacetylene reacts with iron carbonyls, the complexes (V), (VIII), (IX), (XI), and (XIV) are formed, while the product of the reaction of *p*-bromophenylacetylene and $Fe_3(CO)_{12}$ is the complex (X).[23,138,196]

A characteristic feature of the behaviour of ruthenium and osmium dodecacarbonyls is a higher stability of the metal-containing cluster in the reaction with acetylenes compared with the corresponding iron carbonyl. After refluxing tolane with $Ru_3(CO)_{12}$ in petroleum ether, complexes analogous to the corresponding iron complexes (V), (IX), and (XVI) were isolated[197-202]. Under the reaction conditions, the dimethyl ester of acetylenedicarboxylic acid trimerises quantitatively to $C_6(COOCH_3)_6$.

The reaction of $Os_3(CO)_{12}$ with but-2-yne involves the formation of the osmium analogues (V) and (IX)[203]. Tolane gives rise to $(Ph_2C_2)_2Os_3(CO)_9$ (XXIII) which may be represented by the alternative structures (XIIIa) and (XIIIb)[204] and the complex $(Ph_2C_2)_2Os_3(CO)_8$,[204,205] which has the structure (XXIV) according to X-ray diffraction analysis[206]:



(XXIIIa) (XXIIIb)

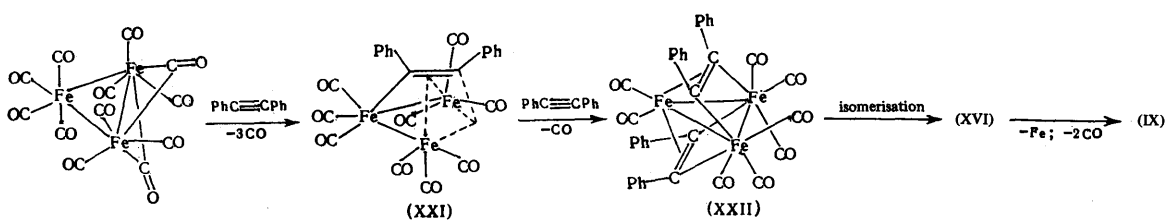


(XXXIV)

When carbon monoxide is allowed to act on (XXIII), the product is an analogue of the complex (IX).

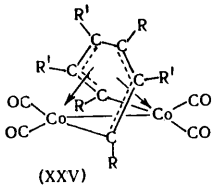
The cobalt carbonyls $Co_2(CO)_8$ and $Co_4(CO)_{12}$ react with acetylenes to form acetylenic π-complexes $RC_2R'CO_2(CO)_6$ and $RC_2R'CO_4(CO)_{10}$ and their cyclo-oligomerisation products—the complexes (XXV) and (XXVI), as well as

Scheme 2

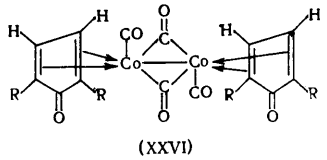


(XXI) (XXII)

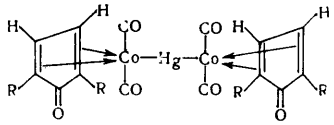
the corresponding cyclopentadienones and benzenes [25,176,207-211]. The structure (XXV) was established by X-ray diffraction [212]:



(XXV)



(XXVI)

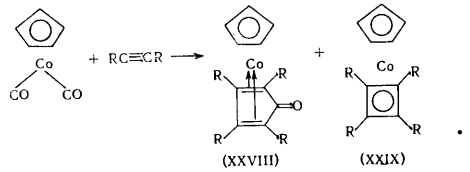


(XXVII)

Mercury tetracarbonylcobaltate reacts with disubstituted acetylenes to form acetylenic complexes, while the reaction involving monosubstituted acetylenes proceeds without the elimination of mercury and with formation of the cyclopentadienone complexes (XXVII) [25,138,213]. The complexes $R_2C_4H_2Co_4Hg_2(CO)_{12}$, which probably contain a cyclobutadiene ligand, have been obtained from certain monosubstituted acetylenes.

When acetylenehexacarbonyldicobalt reacts with acetylenes different from that coordinated to the metal atom, isomers of substituted benzenes and cyclopentadienones, with partial incorporation of the initial acetylene bound in the complex, are produced [25,214-217].

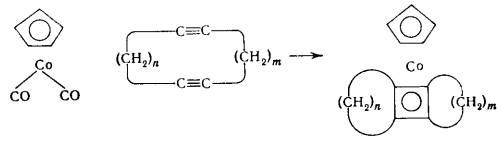
Disubstituted acetylenes dimerise in the presence of π-cyclopentadienylcobalt dicarbonyl with formation of cyclopentadienone (XXVIII) and cyclobutadiene (XXIX) complexes as well as hexa-substituted benzenes and tetrasubstituted cyclopentadienones [218,219]:



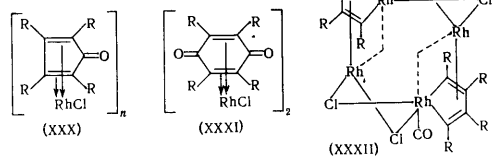
(XXVIII) (XXIX)

X-Ray diffraction structural analysis of compound (XXVIII) has been carried out [220,221].

Depending on R, the reaction involves the formation of complexes (XXVIII) [84,159,222,223] or (XXIX) [224] only. Macrocyclic alkadiynes undergo transannular cyclisation [225,226]:

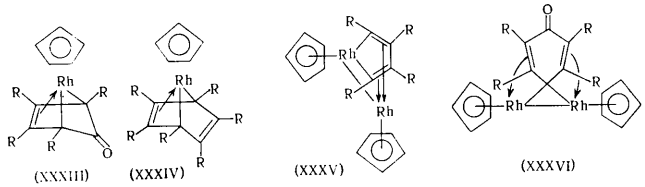


The reaction of disubstituted acetylenes with chlorodicarbonylrhodium leads to the formation, depending on the acetylene, of cyclopentadienones and quinones and their π-complexes (XXX) and (XXXI), as well as complexes with a metal-containing cyclic fragment (XXXII) [33,222,227-229] [the structure (XXXII) was established by X-ray diffraction [230]] and hexasubstituted benzenes:



(XXX) (XXXI) (XXXII)

The reaction of π-cyclopentadienylrhodium carbonyl with HFB leads to the complexes (XXXIII) and (XXXIV) [222] as well as metal-containing cyclic complexes (XXXV) and (XXXVI) [231]. The structure (XXXIV) was established by X-ray diffraction [232]:



(XXXIII) (XXXIV) (XXXV) (XXXVI)

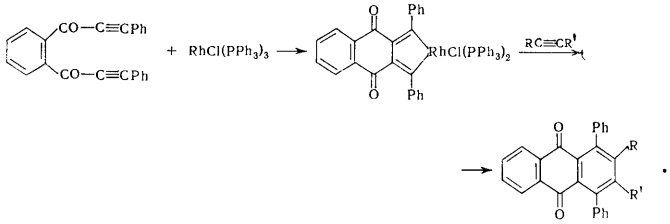
The complexes (XXXIII), (XXXIV), and (XXXVI) were obtained by treating the acetylene complex $[C_5H_5Rh(CO)]_2$. $.(CF_3C_2CF_3)$ with HFB.

Di(pentafluorophenyl)acetylene yielded the pentafluorophenyl analogues of compounds (XXXIII) and (XXXV) and also hexa(pentafluorophenyl)benzene [223,233,234]. The complexes (XXXIV) have also been obtained from $(CH_3)_5C_5M(OAc)_2H_2O$ (M = Rh or Ir) and the dimethyl ester of acetylenedicarboxylic acid in the presence of hydrogen [235].

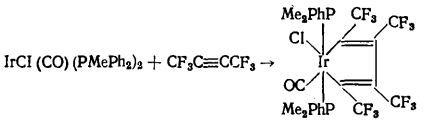
The reaction of $Ni(CO)_4$ with tolane [19] or cyclo-octyne [129] yields the corresponding cyclopentadienones and their nickel complexes.

2. Reactions of Acetylenes with Phosphine, Arsine, and Stibine Metal Complexes

As for the carbonyls, the substitution of phosphine and other similar ligands in the reaction with acetylene is frequently accompanied by the formation of cyclo-oligomerisation products. Rhodium and iridium form metal-containing cyclic products under these conditions. For example, the reactions of $RhCl(MPh_3)_3$ (M = Sb or As) with HFB [236-238] and of $RhCl(PPh_3)_3$ with *o*-di(arylpropionyl)benzene and 2,3-di(phenylpropionyl)naphthalene [239-243] yielded rhodiacyclopentadiene complexes, which can subsequently react with acetylenes whereby they are converted into benzene derivatives:



Similar reactions have been achieved for iridium complexes[244]:



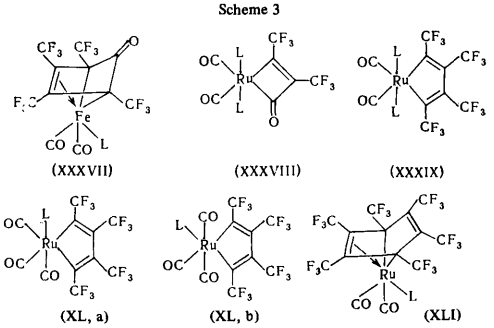
The reactions proceed via intermediate acetylene π-complexes, which were isolated when the reaction was carried out under milder conditions.

The cyclotrimerisation of HFB in the presence of tetra(dimethylphenylarsine)nickel with formation of $(PhMe_2As)_2NiC_6(CF_3)_6$ has been described[245].

3. Reactions of Acetylenes with Carbonylphosphine and Phosphitocarbonyl Complexes of Group (VIII) Metals

The photochemical reaction of HFB with complexes of metals in the iron triad of the type *trans*-$M(CO)_3L_2$, where L = tertiary phosphine or phosphite, has been investigated[246]. The nature of the reaction product depends primarily on the metal and to a lesser extent on the reaction conditions. The reaction of iron with an excess of HFB yielded the complexes (XXXVII). The ruthenium complexes react differently depending on the reaction conditions. The complex (XXXVIII) was obtained from equimolar amounts of $Ru(CO)_3[P(OMe)_3]_2$ and HFB. The complexes (XXXIX) and (XL, a and b) are formed in the presence of HFB. When the reaction is carried out with more prolonged irradiation, the product is the complex (XLI) (see Scheme 3).

Scheme 3



The osmium complexes do not catalyse the cyclo-oligomerisation of HFB.

4. The Reactions of Acetylenes with Certain Transition Metal π-Complexes

At the instant of its formation dicyclopentadienyltitanium reacts with tolane[247] or propyne[248], forming compound (III). Together with a small amount of hexaphenylbenzene, the same complex is formed on thermal decomposition of di-(π-cyclopentadienyl)-σ-diphenyltitanium in the presence of tolane[249].

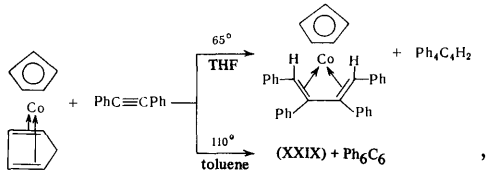
The rhodium complex of norbornadiene (NBD) reacts with an excess of but-2-yne to form an arene complex[250]:

$$[Rh(NBD)]^+ + MeC{\equiv}CMe \rightarrow [Rh(C_6Me_6)(NBD)]^+ .$$

In many instances acetylene substitutes an organic π-ligand, two or three acetylene molecules forming a new ligand.

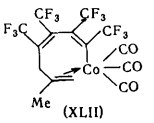
Thus the complexes (XXIX) have been obtained from cobaltocene and disubstituted acetylenes[84,251] including macrocyclic alkadiynes[225]. The complexes (XXIX) are formed also from cyclopentadienylcyclo-octatetraenecobalt[252,253] or cyclopentadienylcyclo-octa-1,5-dienecobalt[251,252].

Tolane reacts with π-cyclopentadienyl-π-cyclopentadienecobalt via the mechanism[253]

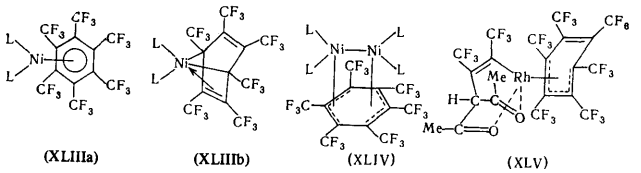


while its reaction with cyclo-octatraeneiron tricarbonyl results in the formation of the complexes (IX) and (XV)[253-255].

Together with polymerisation the reaction of π-2-methylallylcobalt tricarbonyl with HFB leads to the formation of the compound (XLII) produced by the insertion of two acetylene molecules in the cobalt-allyl bond[256]:

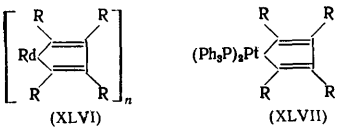


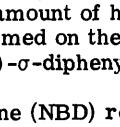
Di(cyclo-octa-1,5-diene)nickel reacts with HFB to form a mononuclear complex (XLIIIa) or (XLIIIb) and a dinuclear complex (XLIV) (L_2 = 1,5-C_8H_{12})[245]:



The displacement of cyclo-octa-1,5-diene by hexafluorobut-2-yne from acetylacetonatocyclo-octadienerhodium has been described[257]. According to X-ray diffraction data, the product has the structure (XLV)[258].

The action of certain acetylenes on dibenzylideneacetone complexes M(DBA)$_2$ (M = Pd or Pt) and Pt(DBA)$_3$ has been investigated[259,260]†. The product of the reaction of the palladium complex with the dimethyl ester of acetylenedicarboxylic acid is palladiacyclopentadiene (XLVI), which gives rise to hexasubstituted benzenes on heating with acetylenes R'S≡CR'. The reaction is catalytic for R' = COOMe:



The structure (XLVI) was established on the basis of the chemical behaviour and also spectroscopic data. The association of individual molecules is due to the involvement of the ester group in coordination to the metal of the type  Pd. Platinum complexes react more slowly with the dimethyl ester of acetylenedicarboxylic acid than the palladium analogue. The metal-containing

†In complexes of this type the metal–ligand bond is formed by the π-electron system of the carbonyl group.

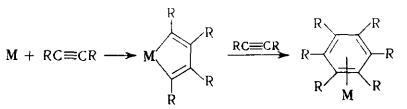
cyclic product was isolated in the form of a triphenylphosphine derivative (XLVII). Hexamethyl mellitate was also isolated from the reaction products, which is evidence of the greater ease of conversion of the metallocyclopentadiene into benzene in the case of platinum.

5. Cyclo-oligomerisation Reactions of Acetylenes Involving σ-Derivatives of Transition Metals

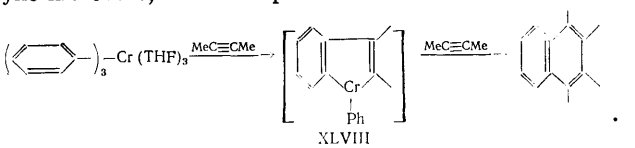
When triphenylchromium tristetrahydrofuranate reacts with but-2-yne, a number of organic and organochromium products are formed[261-264]. The reaction mode depends on the proportions of the reactants. Thus when less than 4 moles of the butyne per mole of Ph_3Cr are employed, the products are 1,2,3,4-tetramethylnaphthalene and its π-complex. An excess of the acetylene promotes the formation of hexamethylbenzene. When the reactant ratio is $Ph_3Cr : C_4H_6 = 1 : 6$, 40% of tetramethylnaphthalene 55% of hexamethylbenzene, and small amounts of the corresponding π-complexes are produced.

The authors believe that the reaction mechanism consists in the stepwise substitution of THF molecules in $Ph_3Cr(THF)_3$ by acetylene. The coordinated acetylene molecules cyclise with formation of aromatic systems and the corresponding π-complexes. The effect of the reactant ratio on the composition of the reaction products is evidence that the displacement of THF by acetylene takes place in steps. The phenyl group linked by a σ bond to chromium can also participate in the intramolecular reaction, which results in the formation of tetramethylnaphthalene.

The possible formation of a five-membered metal-containing ring, which then combines with a third acetylene molecule and is converted into a π-bonded benzene ring, has been suggested[265]:



In order to account for the formation of tetraphenylnaphthalene, a mechanism involving stages in which the butyne is inserted in the phenyl–chromium bond with formation of styrylchromium, its cyclisation to "benzochromole" (XLVIII), and the reaction of benzochromol with a second butyne molecule, has been put forward[266]:



XLVIII

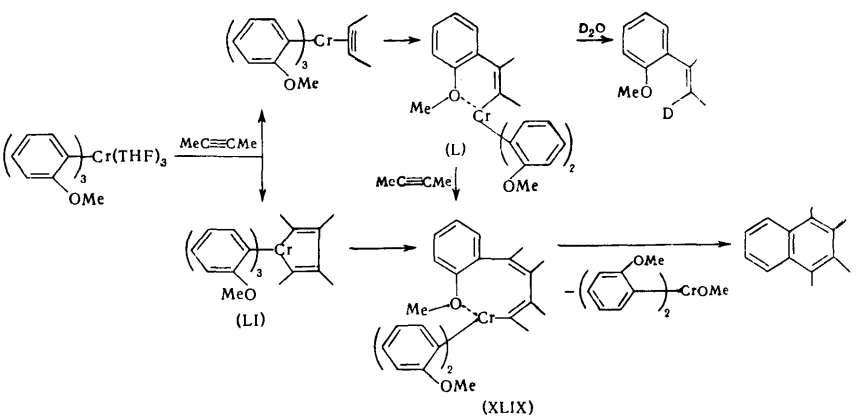
However, objections have been raised to the formation of (XLVIII) as a precursor of tetramethylnaphthalene[267]. When but-2-yne reacts with tri-(2-methoxyphenyl)chromium, 1,2,3,4-tetramethylnaphthalene is formed together with *cis*-2-(2-methoxyphenyl)but-2-yne and 2,3-di-(2-methoxyphenyl)but-2-ene. Since the elimination of the methoxy-group from the *o*-anisyl substituent is observed only in the formation of tetramethylnaphthalene, the authors believe that the *o*-anisylbutadienechromium compound (XLIX) is more likely to be its precursor. The chromium complex can be formed in its turn as a result of the reaction of the σ-vinyl derivative of chromium (L) with a second but-2-yne molecule or as a result of the transfer of the aryl group within the metal-containing ring (LI) formed from two acetylene molecules (see Scheme 4).

Tolane does not form arene complexes with triphenylchromium, the only products being hexaphenylbenzene, tetraphenylnaphthalene, 9,10-diphenylphenanthrene, terphenyl, and tetraphenylethylene[262,268]. Acetylene and monosubstituted acetylenes polymerise. *trans*-Isomers of 1,6-diphenylbuta-1,3-diene and also biphenyl and the conjugated *trans*-polyene $Ph-(-CH=CH-)_n-Ph$ were obtained from acetylene at −70°C.[269] HFB forms a linear polymer[84].

Various aryl derivatives of chromium can be used as cyclising agents[262,270,271]. If the *ortho*-positions are blocked, for example in trimesitylchromium, the only reaction product is a hexa-substituted benzene.

Like the phenyl group, an alkyl group linked by a σ bond to chromium can also participate in the formation of a new ring[263,265,272]. Thus the reaction of tolane with triethylchromium tetrahydrofuranate leads to the formation of 1,2,3,4-tetraphenylbenzene in addition to hexaphenylbenzene, the role of the chromium atom consisting not only in the elimination of the hydrogen atom from the

Scheme 4

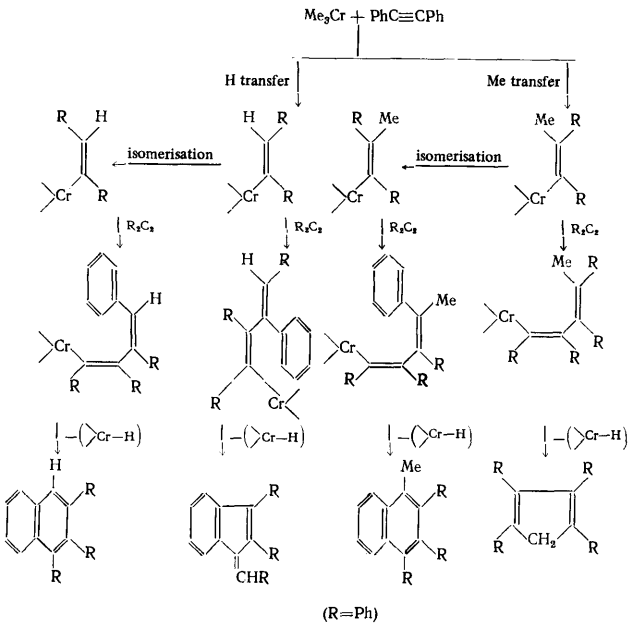


(XLIX)

CH_3 group of the ethyl substituent but also in the dehydrogenation of the resulting dihydrotetraphenylbenzene to an aromatic product. Trimethylchromium gives rise to phenyl derivatives of cyclopentadiene, benzene, and naphthalene [265 269 272-275].

The formation of certain reaction products may be interpreted in terms of metal hydride elimination from isomeric σ-butadienyl derivatives of chromium in accordance with Scheme 5 (Sneeden and Zeiss [276]):

Scheme 5



Tri-n-butylchromium forms with oct-4-yne and but-2-yne a complex mixture of products, from which the corresponding hexa-alkylbenzenes were isolated [270]. Trivinyl chromium [277] and triallylchromium [278] react with but-2-yne to give, together with hexamethylbenzene, condensation products involving σ-groups. Tri-β-styrylchromium forms only hexasubstituted benzenes [279].

The cyclisation of butyne to di(hexamethylbenzene)-chromium on reaction with a mixture of chromyl chloride and triethylaluminium has been described [280, 281]. The methyl derivative of chromium Li_3CrMe_6 does not react with phenylacetylene [273]. The cyclotrimerisation of disubstituted acetylenes in the presence of σ-derivatives of bivalent chromium has been described [273,278,282].

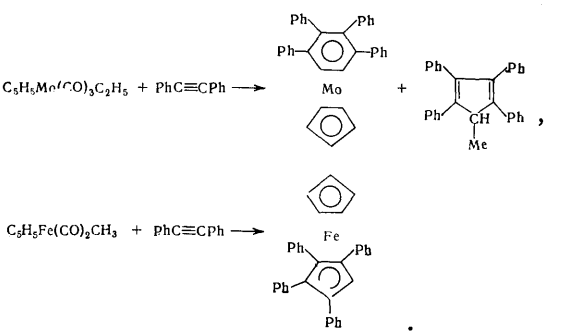
σ-Derivatives of bivalent manganese and cobalt (diphenylmanganese and dimesitylcobalt) cyclotrimerise but-2-yne with formation of hexamethylbenzene and arene π-complexes [283,284]. Naphthalene derivatives are not formed in this case. The π-complex obtained from Ph_2Mn and but-2-yne has the structure of benzene(hexamethylbenzene)manganese(I) [285]. Hexamethylbenzene is formed on cyclotrimerisation of butyne, while the second σ-linked ligand (benzene) is formed from the σ-phenyl group as a result of a σ–π rearrangement.

As a rule acetylene cyclisation reactions in the presence of the organometallic compounds considered are stoichiometric. Dimesitylcobalt, which acts as a catalyst in the reaction with butyne, is an exception. A constant amount (up to 20%) of the corresponding π-complex is always formed in this process. Dimesitylcobalt reacts also with acetylene: the stoichiometric trimerisation to benzene is accompanied by a catalytic reaction involving the formation of a solid polymer. The reaction also yields a certain amount of dibenzenecobalt [286].

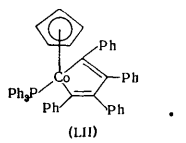
The reaction of tolane with dimesitylnickel(II) results in the formation of hexaphenylbenzene and the complex $[(Ph_2C_2)_4Ni]_n$. [263,282,287] Diethylnickel also induces the cyclisation of tolane to hexaphenylbenzene and provides the ethyl group for mixed cyclisation. However, nickel, being a weaker hydrogen acceptor than chromium, is incapable of abstracting hydrogen from the dihydrobenzene compound (1,2,3,4-tetraphenylcyclohexa-1,3-diene), which is in fact the final product of this reaction [272]. HFB polymerises under the influence of diethylnickel [84] and tolane cyclises also in the presence of dimesityliron [263,282].

The methyl derivatives of many metals $M(Me)_n$ (M = Ti, Zr, V, Nb, Mo, Mn, Fe, Ru, Co, Rh, or Pd) react with tolane to form hexaphenylbenzene, tetraphenylcyclopentadiene, and 1,2,3-triphenylnaphthalene [265,273]. The reaction of tolane with $(Ph_3P)_3RhMe$ yielded the following products: triphenylnaphthalene, tetraphenylbutadiene and a cyclisation product incorporating the σ-methyl group–tetraphenylcyclopentadiene [288].

On reaction with σ-alkyl-π-cyclopentadienyl complexes of molybdenum and iron carbonyls, tolane cyclo-oligomerises with insertion of the alkyl group σ-linked to the metal [254,289]:



The reaction of tolane with π-cyclopentadienyltriphenylphosphinecobalt(III) iodide in the presence of isopropylmagnesium bromide leads to the formation of the metal-containing cyclic complex (LII) [290,291]:



(LII)

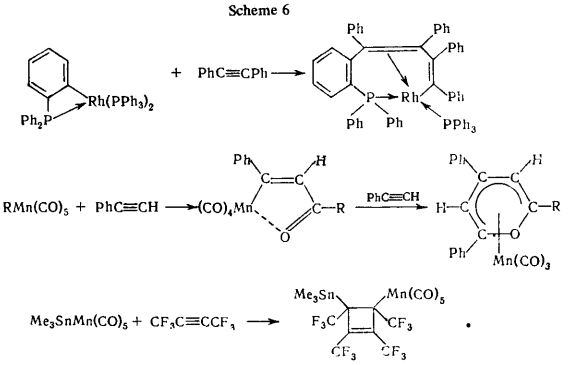
Acetylene and phenylacetylene undergo linear oligomerisation in the presence of σ-methyltris(triphenylphosphine)cobalt(I) [292]. For example:

$$(Ph_3P)_3CoMe + HC{\equiv}CH \rightarrow (Ph_3P)_2Co(CH{=}CH)_nMe .$$

The insertion of two molecules of acetylene derivatives in the σ-bonds Rh–C (Keim [293]) (the structure of the product was confirmed by X-ray diffraction [294]), Mn–C (Booth and

Hargreaves[295]), and Mn–Sn (Bichler et al.[296]) has been described (see Scheme 6).

Scheme 6



The reaction of but-2-yne with a σ-trifluoromethyl derivative of platinum yielded a cyclobutadiene complex[297].

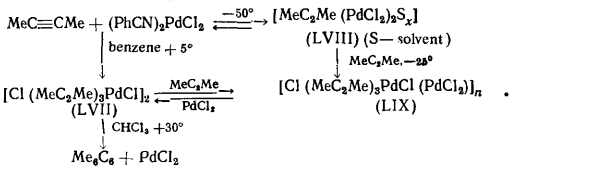
6. Reactions of Acetylenes with Transition Metal Salts

The reaction of acetylenes with bivalent platinum compounds has been investigated in greatest detail. The reaction proceeds in different ways depending on the nature of the substituents, conditions, etc. On treatment with palladium(II) chloride or its benzonitrile complex $(PhCN)_2PdCl_2$ (BNP) in benzene, diarylacetylenes yield π-cyclobutadiene complexes (LIII) together with hexasubstituted benzenes[100–103]. When the reaction is carried out in alcohol[100,103,298–303], the products are the *endo*-ethoxycyclobutenyl complexes (LIV)[103] [the structure of (LIV) has been established by X-ray diffraction[304]], which are converted under the influence of hydrogen halides into cyclobutadiene complexes (LV).

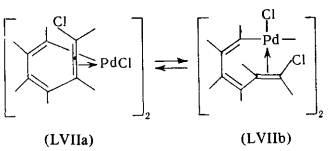
The cyclobutadiene complexes are not intermediates in the synthesis of benzenes[100,260,305]. For example, the reaction of (LIII) with tributylphosphine in the presence of tolane leads to the formation of the corresponding cyclooctatetraene in 92% yield; not even traces of hexaphenylbenzene are formed in this reaction.

The complexes (LV) were obtained from t-butylphenylacetylene and BNP; the formation of cyclotrimerisation products was not observed[173,306]. The structure of the cyclobutadiene complex (LVI) has also been attributed to the complex obtained from *o*-di(phenylethynyl)benzene and $PdCl_2$:[307,308]

Acetylenes containing less bulky substituents behave differently from those discussed above. But-2-yne reacts with $PdCl_2$ in benzene to form the complex (LVII)[260,309,310]. When the reaction was carried out in chloroform, two intermediates—the acetylenic π-complex (LVIII) and the complex (LIX)—differing from (LVII) by including $PdCl_2$ in their composition, were detected:

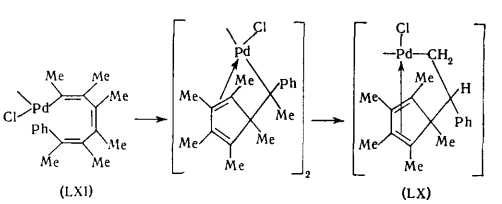


On heating, (LVII) decomposes with formation of hexamethylbenzene; treatment with triphenylphosphine, triphenylarsine, or triphenylstibine in the cold results in the formation of 5-vinylpentamethylcyclopentadiene with a small amounts of hexamethylbenzene. The structure of the product produced by the insertion of three acetylene molecules in the Pd–Cl bond was attributed to the complex on the basis of physicochemical data and the nature of its chemical reactions[260,310,311]. In this complex the ligand can exist as two conformers (LVIIa) and (LVIIb):



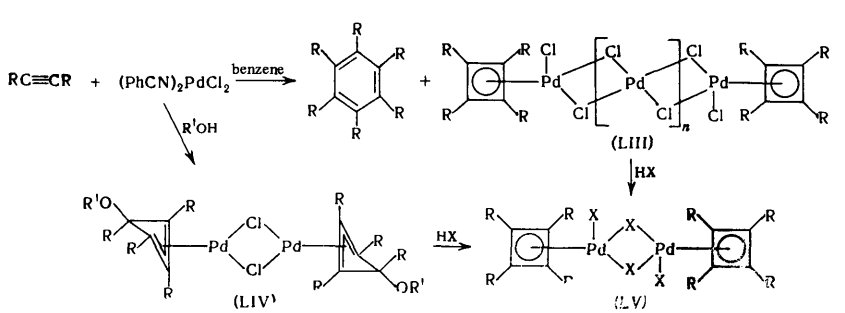
(LVIIa) (LVIIb)

The reaction of but-2-yne with "phenylpalladium chloride" yields a complex having the structure (LX), probably as a result of the cyclisation of (LXI) with a subsequent 1,2-hydride shift[312]:

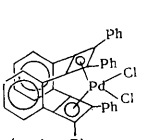


(LXI) (LX)

Together with the expected 1,2,4- and 1,3,5-isomers of trimethyltriphenylbenzene (yields 58 and 39%), the reaction of methylphenylacetylene with BNP in benzene gives rise to a small amount (3%) of the 1,2,3-isomer[102,260,310].



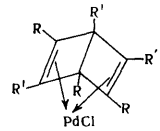
(LIV) (LV)



(LVI)

The formation from methyl- and ethyl-phenylacetylenes in the presence of $PdCl_2$, together with hexasubstituted benzenes, of complexes containing acetylene tetramers and having the compositions $(PhC_2R)_4PdCl$ and $(PhC_2R)_4Pd_2Cl_2$ [299,313] has been reported.

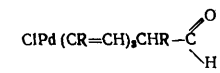
The structure of a complex of Dewar benzene (LXII, R = R' = COOMe) has been attributed to the product of the reaction of the dimethyl ester of acetylenedicarboxylic BNP:[175]



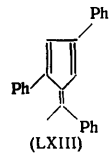
(LXII)

Acetylene and its monosubstituted derivatives undergo linear oligomerisation under the influence of palladium salts. Thus treatment of acetylene with $PdCl_2$ results in the formation of *trans*-alka-1,3,5,7,...polyene as the main product[314]. Stable σ-organometallic polyene products with the general formula $PdCl(CR{=}CR')_nX$ were isolated in the reactions of acetylene, vinylacetylene, and phenylacetylene[315-321]. Acetylene compounds undergo similar reactions in rhodium(III) chloride solutions[321].

The reaction of dialkylethynylmethanols with $PdCl_2$ in aqueous solutions has been investigated[322-325]. The following structure has been proposed for the complexes on the basis of infrared spectra[326-329]:

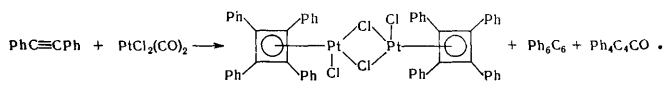


The reaction of phenylacetylene with BNP yielded fulvene (LXIII) and tetramers of unknown structure, tentatively dihydropentalenes[260]. The interaction of BNP with other monosubstituted acetylenes has also been described[310,330-332].

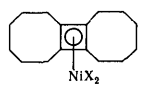


(LXIII)

In contrast to palladium salts, derivatives of bivalent platinum form mainly acetylenic π-complexes with acetylene. The cyclo-oligomerisation reaction has been described in only one instance[333]:



Nickel salts react with cyclo-octyne with formation of a complex to which the cyclobutadiene structure (LXIV) was attributed[129]. Another reaction product is the corresponding benzene derivative:

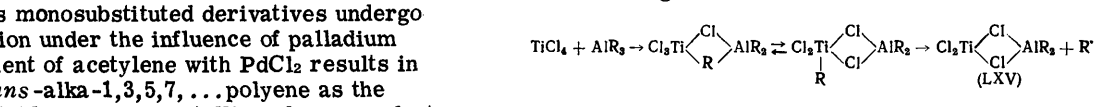


(LXIV)

The possible formation of the cyclobutadienegold complex[334] $[(C_4H_4)AuCl_2]^+$ when acetylene is passed into $AuCl_3$ solutions has been suggested[335].

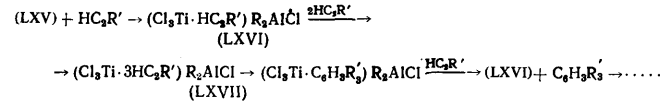
IV. THE MECHANISMS OF ACETYLENE CYCLO-OLIGOMERISATION AND POLYMERISATION REACTIONS IN THE PRESENCE OF TRANSITION METAL COMPOUNDS

The problem of the mechanisms of acetylene cyclo-oligomerisation and polymerisation reactions is now the subject of persistent attention of many chemists. Kinetic investigations involve considerable difficulties in view of the high rate and high heats of these reactions[17]. Such studies have been made on the cyclotrimerisation of hex-1-yne in the presence of the $i\text{-}Bu_3Al\text{-}VOCl_3$ catalytic system, which proceeds at a comparatively low rate. The reaction is described by a second-order equation with respect to the alkyne[57]. It has been shown that a tervalent form of titanium is catalytically active in the presence of $i\text{-}Bu_3Al\text{-}TiCl_4$.[68] The catalytic complex (LXV) is formed via the following mechanism:



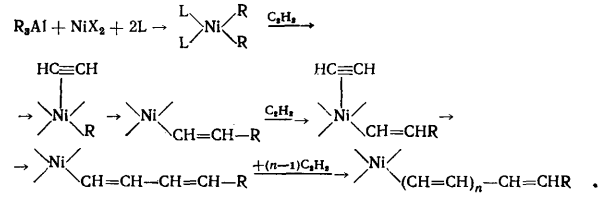
(LXV)

An acetylene molecule reacts with the titanium atom entering into the composition of the catalytic complex with formation of the monoacetylene complex (LXVI), which subsequently combines with two acetylene molecules in the rate-determining stage. In the octahedral complex (LXVII) three acetylene molecules cyclise with formation of a benzene derivative, which is displaced from the complex by a new acetylene molecule, etc.:



It has been shown that the polymerisation of phenylacetylene in the presence of the $Et_3Al\text{-}TiCl_3$ catalytic system is a first-order reaction with respect to the monomer[336]. The authors suggest that the mechanism of the formation of cyclic products is not determined by the simultaneous reaction of three monomeric units in a single step, the rate-determining step involving the abstraction of the linear trimer from the catalytic centre with ring closure.

The kinetics of the polymerisation of acetylene in the presence of $i\text{-}Bu_3Al\text{-}Ni(acac)_2$ have been investigated[337]. The initiation reaction is of first order with respect to the monomer and the order of the propagation reaction is close to zero. The following reaction mechanism including the stage involving the formation of an acetylene π-complex with subsequent insertion of the coordinated acetylene in the Ni–C σ-bond has been proposed:



It proved possible to isolate intermediate complexes incorporating the monomer and having the compositions $i\text{-}Bu_2Ni.C_2H_2.Bipy$ and $i\text{-}Bu_2Ni.C_2H_2.(PPh_3)_2$ in the reaction of acetylene with $i\text{-}Bu_3Al\text{-}Ni(acac)_2$ in heptane in the presence of stabilising ligands (triphenylphosphine or bipyridyl). The complexes polymerise acetylene at −10°C.

The study of the kinetics of the dimerisation of acetylene to vinylacetylene in the presence of copper(I) complexes led to the following mechanism for this reaction involving stages with formation of an acetylene π-complex and its conversion into a σ-acetylide with subsequent insertion of a second acetylene molecule in the Cu–C σ-bond[338–340]:

$$C_2H_2 + [Cu_nCl_{n+1}]^- \rightleftarrows \underset{\pi\text{-complex}}{[C_2H_2Cu_nCl_{n+1}]^-} \underset{-H_3O^+,\,-Cl^-}{\overset{+H_2O}{\rightleftarrows}}$$

$$\rightleftarrows \underset{\sigma\text{-acetylide}}{[Cu_nCl_nC{\equiv}CH]^-} \overset{C_2H_2}{\rightleftarrows} \underset{\pi\text{-complex}}{[Cu_nCl_nC{\equiv}CH\,(C_2H_2)]^-} \xrightarrow{\text{slow}}$$

$$\rightarrow [Cu_nCl_nC_4H_3]^- \xrightarrow[\text{fast}]{+H_3O^+ + Cl^-} [Cu_nCl_{n+1}]^- + C_4H_4 \ .$$

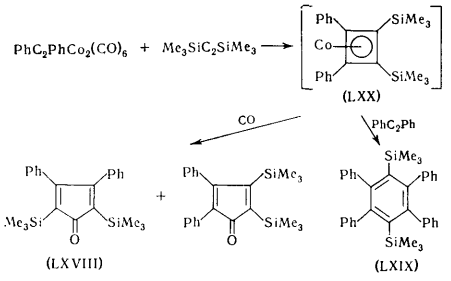
A number of studies have been made on the effect of the polarity of the solvent and various additives on the cyclo-oligomerisation reaction. It was found that the cyclotrimerisation of acetylenes catalysed by metal carbonyls and catalysts of the Ziegler–Natta type is insensitive to a change in solvent polarity. This enabled a number of workers[20,44,88] to put forward the hypothesis that a ionic mechanism of these reactions is unlikely. However, the hypothesis of an ionic mechanism has received increasing recognition recently. These ideas will be considered below.

In most studies ideas concerning the mechanism of the interaction of acetylenes with transition metal compounds were based on the nature of the final reaction products and the structure of intermediates. It is now generally accepted that the first stage of the reaction is a π-complex type of coordination of the acetylene to the metal. The formation of acetylene π-complexes under certain conditions and the possibility of obtaining from them acetylene cyclo-oligomerisation products were frequently pointed out above.

There are two main points of view on the problem of the ways in which coordinated acetylene is subsequently transformed into the final reaction product. The first is that the coordinated acetylene molecules react with one another, the process being accompanied by the formation of new C–C bonds and carbon ring closure. A six- or eight-membered ring can be formed either by the simultaneous formation of three (or four) C–C bonds or via the intermediate formation of the cyclobutadiene ring. The second view presupposes the conversion of the acetylene π-complex into a σ-compound (a metal-containing ring, a σ-ethynyl or a σ-vinyl derivative) with subsequent insertion of acetylene in the metal–carbon bond.

The hypothesis of the intermediate formation of cyclobutadiene complexes has been frequently put forward by a number of workers[142,334,341]. Evidence in support of this hypothesis comes from the conversion of an acetylene complex of niobium into a diacetylene complex and further into a mixed cyclobutadiene–acetylene complex, which splits off hexaphenylbenzene on heating[146,149] (see above).

Heating of diphenylacetylenedicobalt hexacarbonyl with di(trimethylsilyl)acetylene unexpectedly results in the formation, together with other products, of 3,4-diphenyl-2,5-di(trimethylsilyl)cyclopentadienone (LXVIII) and 2,3,5,6-tetraphenyl-1,4-di(trimethylsilyl)benzene (LXIX)[25,138,168]. According to the authors, the most probable mechanism of the synthesis of these products consists in the intermediate formation of the cyclobutadiene complex (LXX), which can then undergo ring expansion in any conceivable manner:



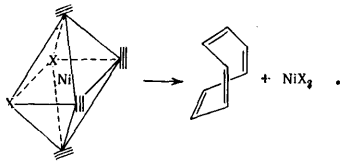
The problem of the possible intermediate formation of cyclobutadiene complexes on cyclotrimerisation of acetylenes was studied in relation to 1,1,1-trideuteriobut-2-yne[266,342,343]. If the reaction proceeds via a cyclobutadiene complex, all three possible isomeric benzenes should presumably be formed. The 1,2,3-$(CD_3)_3$-4,5,6-Me_3C_6 isomer is absent from the products of the reaction involving triphenylchromium, dimesitylcobalt, dicobalt octacarbonyl, di(acrylonitrile)nickel, and i-Bu_3Al–$TiCl_4$. In the presence of Al_3Cl, the 1,2,3-isomer is formed quantitatively (on the assumption of the intermediate formation of a cyclobutadiene structure‡), while on treatment with BNP its yield is intermediate between the two extreme values. As already mentioned, similar results were obtained in the cyclisation of phenylmethylacetylene in the presence of BNP[102,310], which is consistent with the cyclobutadiene hypothesis. However, it has been shown[100,305] that cyclobutadiene complexes of palladium are not intermediates in the synthesis of benzenes. It has been suggested that dynamic processes involving the intermediate complex (LVII), accompanied by the migration of the substituents, are responsible for the "unexpected isomers"[260].

The hypothesis of the simultaneous coordination of several acetylene molecules around the metal atom was put forward for the first time by Reppe[122] and was developed further in subsequent investigations[80,83,345–348] (see also Refs. 349 and 350). The acetylene cyclo-oligomerisation reaction is a many-centre process with simultaneous formation of C–C bonds. These ideas have been developed in detail in relation to the cyclotetramerisation of acetylene under the influence of nickel compounds.

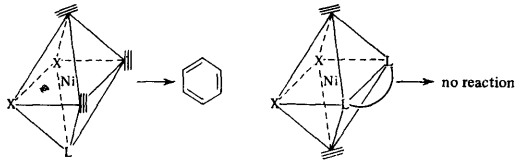
Paramagnetic (at least in solution) nickel(II) complexes with low-field ligands–di(salicylaldehydo), di(acetylacetonato)-, and di-(*N*-alkylsalicylaldimino)-nickel and nickel cyanide are catalytically active in the synthesis of COT. These complexes have an octahedral structure or can readily acquire it. Planar nickel(II) complexes with high-field ligands—phthalocyanine or dimethylglyoxime complexes—are inactive. The yield of COT is proportional to the rate of ligand exchange in the complex. Under the influence of acetylene, the coordinate bonds

‡But-2-yne reacts with $AlCl_3$ under milder conditions with formation of Dewar hexamethylbenzene[344]. This result is also consistent with the hypothesis of the intermediate formation of a cyclobutadiene structure with subsequent addition of an acetylene molecule as in the Diels–Alder reaction.

are ruptured and in the resulting intermediate complexes the four acetylene molecules are arranged favourably for closure of the eight-membered ring:



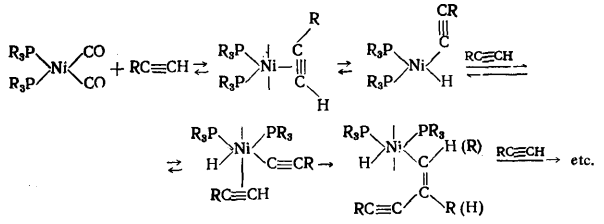
On addition of triphenylphosphine, which blocks one coordination site in the complex, COT is not formed and the reaction product is exclusively benzene. The addition of substances capable of blocking two coordination sites at once [$\alpha\alpha'$-bipyridyl, *o*-phenanthroline, and 1,2-bis-(diphenylphosphino)ethane] fully deactivates the catalyst in the cyclo-oligomerisation reaction:



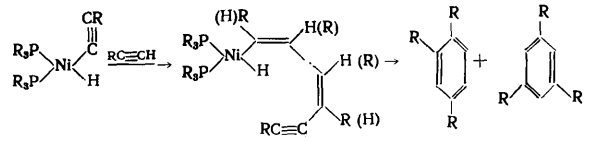
The formation of COT in the presence of $Zn[Co(CO)_4]_2$ can be accounted for by dinuclear catalysis. Two acetylene molecules are coordinated around each of the two cobalt atoms with simultaneous formation of new C–C bonds [121,351]. This hypothesis is open to many objections. In particular it cannot explain the preferential formation of 1,2,4-isomeric substituted benzenes in the cyclotrimerisation of asymmetric acetylenes.

The essential feature of the hypotheses concerning the mechanism of the cyclisation and polymerisation of acetylenes discussed reduces to the postulate of the intermediate formation from the acetylenic π-complex of an organometallic compound with metal–carbon σ-bonds; chain growth takes place as a result of the insertion of π-coordinated acetylene in the M–C bond.

The mechanism proposed [17] explains satisfactorily the formation of linear polymers in the reactions of terminal acetylenes with metal carbonyls. On the basis of the finding that deuteriated hept-1-yne reacts much more slowly with dicarbonyldi(triphenylphosphine)nickel than its non-deuteriated analogue, the authors proposed a mechanism based on the oxidative addition of acetylene to the metal with formation of an acetylide–hydride complex. The insertion of acetylene in the M–C bond leads to the formation of a σ-vinyl derivative:

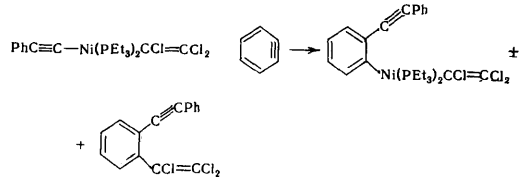


In the presence of a favourable conformation, ring closure may take place with formation of benzene derivatives:

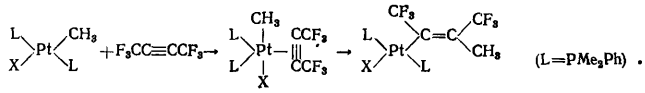


A similar mechanism has been proposed for the polymerisation of alk-1-ynes in the presence of rhodium(I) and iridium(I). [90,91,94]

The occurrence of certain reaction stages has been confirmed experimentally. Thus the formation of hydride-acetylide compounds is observed when certain terminal acetylenes add to the coordination-unsaturated iridium complex $IrCl(CO)(PPh_3)_2$. [352] The insertion of acetylene in the metal-alkynyl group has been described for the interaction of nickel acetylide with dehydrobenzene [353]:



In platinum complexes coordinated acetylene has been inserted in the Pt–CH_3 bond [354–356]:

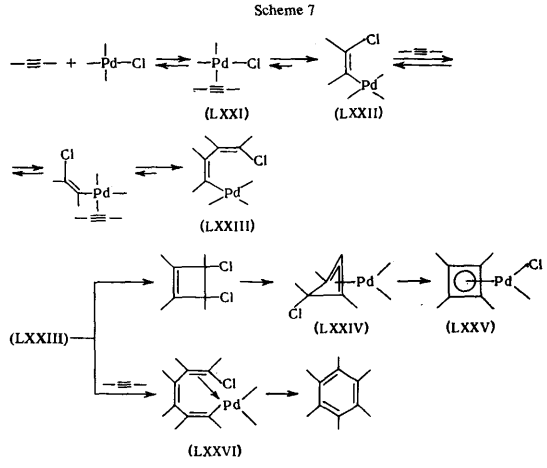


The formation of iridium complexes containing both a σ-vinyl group and a π-acetylenic ligand, $(Ph_3P)_2Ir(CR=CHR)(RC_2R)(CO)$ (R = CF_3 or $COOCH_3$), can also serve as evidence in support of the mechanism proposed [357].

Finally linear polymerisation of phenylacetylene with participation of nickel and platinum acetylide complexes has been achieved [86,87,358].

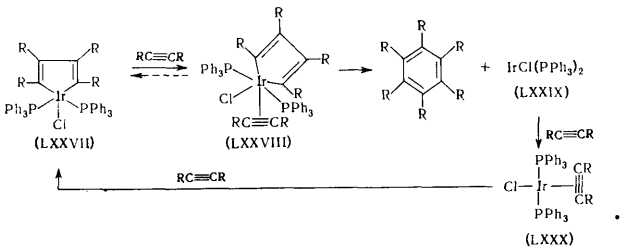
In the polymerisation of alkynes in the presence of transition metal halides of the type $(R_3P)_2NiX_2$, [104] BNP, [100,309] $PdCl_2$, and $RhCl_3$ [321] a σ-vinyl derivative may be formed as a result of the insertion of acetylene in the M–Hal bond. Thus Scheme 7 has been proposed for the cyclo-oligomerisation of acetylene in the presence of BNP. [260,309,310,312] The acetylene π-complex $(RC_2R).(PdCl_2)_2S_X$ (LXXI) formed initially is converted in the rate-determining stage into the σ-vinyl intermediate (LXXII), which subsequently coordinates a second acetylene molecule and is converted into (LXXIII). The reaction pathways of the latter depend on the size of the substituents in acetylene. For bulky substituents (Ph, t-Bu), cyclisation into inactive cyclobutene or cyclobutadiene complexes (LXXIV) or (LXXV) is observed. For small substituents (Me), a third acetylene molecule is inserted with formation of (LXXVI), which cyclises to hexamethylbenzene.

Scheme 7

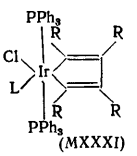


The polymerisation of acetylene in the presence of Ziegler–Natta catalysts can be explained similarly by the insertion of acetylene in an M–R bond[359].

In order to account for the formation of benzene derivatives from disubstituted acetylenes in the presence of nickel catalysts, the hypothesis of the intermediate formation of a metal-containing cyclic complex was put forward[17]. It was developed further in subsequent investigations[5,32,100,290,352,360]. The reaction mechanism for iridium as an example is as follows[361]:



The reversible addition of acetylene to the coordination-unsaturated cyclic iridium compound (LXXVII) leads to the formation of the intermediate complex (LXXVIII), which then decomposes with liberation of hexasubstituted benzene and the moiety (LXXIX). The latter combines with an acetylene molecule to form the acetylene complex (LXXX), which is in turn converted into the cylic iridium complex (LXXVII), etc. The changes involving the conversion of (LXXX) into (LXXVII) and of (LXXVII) into a benzene derivative have been achieved experimentally. The capacity of the coordination-unsaturated complex (LXXVII) to react with CO and tertiary phosphines with formation of the hexacoordinate complex (LXXXI),



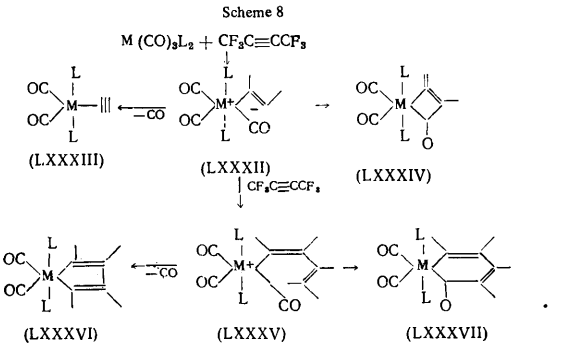
suggests that the stage involving the formation of (LXXVIII) is also likely. A similar series of transformations has been achieved for rhodium complexes[236,239–243].

The employment of the metal-containing cyclic compound hypothesis in relation to non-stoichiometric cyclisation reactions of acetylenes in the presence of σ-alkyl and σ-aryl metal derivatives was described above (Section III).

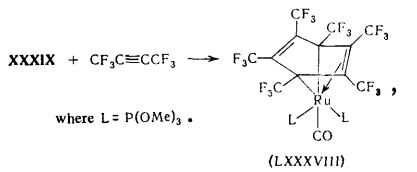
The attempts to apply the metal-containing cyclic compound hypothesis in the version described in order to account for the reaction of HFB with carbonylphosphine (phosphitocarbonyl) complexes of iron, ruthenium and osmium of the type $M(CO)_3L_2$ [L = PMe_2Ph or $P(OMe)_3$] have encountered many objections. In particular the formation of, for example, the complex (LXXXIV) cannot be accounted for in terms of the "insertion reaction" of carbon monoxide (more correctly the migration of the alkyl group), since electronegative substituents in σ-linked alkyl groups are known to hinder strongly the insertion of CO in the M–C bond.

Scheme 8, postulating the formation of an intermediate ionic product (LXXXII), has been proposed as an alternative to the "insertion reaction". This product is either converted into an acetylene π-complex (LXXXIII) with elimination of CO or the metallocyclobutenone (LXXXIV) is formed as a result of the intramolecular attack of the carbanion on the coordinated carbonyl group. Compound (LXXXII) can also react with a second acetylene molecule, forming the ionic intermediate (LXXXV), which yields as a result of similar reactions either the metallocyclopentadiene (LXXXVI) or the complex (LXXXVII) as a precursor of cyclopentadienone.

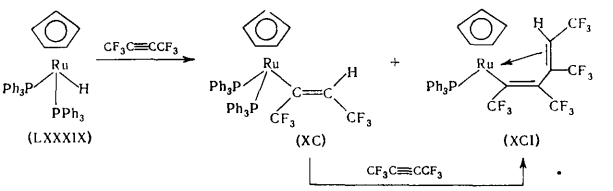
Scheme 8



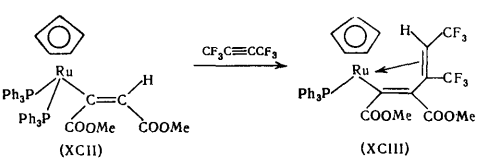
The formation of the complex (LXXXVIII) from (XXXIX) on irradiation is consistent with the hypothesis that the benzene ring is formed from the metallocyclopentadiene:



The mechanism in which the formation of ionic intermediates is postulated has been confirmed in studies by other investigators. When π-cyclopentadienyldi(triphenylphosphine)ruthenium hydride (LXXXIX) reacts with HFB, the complexes (XC) and (XCI) are formed[362]:



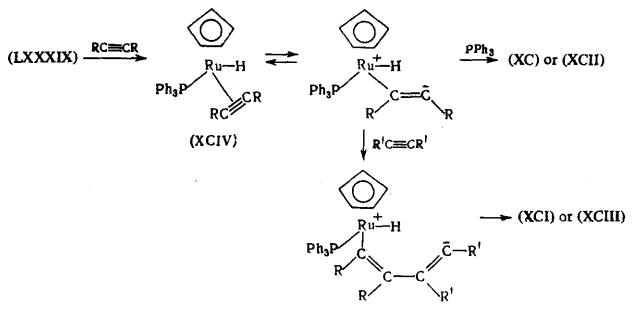
Compound (XCII) was similarly obtained from (LXXXIX) and the dimethyl ester of acetylenedicarboxylic acid. The reaction of (XCII) with HFB yields a complex which has the structure (XCIII) according to X-ray diffraction data:



The formation of (XCIII) cannot be accounted for from the standpoint of the insertion of acetylene in the M–C bond, since one would expect in this case the formation of the isomeric product $C_5H_5Ru(PPh_3)[C(CF_3)=C(CF_3)-C(COOMe)=CH(COOMe)]$. Evidently (XCIII) is formed as a result of the insertion of HFB in the C–H bond in (XCII). Scheme 9, in which the formation of ionic

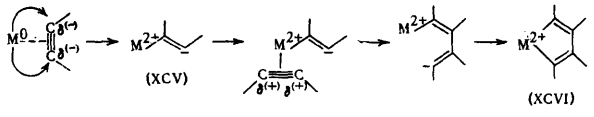
intermediates is postulated as in Scheme 8 discussed above, has been put forward on the basis of the data obtained for the reaction:

Scheme 9

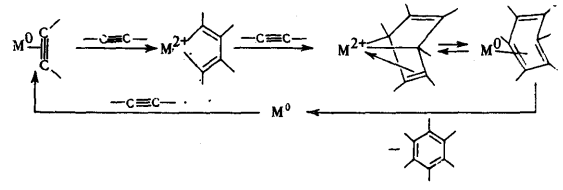


A similar mechanism has been proposed for the cyclo-oligomerisation of acetylenes with participation of zero-valent palladium and platinum complexes (Scheme 10).[260] The hypothesis of the formation of dipolar intermediates (XCV) is based on the observed acceleration of the reactions in polar solvents. A second acetylene molecule is coordinated to the metal which is already in a +2 state of oxidation as a result of which the acetylene is activated in relation to the nucleophilic agent and undergoes intramolecular attack by the vinyl anion:

Scheme 10



It has been suggested that the subsequent conversion of the metal-containing cyclic product (XCVI) into a benzene derivative involves the formation of a π-tetrahaptobenzene complex:



Thus an obligatory stage in all the cyclo-oligomerisation and polymerisation reactions of acetylenes in the presence of transition metal compounds is the formation of acetylene π-complexes. The pathways followed in the subsequent conversion of the π-complexes into the final products can apparently be different depending on the nature of the metal and the acetylene.

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