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Cyclisation reactions involving carbene complexes in the inner coordination sphere of transition metals

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ABSTRACT. The literature data on inner-sphere cyclisation reactions involving carbene complexes in the coordination sphere of transition metals are summarised.

The bibliography includes 136 references.

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I. Introduction

Cyclisation reactions that involve carbene complexes have been known for quite a long time, but they have mainly been studied in relation to the use of organometallic reagents in organic synthesis (see several reviews),[1–6] primarily for the synthesis of derivatives of naphthalene, indene, etc. In the present review we shall summarise those reactions of carbene complexes during which the carbene ligand combines with a molecule of substrate to form a cyclic (or metallacyclic) ligand, with all of the reactions occurring in the inner coordination sphere of the metal. It should be emphasised that there are no strict criteria which could be used to classify a given reaction as intramolecular. Very frequently it is only the structure of the final products that suggest the inner-sphere nature of the processes, since in the majority of cases the corresponding reactions are not typical for the uncoordinated ligands. Thus the term "inner-sphere cyclisation" is fairly arbitrary.

In the present review we shall mainly examine the processes which result in the reaction between a ligand that is already present and a molecule of reagent to form a new cyclic ligand which remains in the coordination sphere. Reactions of the formation of a cyclic ligand on a transition metal atom (template reactions) will be included subsequently, and it is also proposed to include data on catalytic cycloaddition reactions in the presence of transition metal complexes.

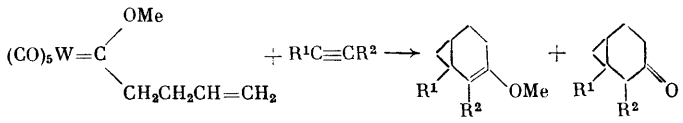
In general cycloaddition reactions have been covered in sufficient detail in the literature, so in this review there is no need to dwell on a detailed examination of them. With regard to cycloaddition reactions in the inner coordination sphere of transition metals, the number of theoretical studies in this area is clearly insufficient to raise the question now about finding a correspondence between theory and practice. In those cases where it was possible to do this, specific examples are given.

This review covers the original literature up to the end of 1989.

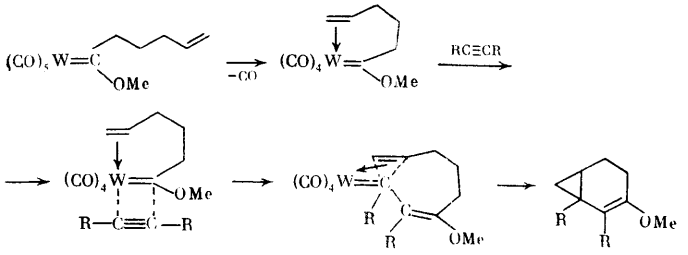
II. Reactions that lead to the formation of three-membered rings

Carbenes are known[6] to react with olefins to give cyclopropanes. The use of carbene complexes of transition metals as transfer agents of a carbene to an olefin in the synthesis of cyclopropanes was first described by Fischer.[7] In the present review there are examples of the formation of cyclopropanes from carbene complexes and acetylenes that occur without the formal cleavage of the metal–carbene bond at the intermediate stages of the reaction.

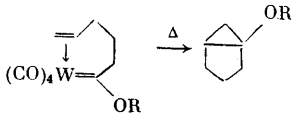
Carbene complexes of tungsten containing a multiple bond on the "periphery" of the carbene ligand react with disubstituted acetylenes to form condensed cyclopropanes:[8,9]



The reactions occur in the following way: at the first stage the alkyne is inserted into the metal–carbene bond to form a dienyl-substituted carbene intermediate in which intramolecular cyclopropanation of the double bond by the carbene ligand then occurs, as described by Fischer.[7] Initially the carbene complex may undergo isomerisation with elimination of CO and formation of a π-olefin carbene complex which can be isolated:[10,11]

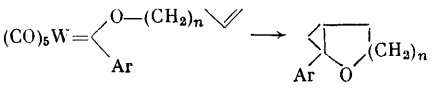


The intermediate π-olefin carbene complex may also form a cyclopropane derivative through intramolecular cyclopropanation:[10,11]



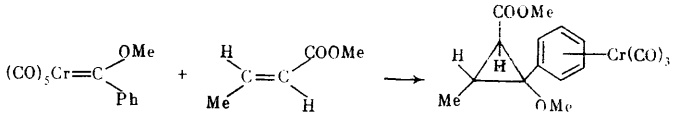
R = Me, Et.

Similar reactions have been reported for carbene complexes with an unsaturated alkoxyl residue:[12]



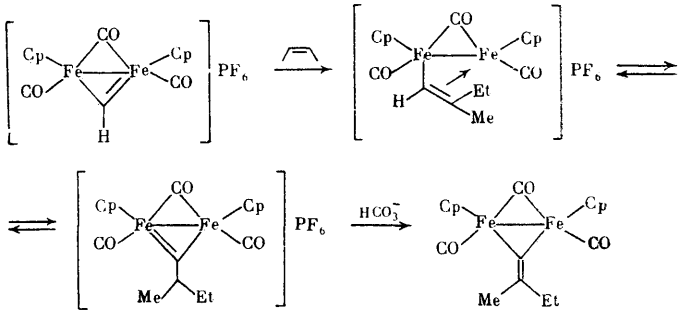
Ar = 4-MeC$_6$H$_4$; n = 2, 3.

When n = 1 only an allyl aryl ketone was isolated. A tungsten π-arene complex was obtained as a by-product. The formation of such π-arene complexes was detected in the cyclopropanation of olefins with chromium π-alkoxybenzylidene complexes:[13]

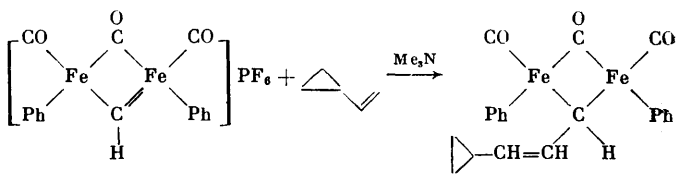


The reaction is stereoselective—a *trans*-cyclopropane is formed from a *trans*-olefin. The enantioselective synthesis of cyclopropanes using chiral iron carbene complexes has been reported.[14]

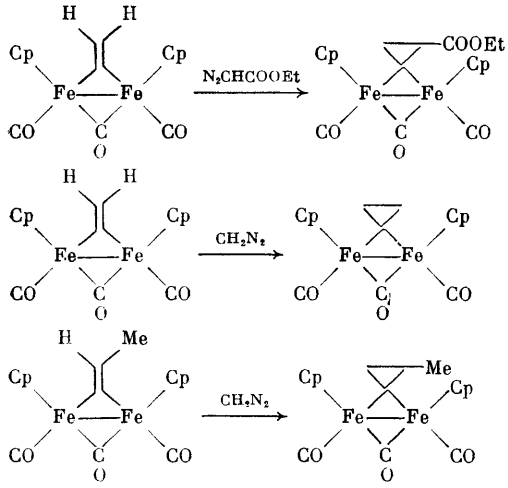
Cationic iron complexes with bridging carbene ligands react with olefins to form diferracyclopropanes:[15]



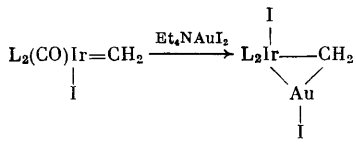
The reaction occurs via σ,π-olefin complexes which are formed as a result of the insertion of the olefin into the "double" C=Fe bond followed by a 1,3-hydrogen shift. Vinylcyclopropane reacts somewhat differently:[16]



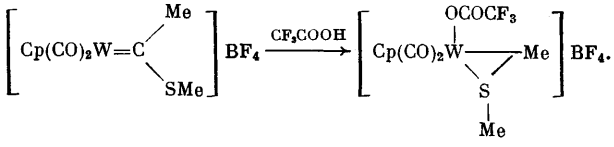
Iron alkylidene complexes obtained by reaction of olefins with bridging carbene derivatives react with diazoalkanes to form diferraspiropentanes:[17–19]



The formation of a three-membered dimetallacycle has been observed[20] in the reaction of an iridium carbene complex with tetraethylammonium diiodoaurate:



This reaction may be regarded as the addition of :AuI to the iridium–carbon double bond. The addition of trifluoroacetic acid to a tungsten–carbon double bond gives a thiatungstacyclopropane:[21]



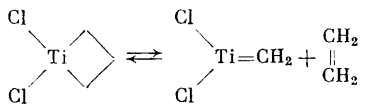
It may be concluded from the material examined that [1 + 2] cycloaddition reactions with the formation of π-cyclopropene or η^3-cyclopropenyl complexes are not typical for carbene compounds of transition metals.

III. Reactions that lead to the formation of four-membered rings

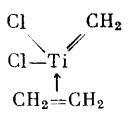
The formation of four-membered rings involving carbene complexes is possible as a result of either [1 + 3] cycloaddition or a [2 + 2] process. In the first case the formation of cyclobutenyl or cyclobutadienyl complexes are to be expected for an inner-sphere reaction, in the second case metallacycles are to be expected. This is true for all concerted reactions; but in the chemistry of organometallic compounds, as a result of a metal atom participating in the reaction, unconcerted multistage reactions are possible. It is

therefore probable that the formation of cyclisation products in the inner coordination sphere cannot always be strictly interpreted in terms of a given limiting mechanism.

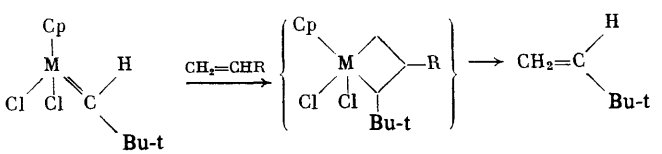
A theoretical analysis of $2\pi + 2\pi$ reactions that occur within the coordination sphere of a transition metal has been carried out for the system titanium alkylidene complex – olefin.[22]



It was found that the intermediate olefin(methylidene) complex

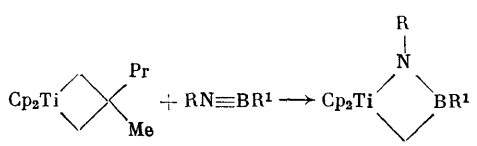


has an energy which exactly corresponds to that of the transition state of the reaction. The initial titanacyclobutane is 11.5 kcal mol^{-1} more stable than the intermediate complex and the conversion to the final products requires a further 10.4 kcal mol^{-1}. Thus, the reaction of olefins with metal carbene complexes with the formation of four-membered metallacycles is thermodynamically favourable. It is likely that the metathesis of olefins with niobium and tantalum (π-cyclopentadienyl)(neopentylidene) dichlorides occurs in this manner:[23]



M = Ta, Nb; R = H, Me, Ph.

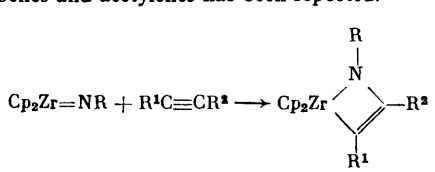
The suggestion of Paetrold et al.[24] that the reaction of a titanacyclobutane complex with $RNBR^1$ occurs via the formation of the intermediate carbene complex $Cp_2Ti{=}CH_2$ is not consistent with the conclusions of Upton and Rappe.[22]



R = iso-Pr, t-Bu; R^1 = iso-Pr, Bu, t-Bu, C_6F_5.

It is clear that the formation of azaboratitanacyclobutenes occurs in some other way, or the presence of the two geminal substituents in the four-membered ring of the initial complex considerably assists the elimination of an olefin with the separation of a methylene complex.

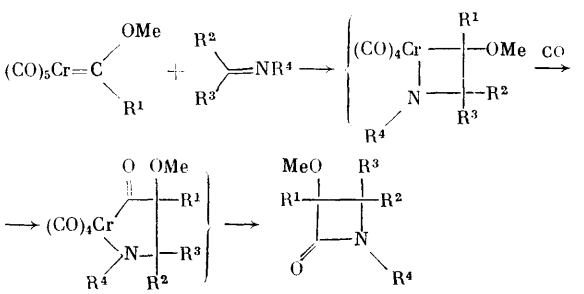
The formation of azazirconacyclobutenes from the aza analogues of carbenes and acetylenes has been reported.[25]



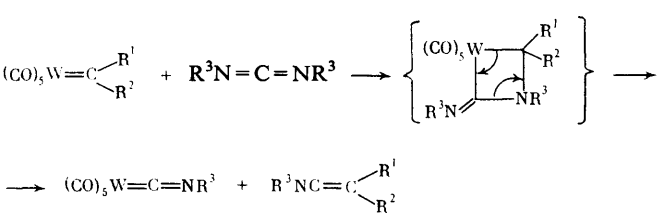
R	R^1	R^2
t-BuC_6H_4	Me	Ph
t-Bu	Ph	Ph
2,6-$Me_2C_6H_3$	Me	Me

The initial imidozirconocenes are generated by thermolysis of the respective products $Cp_2Zr(R^3)NHR$ (R^3 = Me, Ph) or by thermolysis of the bisamides $Cp_2Zr(NHR)_2$. In the case of a bulky substituent (R = t-Bu) the corresponding imide was isolated as an adduct with THF and its structure was established by X-ray diffraction analysis.[25] It is interesting that in the reaction of an imide with the asymmetric $MeC{\equiv}CPh$ only one isomer is formed with the methyl group at the α-position relative to the nitrogen of the heterocycle, i.e., cycloaddition takes place contrary to Markownikoff's rule. The isoelectronic titanamethylidene complex $Cp_2Ti{=}CH_2$ undergoes similar reactions with alkynes.[26–28]

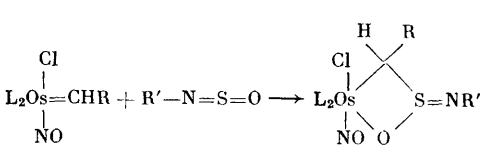
According to McGuize et al.[29,30] β-lactams are obtained in reactions between chromium carbene complexes and imines via azachromacyclobutanes, which are [2 + 2] cycloaddition products:



The metathesis of carbodiimides on treatment with tungsten carbene complexes to form intermediate four-membered metallacycles occurs in a similar manner:[31]

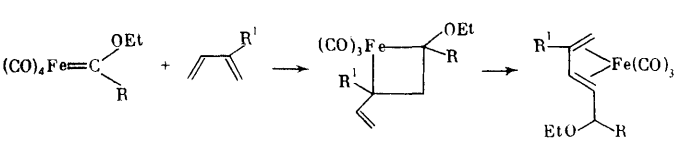


The reaction of sulphinylamines with osmium alkylidene complexes occurs as a [2 + 2] cycloaddition only on the S=O bond pseudocumulene [sic]:[32]



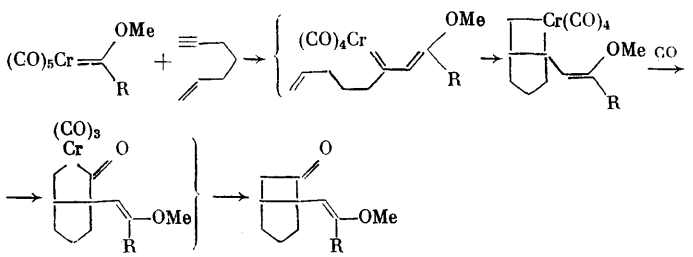
L = PPh_3, R = H, COOEt, R' = Ts.

The reaction of 1,3-dienes with iron carbene derivatives also only takes place on one of the two double bonds:[33,35]

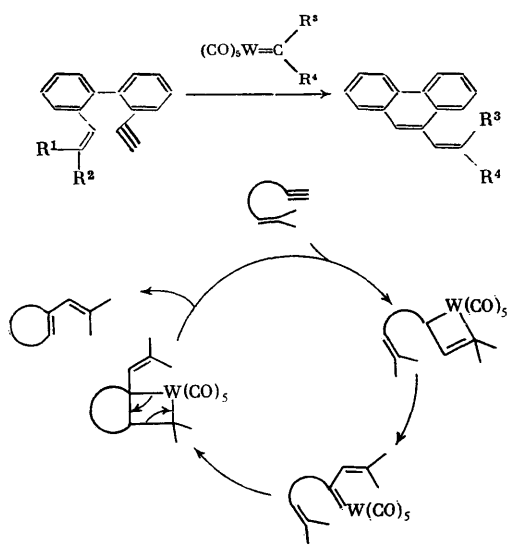


It should be noted that the idea of intermediate four-membered metallacycles being formed has been used to quite a significant extent to account for both catalytic and stoichiometric reactions of transition metal carbene complexes with olefins or acetylenes.

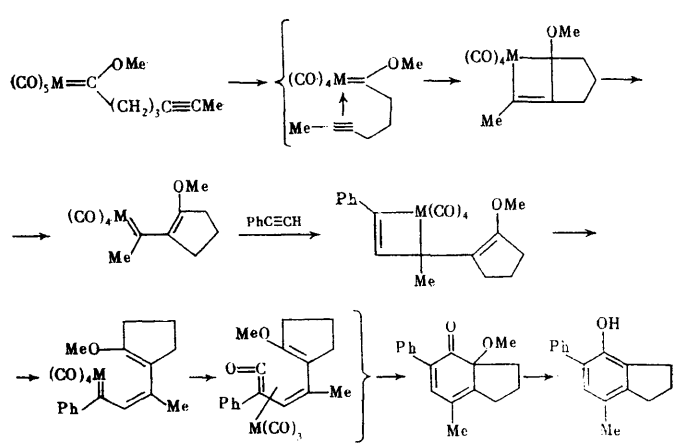
For example, the following scheme has been put forward for the stoichiometric reaction of hept-1-en-6-yne with chromium methoxycarbene complexes, which gives 1-vinyl-substituted bicyclo-[3.2.0]heptanones:[35]

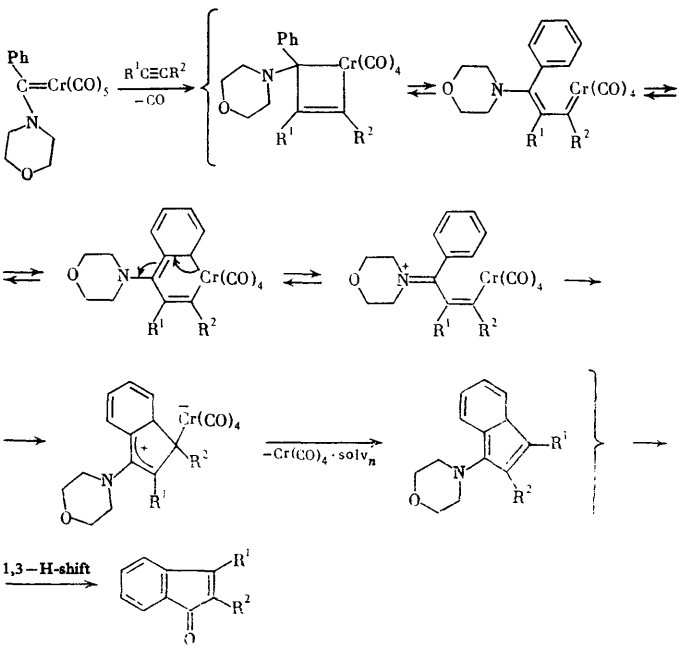


At the first stage acetylene is inserted into the metal–carbene bond, then intramolecular cyclisation, insertion of CO, and elimination take place. The formation of a metallacyclobutane can also occur at the first stage, as has been proposed for the catalytic reaction to obtain 9-vinylphenanthrenes from 1,1′-alkynyl(vinyl)biphenyls:[36]

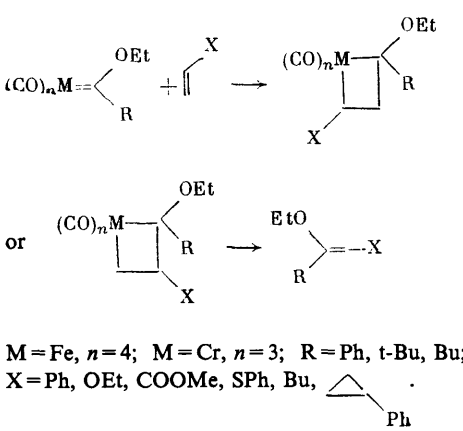


The reactions between alkynes and (1-methoxyhept-5-ynylidene)-pentacarbonylchromium[37] and between acetylenes and [(phenyl)-(morpholino)carbene]pentacarbonylchromium also occur in a similar manner:[38]



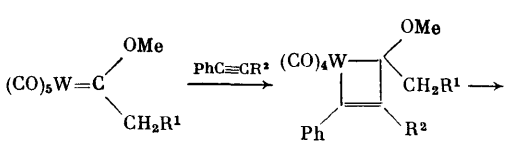


The metathesis of olefins on iron and chromium carbene complexes also occurs via intermediate metallacyclobutanes:[39]



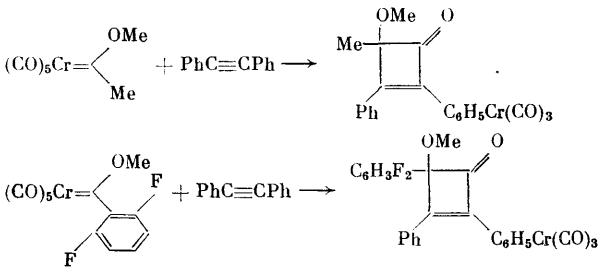
M = Fe, $n = 4$; M = Cr, $n = 3$; R = Ph, t-Bu, Bu;
X = Ph, OEt, COOMe, SPh, Bu, .

as does the addition of coordinated carbene ligands to acetylenes:[40]

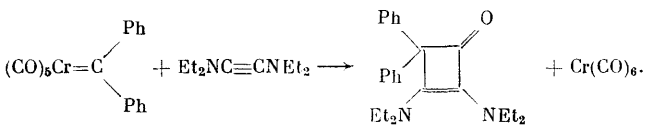


R^1	R^2	(A), %	(B), %
H	Ph	64	—
Me	Me	61	—
Me	Ph	12	50
Me	Me	19	42

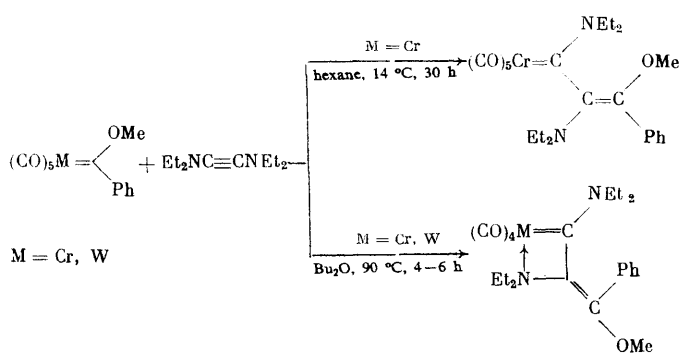
In the case of the addition of diphenylacetylene to a chromium methoxycarbene complex the $Cr(CO)_3$ residue remains coordinated in the reaction products:[41,42]



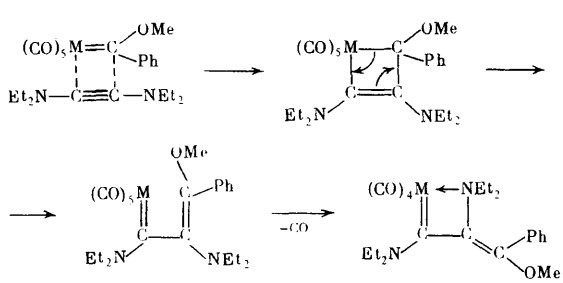
Confirmation of the coordination of $Cr(CO)_3$ with an aryl group of diphenylacetylene is provided by the reaction of bis(diethylamino)-acetylene with a chromium diphenylcarbene complex:[41]



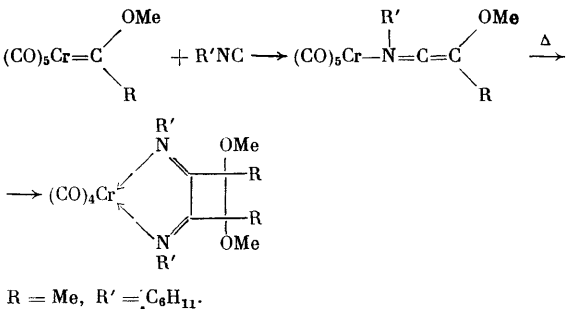
Interestingly, the reaction of bis(diethylamino)acetylene with chromium and tungsten (methoxybenzylidene)pentacarbonyls takes place in a different manner;[43]



However, even in this case the formation of both complexes can be accounted for in terms of a four-membered metallacyclic intermediate:

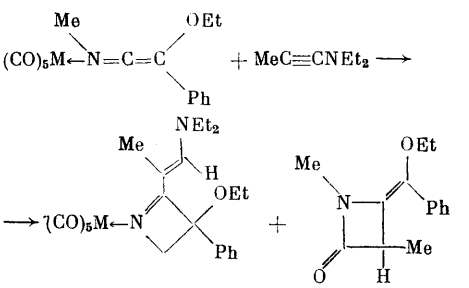


There have been instances reported where reactions of carbene complexes with isonitriles result in the formation of four-membered rings which remain within the coordination sphere of the metal atom by means of Cr–NC bonds with imine groups. These reactions occur as a [2 + 2] cyclisation of intermediate ketenimine complexes:[44,45]

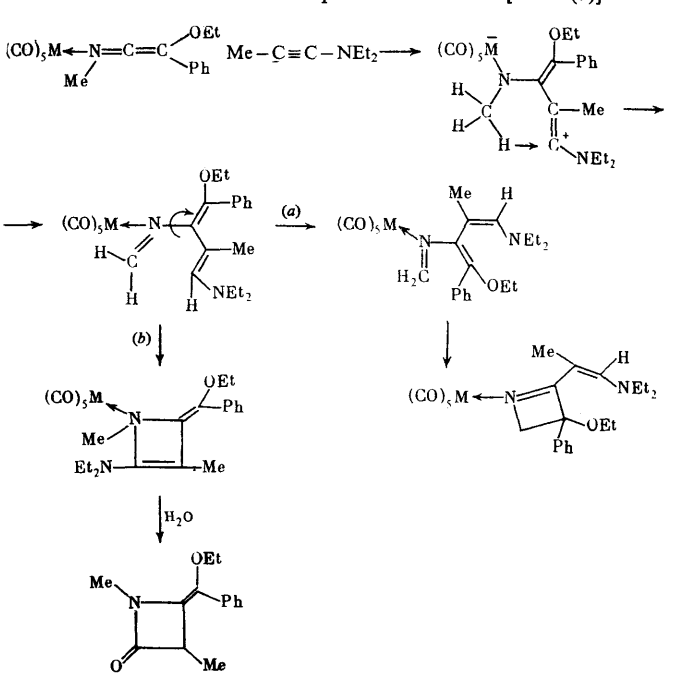


R = Me, R′ = C_6H_{11}.

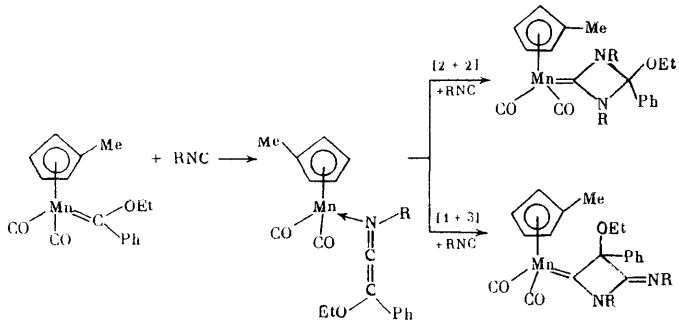
Interestingly, uncoordinated ketenimines dimerise differently, giving azetidines.[44] A similar type of cyclisation occurs[46] occurs in the reaction between chromium and tungsten ketinimine complexes and 1-diethylaminopropyne:



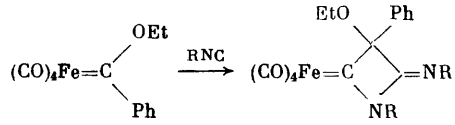
The formation of an azetine complex has been attributed[46] to the initial addition of alkyne to the N=C double bond of the coordinated imine, resulting in a zwitterionic dienamide derivative in which intramolecular addition of hydrogen from the methyl group to the carbocation site occurs with regeneration of an imine complex. The latter may undergo rotation about the C–N bond and a [2 + 2] cyclisation to an azetine [route (*a*); "normal" [2 + 2] cyclisation without rotation results in a complex with a lactam [route (*b*)]:



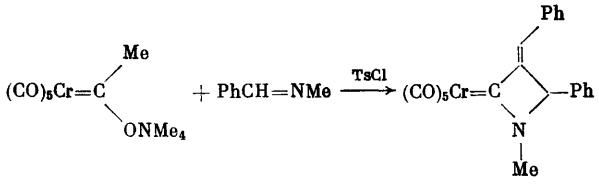
Intermediate ketenimine derivatives can react with excess isonitrile to form products of both [2 + 2] and [1 + 3] cycloaddition:[47]

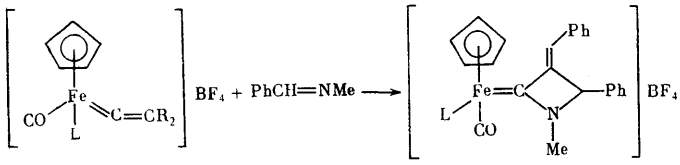


In the case of an iron complex only [1 + 3] cycloaddition occurs:[48]

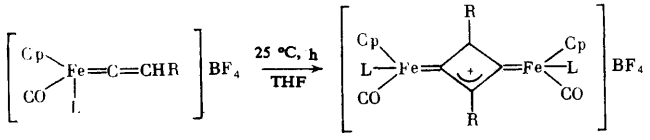


Schiff bases react with chromium[49] and iron[50] carbene complexes in a similar manner

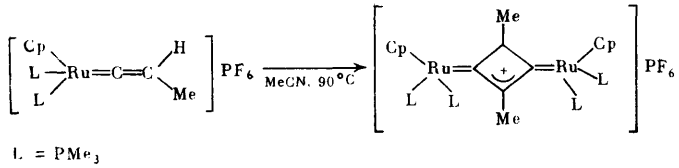




In the case of the chromium derivative the reaction route depends on the solvent—in CH_2Cl_2 or t-BuOH only cyclisation occurs while in MeOH the linear product $(CO)_5Cr=C(OMe)CH=CHPh$ is also formed.[49] Cationic iron[51–53] and ruthenium[54] vinylidene complexes can undergo a [2 + 2] homocyclisation to give very interesting products.

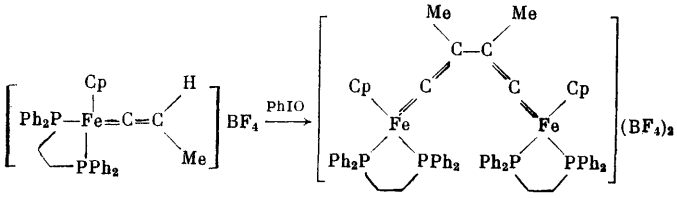


L = CO, PPh_3, $P(C_6H_{11})_3$;
R = H, Ph.

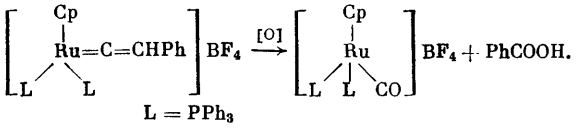


L = PMe_3

An iron vinylidene complex with a chelate diphosphine ligand also dimerises on treatment with iodosylbenzene, but forms a "linear" product:[55]

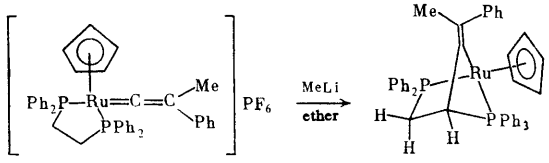


Under these conditions the ruthenium analogue doe not dimerise but its C=C bond is cleaved to form carbonyl derivatives and an acid:[56]



L = PPh_3

Ruthenium vinylidene complexes react with methyllithium quite differently:[57]



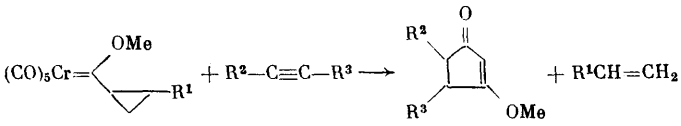
Protophilic attack on the α-CH_2 group of the diphosphine and intramolecular cyclisation with the formally carbocationic α-carbon atom of the vinylidene ligand occur.

In summarising the material presented in this section, it may be concluded that "pure" [1 + 3] cycloaddition reactions of the carbene ligand to form four-member π-ligands do not occur. There is a predominance of [2 + 2] cycloaddition processes to form metallacycles, cyclobutylidene complexes, and azacyclobutane derivatives bound to the metal atom by a coordination bond.

IV. Reactions that lead to the formation of five-membered rings

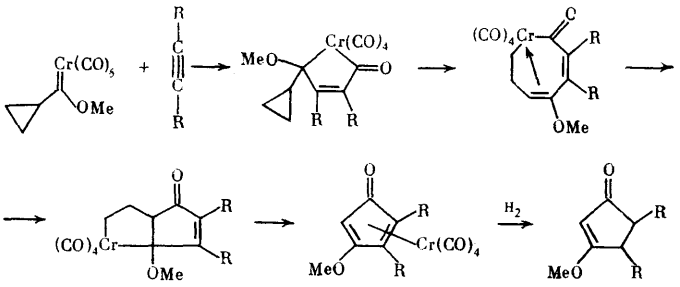
As the material of the previous section demonstrates, attempts to consider inner-sphere cyclisation reactions involving carbene complexes in terms of [*n* + *m*] cycloaddition processes are too formal, since in the majority of cases formation of the final products results from secondary reactions, a carbonyl ligand acting as the "supplier" of a further carbon atom to the ring may participate in ring formation. Strictly speaking, synchronism has not been demonstrated for a single reaction and the stereochemical result of the reactions is not always clear. In the present section an attempt will be made to classify the reactions according to the nature of the final products. Three types of reaction can be distinguished from the existing literature data: the formation of metallacycles, cyclopentylidene complexes, and five-membered rings that remain in the coordination sphere because of the *N*-donor groups present in them. Herndon et al.[58,59] have reported the formation of

cyclopentenes in the reaction between acetylenes and chromium (cyclopropyl)-(methoxy)carbene complexes:



R^1 = H, Ph; R^2 = H, Me, Pr, Ph; R^3 = Pr, Ph, C_5H_{11}.

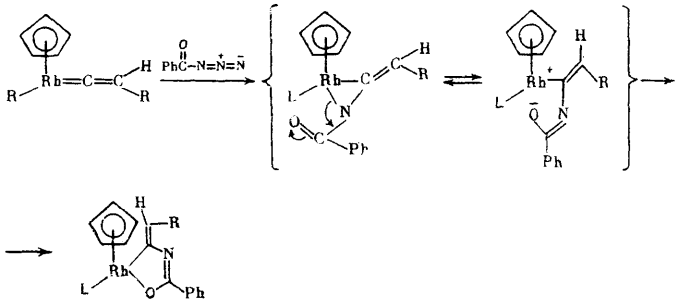
The following reaction scheme has been proposed:[58]



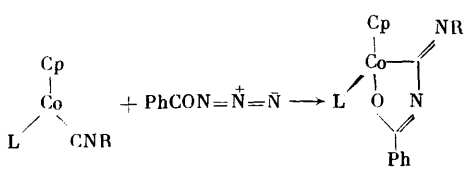
Because of this scheme, which includes intermediate five-membered metallacycles, the two studies of Herndon et al.[58,59] can formally be covered in the present section.

1. Formation of five-membered metallacycles

The reactions of rhodium and osmium vinylidene complexes with benzoyl azide gives metallaoxazoline derivatives,[60,61] these being accompanied by the elimination of nitrogen. It is possible that they take place as a [3 + 2] cycloaddition of the dipolar azide to the polar Ph=C group with initial formation of a five-membered metallacycle, which after elimination of nitrogen is converted to a three-membered metallacycle. The following reaction scheme has been proposed:[61]

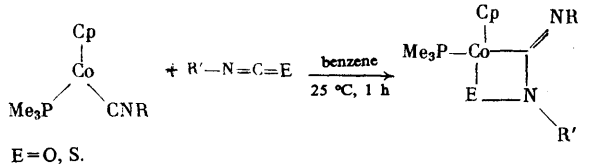


Similar cobaltaoxazoline derivatives are formed in the reaction between benzoyl azide and cobalt isonitrile complexes:[62]



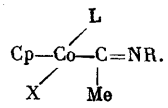
L = PMe_3; R = Ph, Me.

Interestingly, isocyanates and isothiocyanates react with cobalt isonitrile complexes to give four-membered metallacycles:[63]

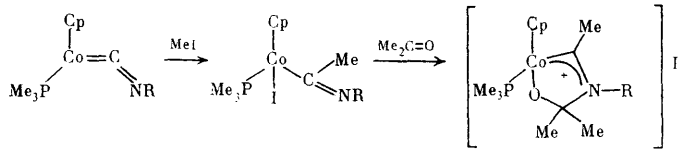


E = O, S.

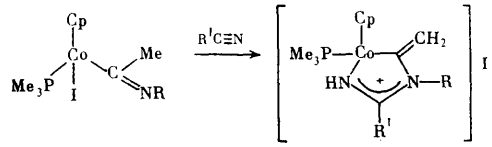
A series of studies[64–67] is devoted to the [3 + 2] cycloaddition reactions of different substrates (carbonyl compounds,[64] nitriles,[65] isothiocyanates,[66] and carbon disulphide[67]) to imidoylcobalt complexes of the type



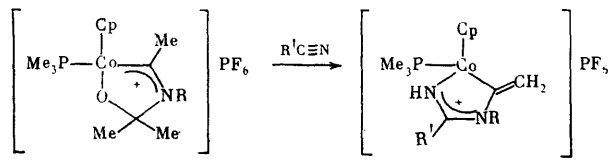
They are readily generated by addition of MeI to the corresponding isonitrile complexes;[64,65] in acetone solution[64] cyclisation to form cobaltaoxazoline occurs:[64]



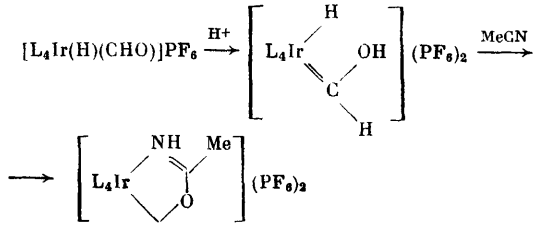
The reaction with aldehydes[64] and nitriles[65,68] occurs in a similar manner:



The same cobaltamidoazolines are formed when the cycloadducts with acetone are treated with nitrile:

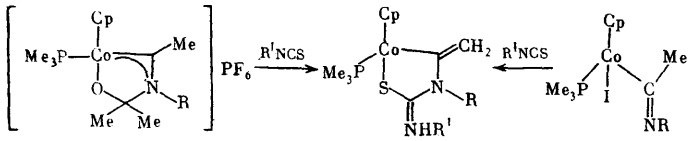


Interestingly, similar metallacycles have been obtained[69] by reaction of acetonitrile with an iridium hydroxycarbene complex:

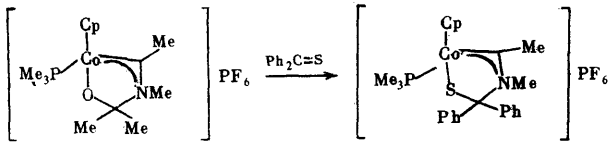


L = PMe_3

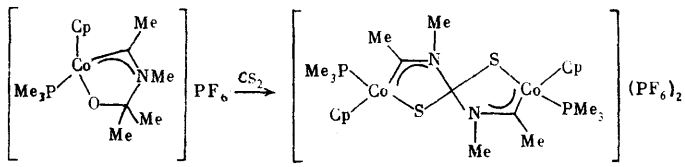
Isothiocyanates react[66] with imidoylcobalt complexes or with their acetone adducts to form cobaltathiazoline derivatives:



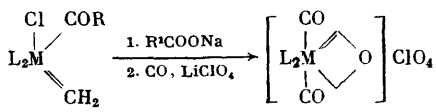
Diphenyl thioketone also displaces acetone from its adduct, giving a new heterocycle:[67]



Under these conditions carbon disulphide forms a spirocyclic complex:[67]

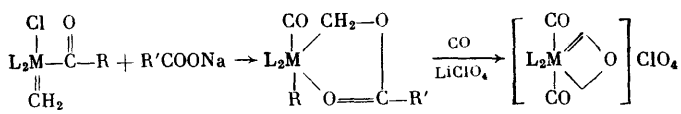


The complexes obtained by Werner et al.[64–67] contain a metallacycle with a multiple carbon–metal bond. Formally they are products of addition to the M=C bond in pseudocarbene complexes. Bohle et al.[70] have reported an example of intramolecular combination of a carbene ligand with an acyl residue:

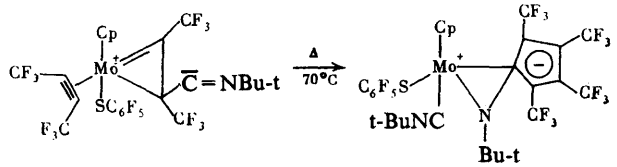


M = Ru, Os; L = PPh_3; R = Ph, $MeOC_6H_4$.

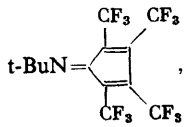
These authors assume that initially a five-membered metallacycle is formed through the addition of R'COONa to the $M=CH_2$ bond:



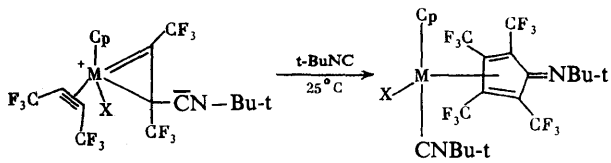
The preparation of a quite unusual cyclopentadienyl anion has been reported:[71]



On heating the cyclic carbene complex in a sealed ampoule, the sole product isolated is a complex containing the iminocyclopentadiene ligand

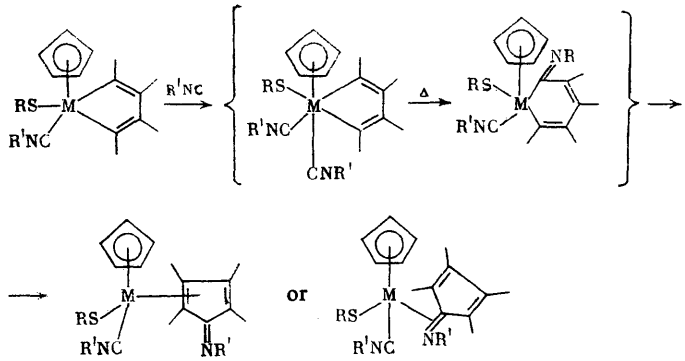


which does not have η^4-type coordination as occurs for the complexes reported by Carlton and Davidson[72]



M = Mo, W; X = CF_3, Cl.

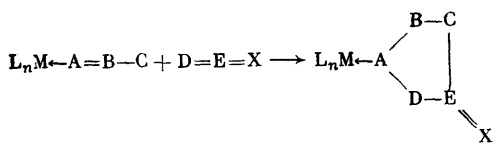
but has η^2-coordination via the imine bond. The preference for a given form of coordination in an iminocyclopentadiene is dictated by thermodynamic and kinetic factors. It is possible that the η^2-bonded isomer is generated from an initially formed η^4-complex.[71]



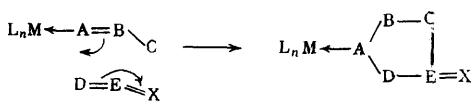
It is thought[71,73] that both isomers are derived from the same metallacyclopentadiene precursor.

2. Formation of cyclopentylidene complexes

In the present subsection we shall consider reactions of the following type:

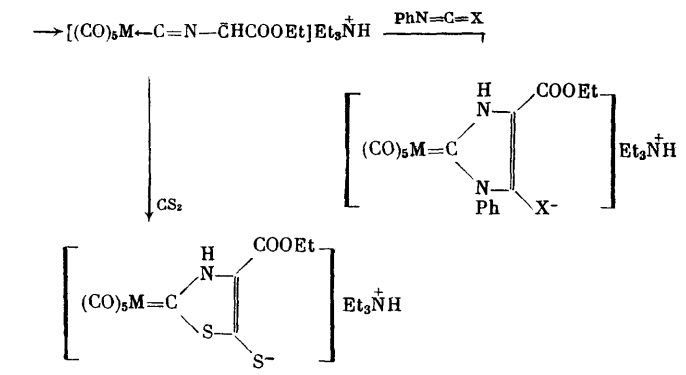


This is, in effect, a [3 + 2] cycloaddition:



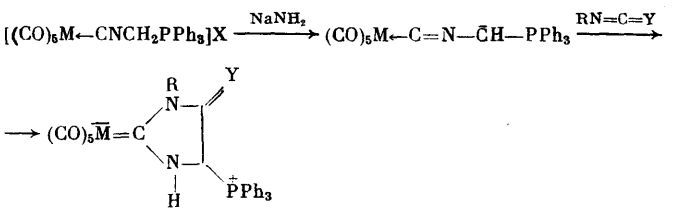
Whether these reactions are concerted or occur in stages is a question which most frequently remains outside the scope of investigation, but the authors of all the studies cited below adhere to the terminology of [*m* + *n*] processes. A necessary condition for

such reactions to occur is the presence in the initial complex of a multiple A=B bond. It is also desirable that the A=B–C residue should have a 1,3-dipole nature. This is achieved in various ways. For example, in the reaction of isocyanates, isothiocyanates,[74] and carbon disulphide[75] with chromium or tungsten ethoxycarbonylmethylisocyano derivatives, a base (Et_3N, t-BuOK) is used as a catalyst, removing a proton from the methylene group, as a result of which a 1,3-dipolar intermediate is formed. The latter undergoes cyclisation:



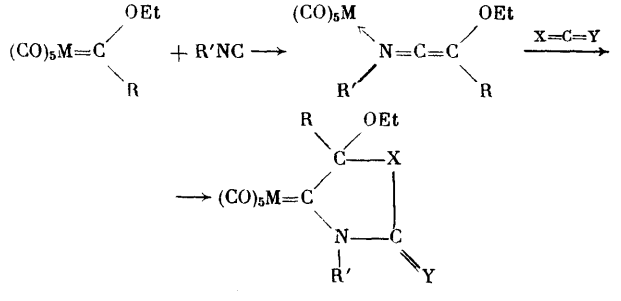
X = O, S.

In the case of complexes with triphenylphosphoranylmethylisonitrile deprotonation occurs on treatment with sodamide.[76,77] The resulting isocyanomethylenephosphoranes undergo a [3 + 2] cycloaddition reaction with isocyanates, isothiocyanates, carbon disulphide, nitriles, olefins, and acetylenes:



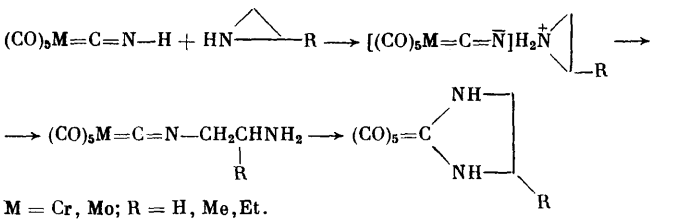
M = Cr, W; R = Ph, Me; X = Cl, PF_6; Y = O, S.

The reactions are similar[78,79] for metal ketenimine complexes (mention has been made of ketenimine complexes in Section III), which are formed by treatment of carbene derivatives with isonitriles:[78–80]



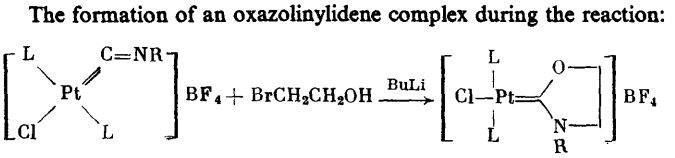
M = Cr, Mo; R = Ph, C_6H_{11}, $C_6H_3Me_2$-2,6;
R' = Ph, 2-thienyl;
X = O, NPh, NMe;
Y = O, NBu-t, NC_6H_{11}.

Isonitrilic acid complexes react with aziridines to form cyclic diaminocarbene derivatives.[81] In this case the aziridine acts both as a base and as part of the ring being formed:



M = Cr, Mo; R = H, Me, Et.

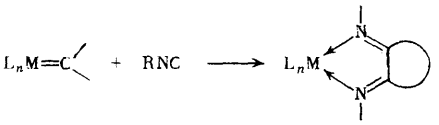
The formation of an oxazolinylidene complex during the reaction:



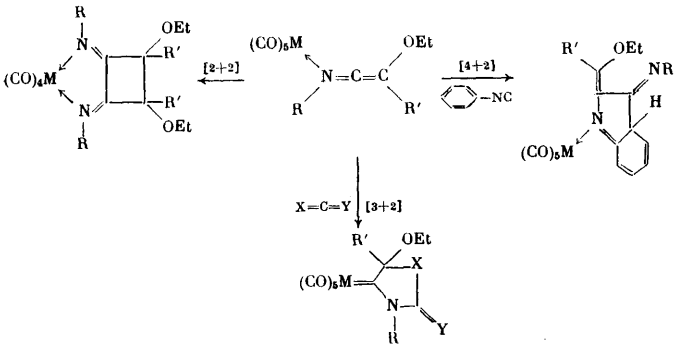
can be interpreted as attack by the dianion $^-CH_2CH_2O^-$ on the suitably polarised C=N bond of the isonitrile ligand.[82]

3. Formation of five-membered rings coordinated with *N*-donor groups

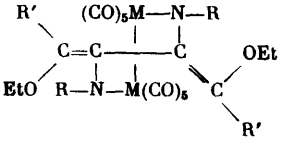
In this subsection we shall summarise reactions of the following type:



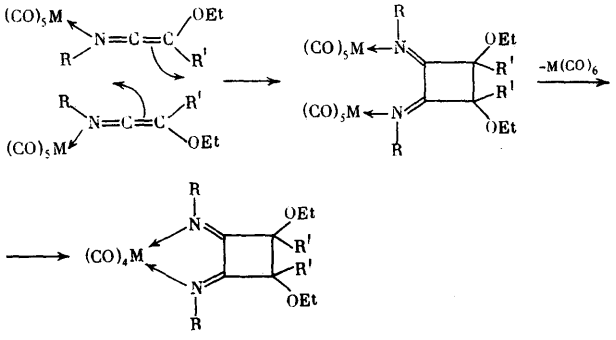
All of these reactions take place with the formation of intermediate ketenimine complexes $L_uM{\leftarrow}N(R){=}C{=}C\lessdot$ (see Section III), which have been isolated in a number of cases.[83–85] According to the data of Aumann et al.,[44,45,79] the ketenimine residues can undergo [2 + 2], [2 + 3], and [2 + 4] cycloaddition:



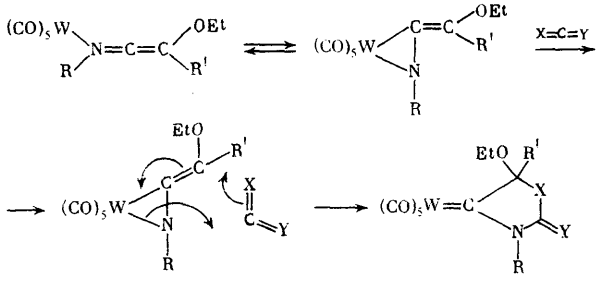
The [2 + 2] cycloaddition takes place via an intermediate of the type:



which is formed by treatment of the initial ketenimine complexes with isonitrile. The occurrence of a concerted process should also not be excluded:

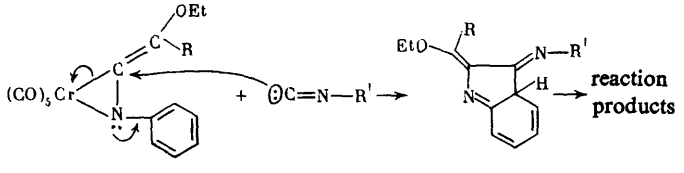


In order to account for the [3 + 2] reaction, the concept of an equilibrium between *N*- and π-coordinated ketenimine complexes (see Section III) has been adopted;[79] the π-imine derivative then undergoes a normal [3 + 2] cycloaddition:

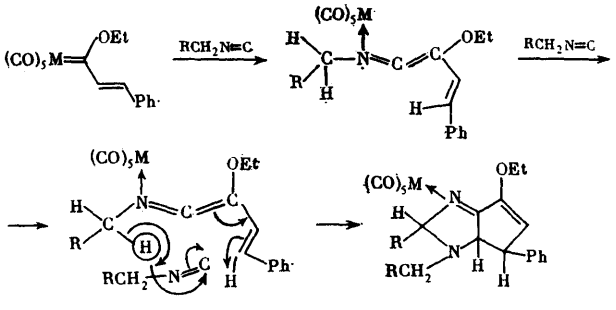


The choice between [2 + 2] and [3 + 2] processes is governed by steric factors—as steric hindrance increases the [3 + 2] cycloaddition predominates.

The interpretation of the [4 + 2] reactions is somewhat more complex.[79] The participation of a π-ketenimine intermediate and the C=C bond of the aromatic ring has been suggested:

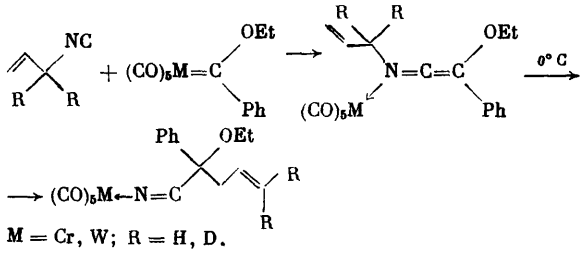


The formation of five-membered rings in two studies by Aumann et al.[83,85] is accounted for in terms of a [4 + 1] cycloaddition involving four double bonds and a single α-C–H bond of the isonitrile ligand:



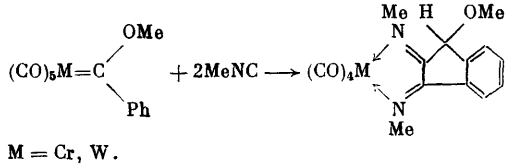
M = Cr, W ; R = H, Ph, CH_2=CH.

Allylisonitriles react with carbene complexes that do not contain a multiple bond in the carbene ligand without forming cyclic products. At low temperatures the intermediate ketenimine complexes rearrange to but-4-enylisonitrile complexes:[84]



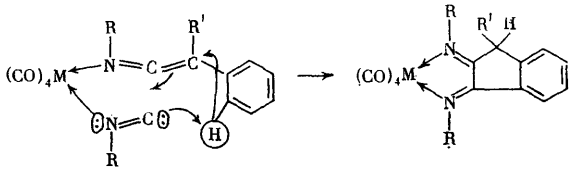
M = Cr, W; R = H, D.

In some cases the intermediate ketenimine adduct is not isolated:[86]

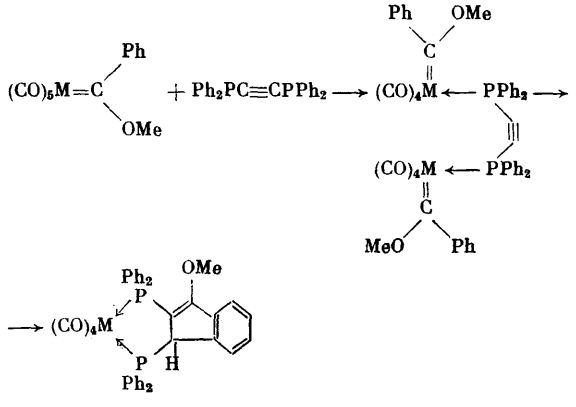


M = Cr, W.

In this case α- and *ipso*-carbon atoms of the aryl group of the carbene ligand participate in reaction. It is quite clear that this reaction is not synchronous. At the first stage a ketenimine intermediate is formed which adds a second isonitrile molecule, while the hydrogen on the α-carbon atom undergoes a 1,3-shift



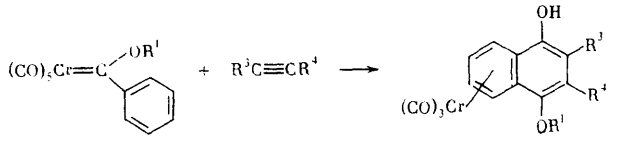
The formation of a chromium phosphine complex as described by Dötz et al.[97] is likely to occur in a similar manner:



Thus, despite the formalism of the concept of [*n* + *m*] cycloaddition (see beginning of Section IV) the attempt to classify the reactions according to the final products has essentially led to the same concept. It is clear from the material in this section that the formation of five-membered rings involving carbene complexes can result from [4 + 1], [3 + 2], and [2 + 2] reactions. In the latter case metallacycles are formed because of the participation of the metal atom.

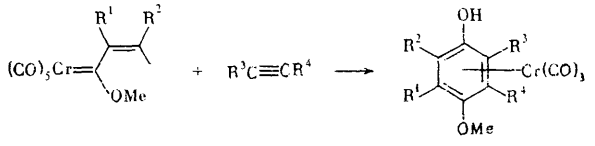
V. Reactions that lead to the formation of six-membered rings

There exists a considerable number of studies (see several reviews)[1-5,88] in which is described the formation of chromium arene complexes by reaction of alkynes with pentacarbonylchromium carbene derivatives containing an aryl substituent on the carbene carbon atom:



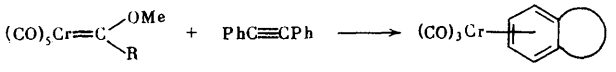
It is quite clear that the α-carbon atom of the phenyl group of the carbene ligand and one of the carbonyl groups bound to chromium participate in the reaction.

Another type of reaction that leads to arene complexes is characterised by the presence of a vinyl group on the carbene carbon atom:



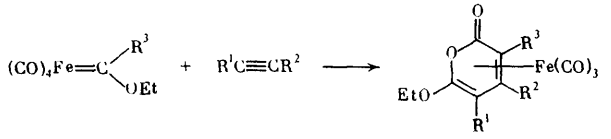
It is possible that this is a special case of the process shown above, since methoxyallylidene complexes can be formed by the reaction of alkynes with carbene complexes.

The synthesis of arene complexes from carbene derivatives with a five-membered ring on the carbene carbon atom has also been reported:



R = ferrocenyl, cycloalkenyl, pyrrolidinyl, furyl, thienyl, pyrrolyl.

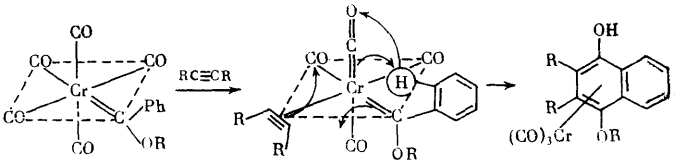
It is likely that in this case the formation of arene complexes is a secondary process. And finally, there is a small group of reactions leading to the formation of α-pyrone complexes:



These reactions take place in the presence of CO.

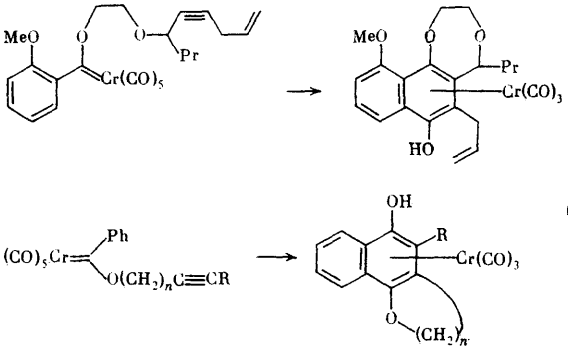
1. Formation of arene complexes from α-alkoxybenzylidene derivatives

In order for the formation of arene complexes from metal α-alkoxybenzylidene derivatives to occur successfully it is necessary for three components—alkyne, carbene, and carbonyl—to coordinate with the metal site at the same time. In order to coordinate the alkyne it is necessary to displace one carbonyl ligand from the coordination sphere. According to the data of two studies,[89,90] the CO ligand that is situated *cis* to the carbene ligand in chromium pentacarbonyl carbene complexes is the most readily replaced. As a result a *fac*-(alkyne)(carbene)carbonyl intermediate is formed, and the subsequent reaction may be regarded as a [3 + 2 + 1] cycloaddition:[2]



Under kinetically controlled conditions (low temperatures, short reaction time) a complex is obtained in which the metal is bound to the newly formed ring (1-8*a*-η^6-coordination). At higher temperatures and long reaction times the $Cr(CO)_3$ group migrates to the free ring, and the naphthalene ligand has 4*a*-8*a*-η^6-coordination in the complexes isolated. The literature data on the synthesis of chromium arene complexes starting from alkynes and α-alkoxybenzylidenepentacarbonylchromium are summarised in Table 1.

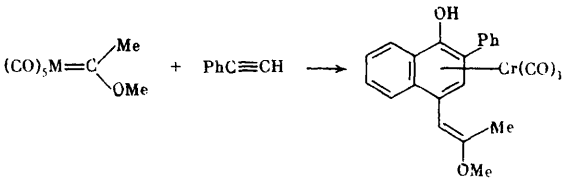
An intramolecular form of the reaction is possible when all three components—alkyne, carbene, and carbonyl—are present in the same molecule:[101,102]



n = 2 ÷ 4; R = H, Me

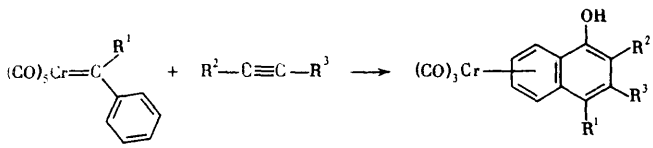
These reactions represent key stages in the synthesis of anthracyclinone antibiotics (desoxyfrenolicin, daunomycinone).[2] The regioselective reaction in the case of the *ortho* substituent in the benzene ring attacts attention. Two studies[103,104] have been devoted to this phenomenon.

In a number of cases[105,106] chromium tricarbonyl complexes of α-naphthols are formed in reactions with chromium carbene derivatives in which there is no aryl substituent on the carbene carbon atom:



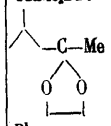
It is quite clear that a phenyl group of phenylacetylene participates in the formation of the naphthalene skeleton. It is thought[105] that in contrast to the [3 + 2 + 1] mechanism (see beginning of

Table 1. Chromium arene complexes obtained by the reaction



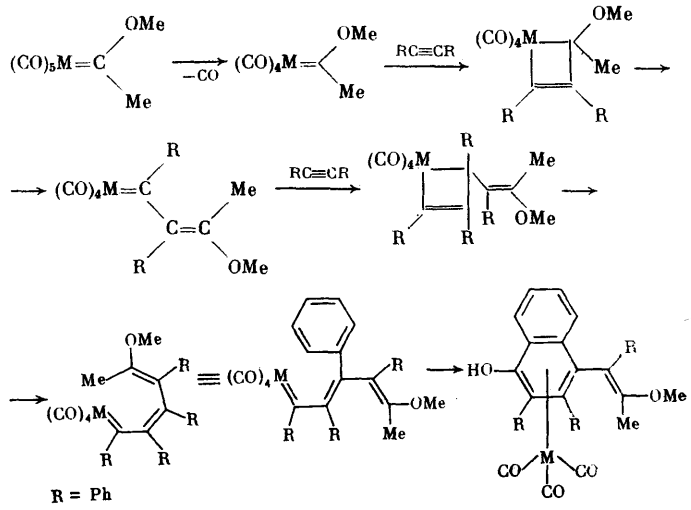
R^1	R^2	R^3	Yield, %	Refs.	Notes
OMe	Ph	Ph	62	[91]	
OMe	Ph	Ph	18	[92]	
OMe	Me	H	63	[93]	Isolated after oxidation as 2-methyl-1,4-naphthoquinone
OMe	Me	Phytyl *1	48	[93]	Isolated after oxidation as 3-methyl-2-(3,7,11,15-tetramethylhexadec-2-enyl)-1,4-naphthoquinone
OMe	Pr	H	45	[94]	Isolated as the 8a-4a-η^6-isomer
OMe	C_6H_{17}	H	59	[94]	8a-4a-η^6-isomer
OMe	t-Bu	H	79	[94]	ditto
OMe	Et	Pr	62	[94]	"
OMe	Et	t-Bu	66	[94]	"
OMe	Pr	Bu	62	[94]	"
OMe	Ph	Me	73	[94]	"
OMe	Et	Me	56	[94]	"
OMe	Pr	Me	80	[94]	"
OMe	t-Bu	Me	59	[94]	"
OMe	Phytyl *1	Me	58	[94]	"
OMe	Me	Phytyl *1	34	[94]	"
OMe	Ph	4-MeC_6H_4	52	[94]	"
OMe	Ph	4-$CF_3C_6H_4$	66	[94]	"
OMe	4-$CH_3C_6H_4$	4-$CF_3C_6H_4$	62	[94]	"
OMe	Me	Et	60	[95]	"
OMe	Et	H	35	[96]	"
OMe	Me	Me	68	[96]	"
OMe	Pr	H	45	[96]	"
OMe	Bu	H	45	[96]	"
OMe	Pr	Me	58	[96]	"
OMe	Et	Et	65	[96]	"
OMe	Me	Me	36	[96]	"
OMe	Pr	H	32	[96]	"
OMe	Bu	H	30	[96]	"
Ph	Me	Me	12	[96]	"
Ph	Pr	H	11	[96]	"
Ph	Ph	H	27	[96]	"
Ph	Ph	Ph	20	[96]	"
Ph	Ph	COOEt	7	[96]	"
Ph	H	H	9	[96]	"
OMe	Ph	Ph	61	[96]	Obtained from diphenylacetylene and a tris(4-fluorophenyl)phosphine complex
OMe	Ph	Ph	11	[96]	Obtained from diphenylacetylene and a tributylphosphine complex
OMe	Me_3Si	H	76	[97]	Isolated as the 8a-4a-η^6-isomer
OMe	Me	Phytyl *1	58	[98]	ditto
OMe	Phytyl *1	Me	34	[98]	"
OMe	H	$CH_2CH{=}CMe_2$	60	[98]	"
OMe	Me	$CH_2CH{=}CMe_2$	85	[98]	Isolated as the 8a-4a-η^6-isomer
OMe	Me	$C_{10}H_{17}$ *2	91	[98]	ditto
OMe	Me	$C_{15}H_{25}$ *3	90	[98]	"
OMe	Ph	Ph	—	[99]	"
OMe	Ph	4-MeC_6H_4	52	[99]	Mixture of 8a-4a-η^6- and 4a-8a-η^6-isomers
OMe	Ph	4-$CF_3C_6H_4$	66	[99]	ditto
OMe	4-$CH_3C_6H_4$	4-$CF_3C_6H_4$	62	[99]	"
OMe	Ph	Me	73	[99]	Isolated as the 8a-4a-η^6-isomer

Table 1 (cont.).

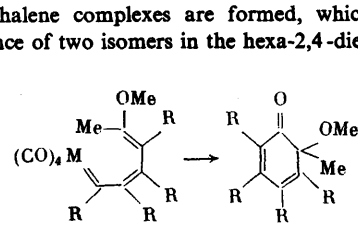
R^1	R^2	R^3	Yield, %	Refs.	Notes
OMe	Ac	H	42	[100]	Isolated after oxidation as the respective 2-substituted 4-methoxy-α-naphthol
OMe	EtOCO	H	41	[100]	ditto
OMe	t-$BuMe_2SiOCMe_2$–	EtO	54	[100]	"
OMe	$OSiMe_2Bu$-t	EtO	45	[100]	"
					
OMe	Ph	COOEt	22	[100]	Isolated after oxidation as the respective substituted 4-methoxy-α-naphthol
OMe	C_5H_{11}	COOEt	60	[100]	ditto
OMe	Et	COOEt	38	[100]	"

*1 Phytyl = 3,7,11,15-tetramethylhexadec-2-enyl.
*2 $R^3 = CH_2CH{=}C(Me)CH_2CH_2CH{=}CMe_2$.
*3 $R^3 = CH_2CH{=}C(Me)CH_2CH_2CH{=}C(Me)CH_2CH{=}CMe_2$.

Section V.1), in this case a [2 + 2 + 2] cycloaddition involving two alkyne molecules occurs:

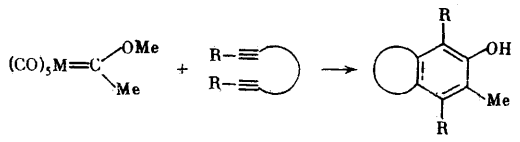


When R = alkyl, cyclohexadienone complexes rather than naphthalene complexes are formed, which is attributed[105] to the presence of two isomers in the hexa-2,4-dienylidene intermediate:

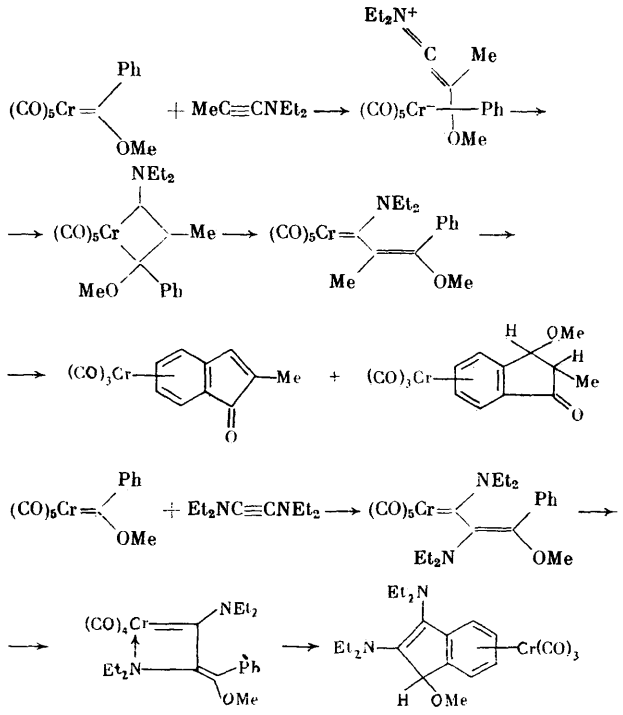


R = Me, Pr.

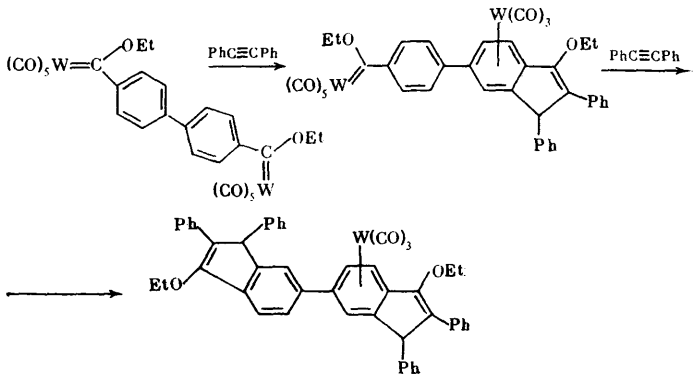
Annelation reactions involving two alkynyl residues can be carried out in an intramolecular form:[106]



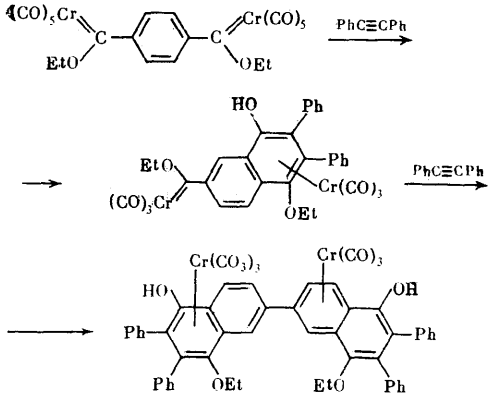
Derivatives of indene and naphthalene are obtained in this manner.[107] According to Dötz,[2] the formation of compounds with an indene skeleton occurs by insertion of alkyne into the metal–carbene bond, possibly via a four-membered metallacyclic intermediate. Nucleophilic alkynes as a rule participate in such reactions:[108–110]



However, the formation of indenes is also possible in reactions with normal alkynes such as diphenylacetylene.[92,111] An interesting reaction has been reported by Hoa and Lefloch.[112]



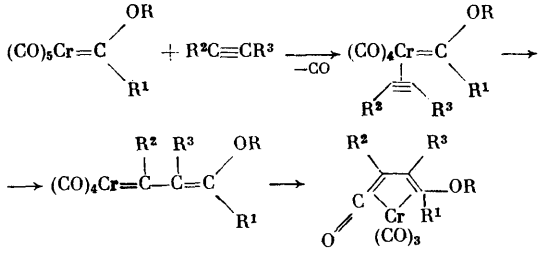
In the case of the chromium analogue a chromium naphthalene complex is formed:[122]



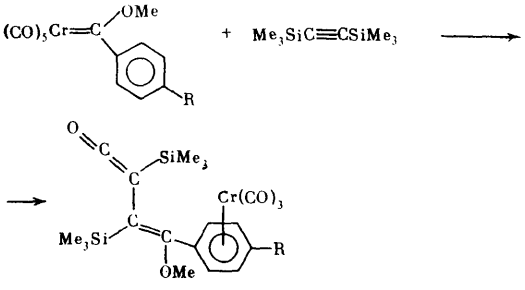
In contrast to tungsten the μ-η^6:η^6-derivative was isolated.

2. Formation of arene complexes from α-alkoxyallylidene derivatives

As was indicated above, α-alkoxyallylidene intermediates can be formed by reaction of alkynes with transition metal carbene complexes. In some instances[97,105] this is only postulated, but in a number of cases, especially for nucleophilic alkynes,[113–118] these intermediates have been isolated. They can participate in subsequent reactions. One of these is the insertion of a carbonyl ligand into the metal–carbene bond to form ketene derivatives:[97,117,119]

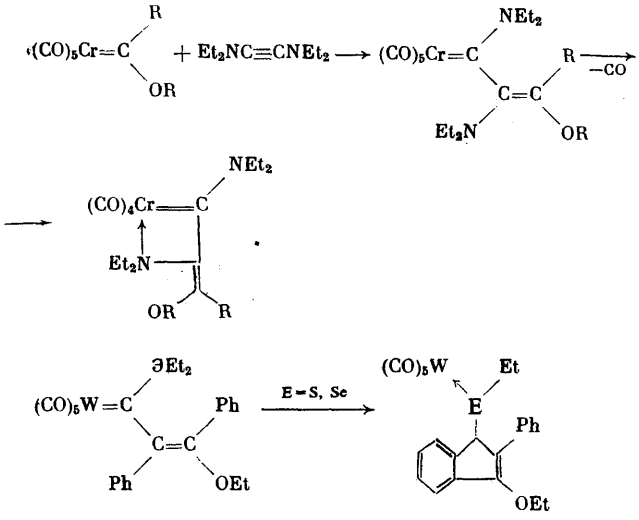


In fact, in a number of cases[97] such ketenes have been isolated, for example

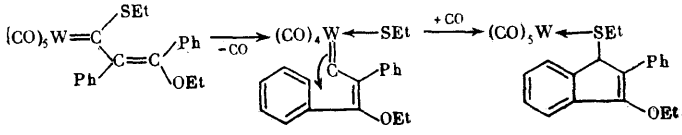


R = H, Me, OMe, CF_3.

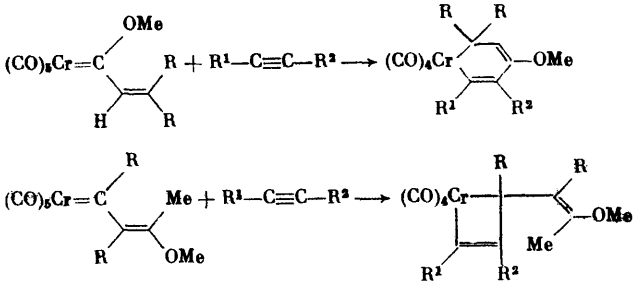
Another reaction is intramolecular cyclisation through coordination of the metal atom with *N*-donor groups present in the alkyne molecule:[110,120]



The latter reaction appears to be unusual. It can be given by a scheme, one of the stages of which is formation of a three-membered metallacyclic intermediate. This metallacycle subsequently decomposes through cleavage of the metal–carbon double bond of the carbene ligand, with a five-membered ring being formed:

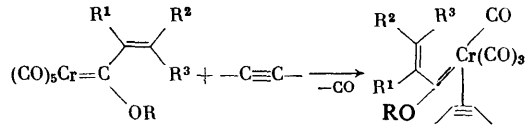


The formation of "true" metallacycles with metal–carbon σ-bonds is also possible:[105,121]

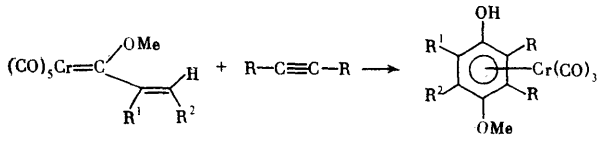


Interestingly, whatever the size of the ring in the resulting intermediate, in the latter two cases the same final product—2-methoxy-2-methyl-3,4,5,6-tetrasubstituted cyclohexa-3,5-dienone—was isolated, although Tang and Wulff[121] in the case of the six-membered metallacyclic intermediate expected to obtain a 3-methoxycyclopentadiene—a product derived from the β-elimination of $HCr(CO)_5$. However, Herndon et al.[122] on reacting pentacarbonyl[(methoxy)(cyclopropyl)carbene]chromium with diphenylacetylene isolated 4,5-diphenylcyclopent-3-enone—the expected reaction product.

Thus, all reactions of α-substituted allylidene complexes with alkynes can be represented[2] by the formation of an (alkyne)(carbene)carbonyl intermediate:



This is essentially the same intermediate as that depicted at the beginning of Section V.1, and its subsequent fate depends on the nature of substituents R^1, R^2, and R^3. When R^3 = H, arene complexes are formed:[123–126]

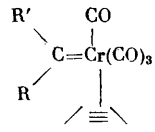


R^1 = Me, H; R^2 = H, Me, Ph; R^1, R^2 = $-(CH_2)_n-$, where n = 3, 4.

Terminal acetylenes react regioselectively, the substituent going into the *ortho* position relative to the OH group.[125]

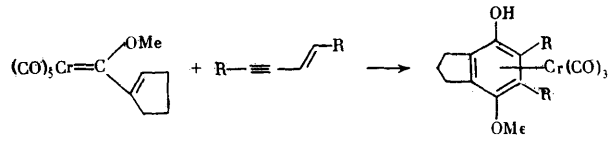
3. Formation of arene complexes from carbene complexes with a five-membered ring on the carbene carbon atom

The five-membered ring on the carbene carbon atom in carbene complexes can be a heterocycle,[117,127–132] alicycle,[125,127] or cyclopentadienyl ring of a ferrocenyl residue.[133] In all cases the results (alkyne)(carbene)carbonyl intermediate (see Section V.1) takes the following form:

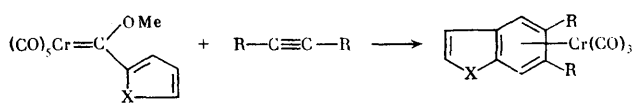


R′ = five-membered ring.

The fate of this intermediate is known[125,127] when R′ is an alicyclic group—η^6-indane derivatives are formed. It is interesting that in the reaction



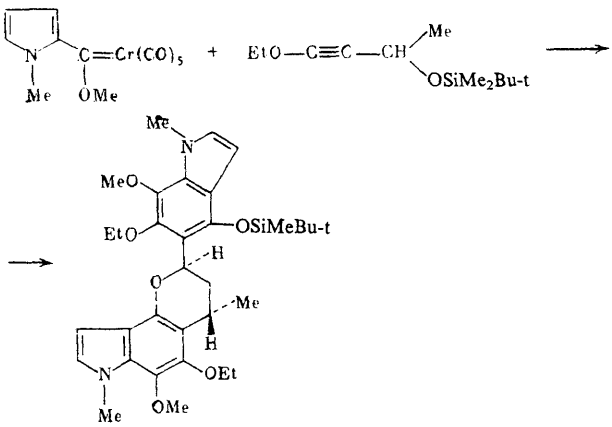
the C=C double bond of the ring rather than that of vinylacetylene is involved in the cycloaddition process.[125] When R′ - α-pyrrolyl,[129] α-furyl,[127,132] and α-thienyl[127] annelation also occurs in a normal manner—the corresponding benzo derivatives of the heterocycles are formed:



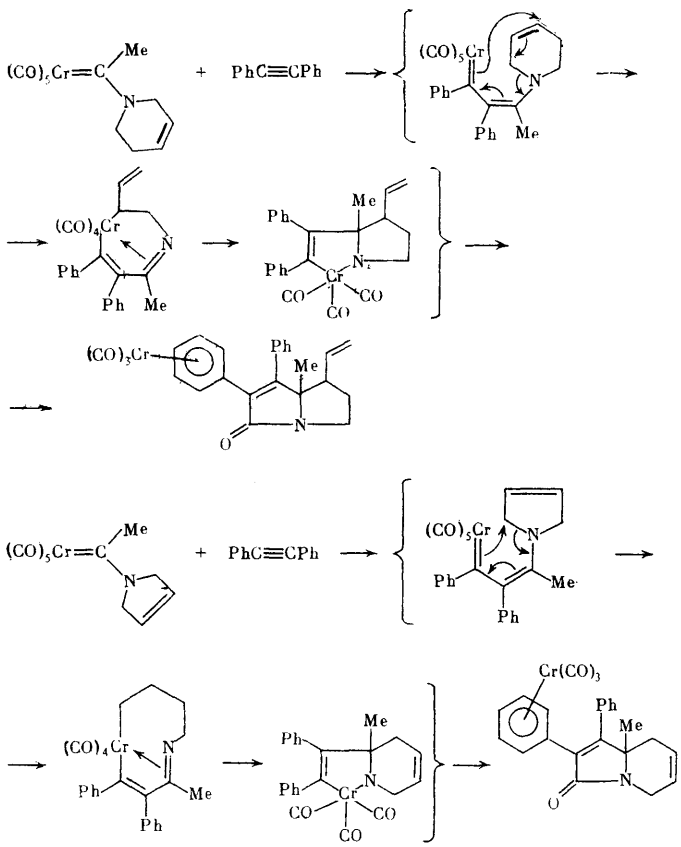
X=O, S, NMe; R = H, Me, Et, EtO, COOMe, Bu, Ph.

However, there are exceptions. For example, the reaction of a chromium α-pyrrolylcarbene derivative with 1-ethoxy-3-[dimethyl-

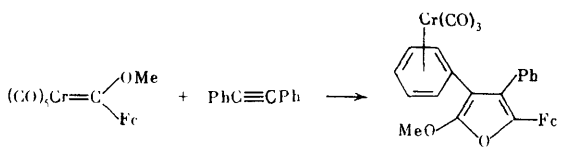
(t-butyl)siloxy]but-2-yne yields its dimer rather than the expected indole:[128]



Annelation can also occur through a more remote double bond:[130,131]

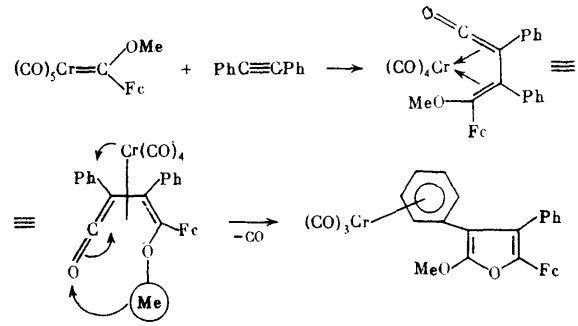


In the case of an α-ferrocenylcarbene complex a furan derivative is formed:[133]



Fc = C_5H_4FeCp.

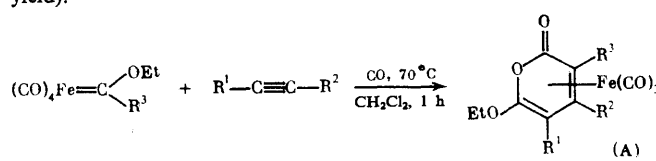
It is possible that the reaction occurs via a ketene intermediate:



The structure of the resulting ferrocene-benzenechromium tricarbonyl derivative has been established by X-ray diffraction analysis.[133]

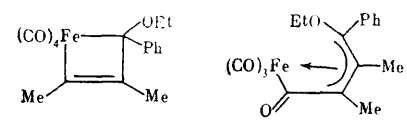
4. Formation of iron α-pyrone complexes

The reaction of iron alkylidene compounds with various alkynes under pressure in an atmosphere of carbon monoxide leads to the formation of complexes of iron with an α-pyrone ligand (in high yield):[134]

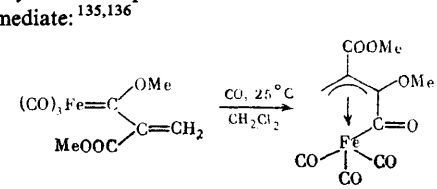


R^1	R^2	R^3	Yield (A), %
Me	Me	Ph	89
Ph	H	Ph	74
Et	H	Ph	33
Ph	Ph	Ph	93
COOMe	Me	Ph	15
Me	Me	t-Bu	60
Ph	H	t-Bu	39
Me	Me	Bu	33

The structure of the complexes obtained (A) has been established by X-ray diffraction analysis. The formation of the α-pyrone skeleton requires the participation of two carbonyl ligands. Moreover, migration of the ethoxyl group from the carbene carbon atom occurs during reaction. When the reaction was carried out in the absence of carbon monoxide, an unstable product was isolated, for which two alternative structures—metallacyclic and π-allylacyl—were proposed on the basis of the ^1H NMR and IR spectra:

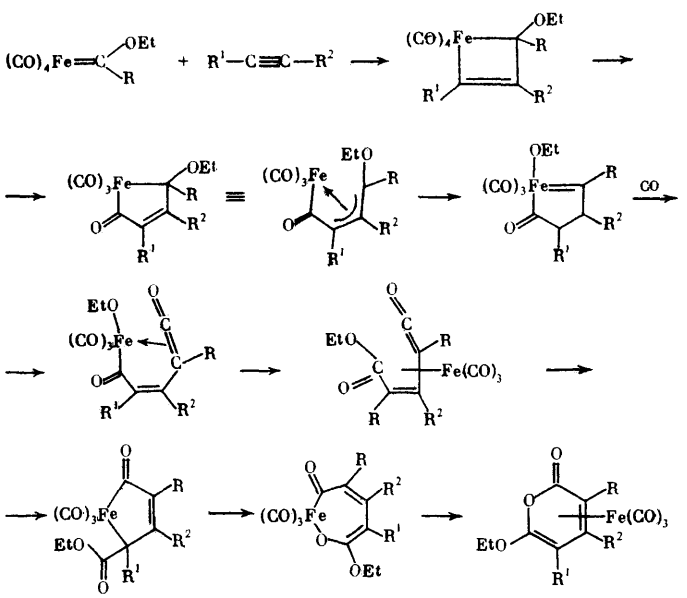


The fact that a π-allylacyl complex is formed when carbon monoxide reacts with a (1-methoxy-2-methoxycarbonylprop-2-enylidene)tricarbonyliron compound is evidence in favour of the second intermediate:[135,136]



However, Semmelhack et al.[134] favour a metallacyclic intermediate, since in the ^{13}C NMR spectrum of the isolated complex there is no signal due to an acyl carbon atom. They

proposed the following scheme for formation of α-pyrone complexes:[134]



This scheme includes the two alternative intermediates. The formation of intermediate ketene complexes is also known,[97] so this sequence of reactions reflects the process mechanism sufficiently objectively.

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Thus, the "carbene site" in transition metal complexes represents a unique matrix on which the most varied cyclic ligands can be built up as a result of an inner-sphere reaction. These processes are treated as [*n* + *m*] cycloaddition reactions, although they are not such types and occur in an unconcerted manner, including stages that are typical of the chemistry of π-complexes such as the initial coordination of substrate, insertion of ligands, elimination, etc. These ring-formation processes in the inner coordination sphere involving carbene complexes are of interest to organic chemists since they act as convenient models for an understanding of the reaction mechanisms of organic compounds in the presence of transition metal complexes.

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