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Transition metal complexes of unsaturated carbenes: synthesis, structure, and reactivity

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ABSTRACT. The methods of synthesis, structure, physicochemical properties, and reactivity of transition metal complexes containing unsaturated carbene ligands (vinylidenes, allenylidenes, and heterocumulenylidenes) are examined. Attention is concentrated on heterometallic compounds. The prospects for the development of the chemistry of unsaturated carbene complexes and their use in organic and organometallic synthesis are discussed.

The bibliography includes 280 references.

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I. Introduction

The chemistry of unsaturated carbene complexes (UCC) is a new field which has arisen at the junction between organometallic, coordination, and organic chemistry and has been developing vigorously during the last decade. Unsaturated carbenes include unsaturated species with an unshared electron pair at an *sp*-hybridised carbon atom C_α and a $C_\alpha=C_\beta$ double bond: vinylidene (ethenylidene) $:C=CH_2$ and its homologues $:C=CHR$ and $:C=CRR'$, allenylidenes (propadienylidenes) $:C=C=CR_2$, ketenylidene $:C=C=O$, and other heterocumulenylidenes $:C=C=S$, $:C=C=C=O$. The involvement of unsaturated carbenes in organic reactions has been described in Stang's reviews.[1–3]

Unsaturated carbenes, which are unstable in a free state, can be stabilised by coordination to Group V–VIII transition metal atoms in low oxidation states. The first structurally characterised complex $(CO)_8Fe_2(\mu\text{-}C=CPh_2)$ was obtained in 1966 by Pauson and Bagga[4] in 3% yield by the interaction of diphenylketen with iron carbonyl. After the discovery in 1974–1978 of the possibility of the formation of UCC from acetylenes and metal carbonyl complexes[5–7] and also from π-acetylenic[8] and σ-alkynyl[9] complexes, simple general methods of synthesis were developed, which made UCC quite readily available. This stimulated a rapid development of their chemistry.

According to the review of Bruce and Swincer,[10] about 150 stable UCC were known in 1983; in their molecules the vinylidene, allenylidene, and heterocumulenylidene ligands were bound to one or several identical or different metal atoms: Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, and Ni. During the last 6 years, the number of such complexes has trebled. The first UCC containing Pt,[11–13] Pd,[14] Ir,[15] and Ta[16] have been synthesised. A new type of bonding of unsaturated carbenes in dinuclear complexes—lateral bridge-type η^1, η^2-coordination—has been discovered.[17–19]

The heterometallic UCC, the first representative of which—$Cp_2(CO)_4MnRe(\mu\text{-}C=CHPh)$—was obtained in 1978,[20] are of special interest. Exotic cluster UCC, such as $CpNiRu_3.(\mu_4\text{-}C=CHR)(\mu\text{-}H)(CO)_9$,[21,22] $CpWOs_3(\mu\text{-}C=CHC_6H_4Me)(\mu\text{-}H).(\mu\text{-}O)(CO)_9$,[23] and $(Ph_3P)_2Au_2Ru_3(\mu_3\text{-}C=CHBu^t)(CO)_9$ [24] have been synthesised by various methods. A general approach to the synthesis of dinuclear and polynuclear complexes, in which mononuclear and dinuclear UCC are used as "building blocks", has been recently discovered on the basis of the application of Hoffmann's isolobal principle[25] (see Section IV, subsection 2). This makes it possible to obtain compounds containing the atoms of two and three different transition metals, including platinum metals, in specified combinations and proportions. Heterometallic UCC can be applied in homogeneous and heterogeneous catalysis. Their employment for the creation of new polymetallic materials (powders, coatings, etc.), necessary for different branches of modern engineering, is promising.

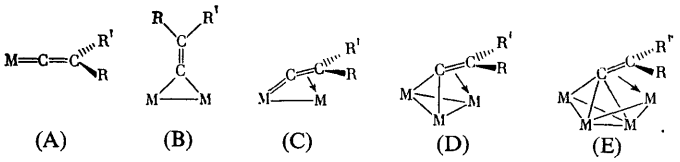
At the present time UCC have been segregated as a special class of organometallic compounds with unusual electronic structures and reactivities. The ease of the formation of UCC from a wide variety of sources and the multiplicity of their reactions suggest that they can be active intermediates in many catalytic reactions involving transition metal atoms. The first examples of the direct use of UCC as catalysts of organic synthetic processes and stoichiometric reactions, leading to valuable organic substances which are difficult to obtain otherwise, have appeared.

In the present review, attention is concentrated on studies performed during the last five years; references to investigations published up to 1982 are given in another exhaustive review.[10]

II. Types of coordination of unsaturated carbenes to metal atoms. The structural and spectroscopic characteristics of the complexes

In contrast to the carbenes $:CR_2$ and :CRX (R = H, alkyl, aryl; X = halogen, OR, NR_2, etc.), which form bonds with only one or

two metal atoms,[26–30] five types of coordination are known for vinylidenes:

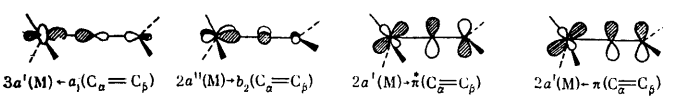


(A) (B) (C) (D) (E)

Coordinations of types (A)–(D) are now known for cumulenylidene complexes.

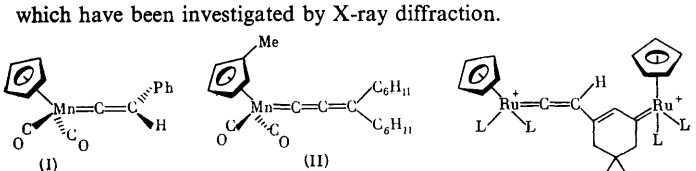
A detailed analysis of the nature of the bonding of unsaturated carbenes to metal atoms has been carried out only for the simplest of such species—vinylidene :C=CH$_2$. The occupied a_1 and π Mo and the unoccupied b_2 and π^* MO of vinylidene participate in the formation of bonds with the metal.[31–33] The character of the bonding of other unsaturated carbenes, isolobal with vinylidene, to metal atoms is apparently similar.

Vinylidene complexes and allenylidene complexes of type (A) contain a linear metallallene M=C=C or metallacumulene M=C=C=C system. Their M–C$_\alpha$ σ-bond is formed as a result of the overlap of the a_1 HOMO of the ligand with $3a'$ LUMO of the metallic fragment. The π-component of the M–C$_\alpha$ bond is formed as a result of the reverse transfer of electron density from the occupied $2a''$ and $2a'$ orbitals of the metal to the unoccupied b_2 and π^* MO of the ligand. Ultimately, the M–C$_\alpha$ bond should have a character intermediate between that of a double and triple bond.

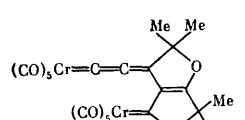


$3a'(M) \leftarrow a_1(C_\alpha{=}C_\beta)$ $2a''(M) \rightarrow b_2(C_\alpha{=}C_\beta)$ $2a'(M) \rightarrow \pi^*(C_\alpha{=}C_\beta)$ $2a'(M) \leftarrow \pi(C_\alpha{=}C_\beta)$

Indeed, very short M–C$_\alpha$ distances have been found in the molecules of vinylidene complexes[10,15,34–48] and allenylidene complexes,[49–53] which have been investigated by X-ray diffraction.



(I) (II) (III), L = PPh_3



(IV)

The Mn=C$_\alpha$ bond lengths in the vinylidene derivatives of cymantrene [1.68(2) Å in the complex (I),[6,34] 1.79(2) Å in $(C_5H_4Me)(CO)_2Mn{=}C{=}CMe_2$,[54] and 1.75(2) Å in $Cp(CO)_2Mn{=}C{=}CHC_6H_4CBr{=}CH_2$ [45]] and in the allenylidene complex (II) (1.806 Å [51]) are smaller than in the dimethylcarbene compound $Cp(CO)_2Mn{=}CMe_2$ (1.872 Å [55]) and approach the length of the Mn≡C triple bond (1.665 Å) in the carbyne complex $[Cp(CO)_2Mn{\equiv}C{-}CH{=}CPh_2]^+$.[56] The Ru=C distance in $Cp(PMe_3)_2Ru{=}C{=}C{=}CPh_2$ [1.884(5) Å [52]] and the Ru=C (vinylidene) distance (1.83 Å) in the bimetallic complex (III)[48] are shorter than the Ru=C (carbene) distance in compound (III) (1.93 Å). The Cr=C (allenylidene) and Cr=C (carbene) distances in the furofurandiylidene complex (IV) are respectively 1.913(7) and 9.73(6) Å.[50]

According to MO calculations,[31,32] the horizontal conformation of vinylidene and the vertical conformation of allenylidene are more favourable in type (A) complexes. Such conformations have in fact been established by X-ray diffraction for the majority of the complexes, for example, in (I) and (II). However, the barrier to rotation about the M–C$_\alpha$ bond is low (~4 kcal mol^{-1}).[32] In the NMR spectra of type A complexes with a $=CR_2$ (R = H or alkyl) terminal group, magnetic equivalence of the substituents R is therefore frequently observed.[8,57,58] The vertical conformation of phenylvinylidene has been observed in the crystal structure of $Cp[P(OMe)_3](Br)Mo{=}C{=}CHPh$.[36]

Owing to the presence of two unoccupied orbitals available for bonding to the metal, vinylidenes are some of the strongest π acceptors. Analysis of the IR spectra of the complexes $Cp(CO)_2MnL$ established the series based on the diminution of the electron-accepting properties of L:

$$SO_2 > CS > \boxed{C{=}CHPh} > AsF_3 > CO > PF_3 > \eta^2\text{-}PhC{\equiv}CPh > CPh_2 > PPh_3.$$

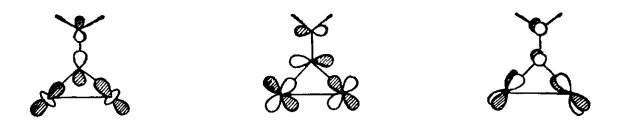
According to this series, the vinylidene ligand C=CHPh is greatly superior to carbenes and π-acetylenes in its electron-accepting capacity.[7]

In the vinylidene complexes, the LUMO is mainly concentrated on the C$_\alpha$ atom, while the HOMO is concentrated on the C$_\beta$ atom.[32] Accordingly, in the vinylidene complexes the attack by the nucleophile is directed to the C$_\alpha$ atom and that by electrophiles is directed to the C$_\beta$ atom. In the allenylidene complexes, there are two electrophilic centres (C$_\alpha$ and C$_\gamma$) and one nucleophilic centre (C$_\beta$). By virtue of the presence of the electrophilic centre, the electrochemical reduction of the complex (I) is much easier ($E_{1/2}$ = –1.99 V)[59] than the reduction of the isoelectronic complexes $Cp(CO)_2MnL$ (L = CO: $E_{1/2}$ = –2.70 V; L = η^2-HC≡CPh: $E_{1/2}$ = –2.38 V).[60]

The presence in the ^{13}C NMR spectra of type (A) complexes of a signal at very low field is consistent with reduced electron density at the C$_\alpha$ atom: δ = 320–390 p.p.m. for vinylidene complexes (Fig. 1), δ = 250–380 p.p.m. for allenylidene complexes, and even δ = 440.6 p.p.m. in the spectrum of $(CO)_5Cr{=}C{=}C{=}C{=}O$.[61] The C$_\beta$ chemical shifts are in the range δ = 100–145 p.p.m. for vinylidene complexes and 140–190 p.p.m. for allenylidene complexes.

The C$_\alpha$=C$_\beta$ bond length in type (A) vinylidene complexes (1.30–1.38 Å) differs little from the C=C bond length in alkenes, whereas in allenylidene complexes it is somewhat shorter (~1.25 Å). The ν(C=C) frequencies in the IR spectra of vinylidene ligands are in the range 1590–1690 cm^{-1}, while the ν(C=C=C) frequencies of the allenylidene ligands are in the range 1900–1940 cm^{-1}.[62]

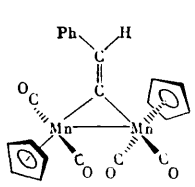
In the type (B) complexes, where the unsaturated carbene bridging ligand is linked symmetrically to two metal atoms, there are two M–C$_\alpha$ σ-bonds, which are formed as a result of the overlap of the a_1 and b_2 MO of the ligand with the MO of the metallic fragments, consisting mainly of the d_{z^2} and d_{xz} AO of the metal atoms.

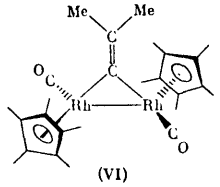


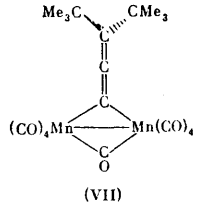
$d_{z^2}(M) \leftarrow a_1(C_\alpha{=}C_\beta)$ $d_{xz}(M) \rightarrow b_2(C_\alpha{=}C_\beta)$ $d_{yz}(M) \leftarrow \pi(C_\alpha{=}C_\beta)$

The optimum overlap is achieved when the b_2 MO of the ligand is arranged parallel to the metal–metal bond axis. This leads to the formation of the planar methylene dimetallacyclopropane system in the μ-vinylidene complexes. The coplanarity of the metallocycle and the =CRR′ fragment has been established in X-ray diffraction studies of a large number of vinylidene complexes of type (B),[10,12,13,23,63–76] for example, in the complexes (V)[6,76] and (VI).[65]

In the μ-allenylidene complexes $[(CO)_5W]_2(\mu\text{-}C=C=CPh_2)$ [77] and (VII),[78] the substituents at the C_γ atom are in a plane perpendicular to that of the metallocycle.


(V)


(VI)

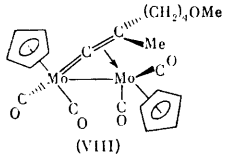

(VII)

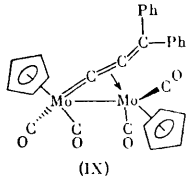
In type (B) complexes there is a possibility of the partial conjugation of the M–C_α and $C_\alpha=C_\beta$ bonds as a result of the overlap of the π and π* MO of the ligand with the MO, having a suitable symmetry, of the metal-containing fragments, the degree of which should depend on the donor–acceptor characteristics of the latter. Indeed, the M–C_α bonds in μ-vinylidene complexes are appreciably stronger[79] than in the related compounds with the μ-CR_2 or μ-CRX ligands, for which such conjugation is impossible.[28,80,81]

In type (B) UCC, there is apparently a higher electron density at the C_α atom than at the C_α atom in mononuclear type (A) compounds. This is indicated by the appreciable upfield shift of the C_α signal in the ^{13}C NMR spectra of type (B) complexes (δ = 240–290 p.p.m.) (see Table 1). The results of a polarographic study indicate a decrease in the electrophilicity of the bridging carbon atom in the complex (V) compared with the C_α atom of the terminal vinylidene ligand in the complex (I): the first stage in the reduction of compound (V) (2*e*, $E_{1/2}$ = –1.81 V) corresponds to the homolytic cleavage of the Mn–Mn bond and one of the Mn–C_α bonds is cleaved only in the second stage (1*e*, $E_{1/2}$ = –2.23 V).[59]

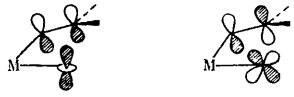
In contrast to the UCC of types (A) and (B), where the ligand supplies two electrons to the metal atoms, in complexes of types (C)–(E), the unshared electron pair of the C_α atom and the π-system of the $C_\alpha=C_\beta$ bond particpate in the bonding to the metal atoms and the unsaturated carbene thus becomes a donor of four electrons.

In the recently synthesised type (C) compounds with the lateral η^1, η^2-coordination of the unsaturated carbene,[17–19] for example in the complexes (VIII) and (IX)


(VIII)


(IX)

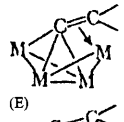
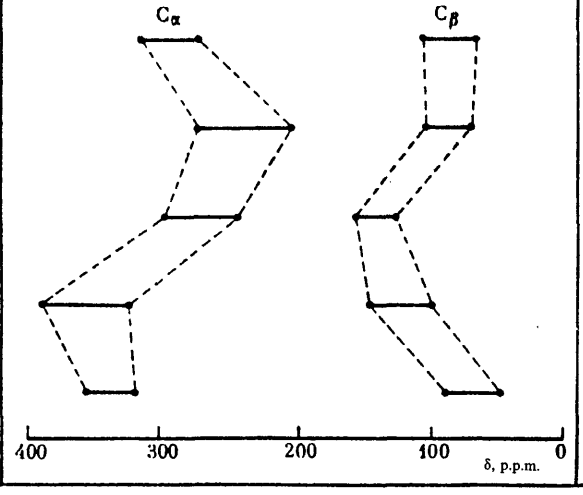
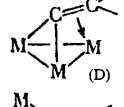
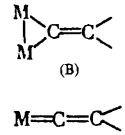
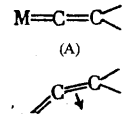
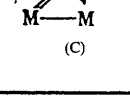
the C_α atom is linked to one of the metal atoms by a double bond similar to the M=C_α bond in mononuclear type (A) UCC. The bond between the unsaturated carbene and the second metal atom is formed as a result of the overlap of the π and π* MO of the $C_\alpha=C_\beta$ bond with the *d* orbitals of the metal.



The ^{13}C NMR spectroscopic data for type (C) complexes agree well with this bonding pattern: the C_α chemical shift is at very low field (δ = 320–340 p.p.m.), while the C_β chemical shift has undergone an upfield shift (δ = 45–85 p.p.m.) as a consequence of electron transfer from the second M atom to the π* MO of the $C_\alpha=C_\beta$ bond, compared with compounds of types (A) and (B) (Fig. 1). Thus the difference between the chemical shifts of the C_α and C_β signals in the type (C) complexes reaches ~300 p.p.m.

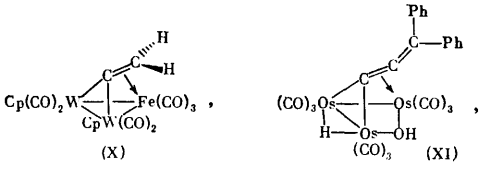
The η^2-coordination of the $C_\alpha=C_\beta$ bond to the metal lengthens it slightly [to 1.380 Å in the complex (VIII)[18] and to 1.336 Å in the complex (IX) [19]] and bends the metallacumulene chain [the

Table 1. Characteristics of the vinylidene ligands.

Type of complex	^{13}C NMR spectrum	C=C bond length, Å
 (E)		1.41–1.45
 (D)		1.37–1.43
 (B)		1.29–1.38
 (A)		1.29–1.34
 (C)		1.38

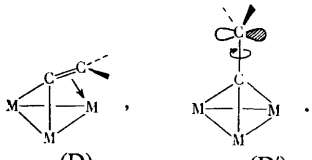
Mo–C_α–C_β valence angle is 168.5° in compound (VIII) and 167.2° in compound (IX), while the C_α–C_β–C_γ angle in compound (IX) is 144.5°].

Type (D) coordination combines elements characteristic of types (B) and (C). In the μ_3-vinylidene and μ_3-allenylidene complexes, examples of which are compounds (X)[82] and (XI),[83] i.e.



(X) (XI)

the unsaturated carbene forms two C_α–M σ-bonds with two metal atoms and a π-bond with the third metal atom:

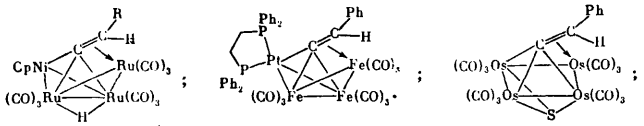


(D) (D′)

According to X-ray diffraction data,[10,24,82–88] the M–C_β distances in all type (D) compounds are appreciably longer than the M–C_α distances, while the $C_\alpha=C_\beta$ bonds are significantly extended (1.37–1.43 Å). The frequencies ν(C=C) in the IR spectra of complexes of this type are also displaced to the region below 1400 cm^{-1}.[89] According to MO calculations for $[(CO)_9Co_3(\mu_3\text{-}C=CH_2)]^+$,[90,91] the lateral μ_3,η^2-coordination of the vinylidene ligand (D) is more favourable than the centrosymmetrical μ_3-coordination (D′), but the difference between their energies is small. The stereochemical non-rigidity of the μ_3-vinylidene complexes, observed in the NMR spectra, is probably caused by the presence in these compounds of a weak M–C_β bond and the possibility of the transition of the molecules in solutions to the (D′) configuration.

By virtue of the transfer of electron density from the three M atoms to the C_α atom, the latter can apparently acquire nucleophilic properties. This is especially characteristic of μ_3-ketenylidene complexes,[92,96] for example, $[(CO)_9Fe_3(\mu_3\text{-}C=C=O)]^{2-}$.[96] The reduction of the electrophilicity of the C_α atom in type (D) vinylidene complexes is apparently indicated by the appreciable upfield shift of the C_α signal in their ^{13}C NMR spectra (δ = 200–280 p.p.m.) compared with types (A)–(C) (see Table 1).

In the μ_4-vinylidene complexes of type (E),[21,22,97–104] for example, in the complexes (XII),[22] (XIII),[104] and (XIV),[101] the unsaturated carbene is linked by C_α–M σ-bonds to three metal atoms and the $C_\alpha=C_\beta$ fragment is π-coordinated to the fourth metal atom:



(XIIa): R = Bu^t
(XIIb): R = Pr^i (XIII) (XIV)

X-Ray diffraction analysis has shown that the M–C_α bonds in type (E) complexes are stronger than the M– C_β bonds and that the C_α–C_β distance (1.41–1.45 Å) approaches the length of a C_{sp^2}–C_{sp^2} single bond (1.46 Å). The downfield shift of the C_α signal in the ^{13}C NMR spectra (δ = 270–310 p.p.m.) suggests an electrophilic character of this atom in type (E) compounds, whose chemical properties have not yet been investigated.

It is noteworthy that the positions of the C_α and C_β signals in the ^{13}C NMR spectra of the complexes examined are greatly influenced not only by the mode of coordination of the unsaturated carbene[105] but also by the nature of the metal atoms and their surrounding ligands, which is reflected in the wide ranges of the chemical shifts illustrated in Table 1. At the same time, the difference Δδ between the C_α and C_β chemical shifts for the majority of types of UCC is more individual than the positions of the C_α and C_β signals themselves. This makes it possible to establish reliably the type of coordination of the unsaturated carbene ligand on the basis of the ^{13}C NMR spectra for many UCC with a known number of metal atoms.

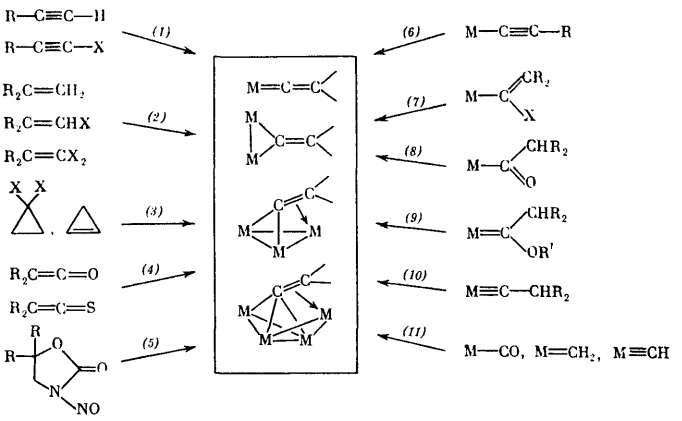
III. The synthesis of unsaturated carbene complexes

The sources and methods of formation of unsaturated carbenes in the coordination spheres of transition metal atoms are much more varied than in organic chemistry.[1] Unsaturated carbene ligands are formed both from organic molecules (alkynes, alkenes, cyclopropanes, cyclopropenes, ketens, *N*-nitrosooxazolidinones) and from the organic ligands forming part of the composition of the complexes (acetylide, vinyl, acyl, carbene, carbyne) (Scheme 1). The formation of vinylidene ligands at metallic centres also from single-carbon fragments (CO, CH_2, CH) is known.

Since it is impossible to give an exhaustive survey of all the methods of synthesis of UCC within the framework of a general publication, in this Section we shall consider only the most general or especially interesting methods of preparation of these compounds.

Scheme 1

Sources of unsaturated carbene ligands



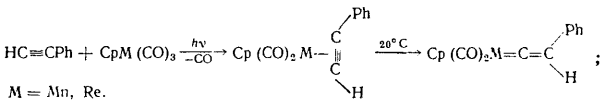
(*1*): M=Cr [50, 106], Mo [36, 107], W [37, 108, 109], Mn [5–7, 45, 78, 110], Re [35, 39, 78, 111], Fe [53, 58, 112], Ru [43, 48, 58, 64, 84, 109, 113–116], Os [46, 101–103], Co [84, 109, 113, 117], Rh [15, 38, 118–120], Ir [151, Pt [121].
(*2*): M=Ta [16], Fe [67, 68, 122], Ru [123], Os [123–125], Co [66, 126], Pd [14].
(*3*): M=Mo [87], Fe [127], Os [128].
(*4*): M=Fe [4, 40, 129].
(*5*): M=Co, Rh [65, 69].
(*6*): M=W [130, 131], Fe [58, 132], Ru [9, 21, 22, 24, 41, 42, 44, 47, 83, 100, 116, 133], Os [85, 134–136], Pt [13].
(*7*): M=Mo, W [137], Fe, Co [138], Os [139–142], Rh [142].
(*8*): M=Fe [143].
(*9*): M=Cr, W [49], W, Pt [12].
(*10*): M=Mo [144, 145], W [12, 72, 82], Fe [82, 86, 146–152], Ru [64, 153, 154], Os [72, 155], Ir [156], Pt [12].
(*11*): M=Mn [143], Fe [147–149, 157–164], Ru [153, 164–167], Co [74].

Note. Here the numerals in square brackets denote references (Ed. of Translation).

1. Generation of unsaturated carbene ligands from organic molecules

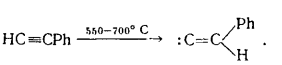
(a) The acetylene–vinylidene rearrangement

The most general method of synthesis of complexes with monosubstituted vinylidenes involves the acetylene–vinylidene rearrangement (AVR) at metallic centres. AVR was first observed for Mn and Re complexes:[5–7,35]



M = Mn, Re.

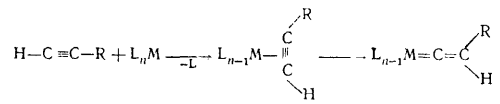
The isomerisation of free acetylenes to vinylidenes is known[1] to occur under severe conditions:



According to calculations,[33] the energy of acetylene is lower by 44 kcal mol^{-1} than that of vinylidene and the activation energy for the AVR is 76 kcal mol^{-1}. On coordination to the metal, the thermodynamic stabilities of acetylene and vinylidene are reversed: $Cp(CO)_2Mn=C=CH_2$ has an energy lower by 32 kcal mol^{-1} than the π-acetylene isomer. This is responsible for the easier occurrence of the AVR at a metallic centre at 5–65 °C.

The principle features of the AVR, its mechanism, and its driving force can be elucidated only now as a result of the accumulation of information about the conditions governing the occurrence of the reaction for a large number of metals (see Scheme 1 and the bibliography quoted in it as well as the review of Bruce and Swincer[10]) with different ligand environments.

In all cases, the synthesis of unsaturated carbenes from acetylenes proceeds via the intermediate formation of π-acetylene complexes:



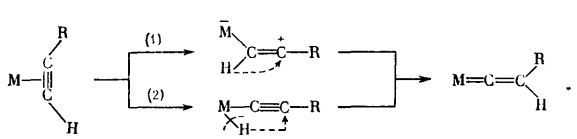
R = H, Alk, Ar, C(OH)R$_2$, COOR etc.

However, they frequently cannot be detected because of the high rate of the AVR, for example, in the formation of $Cl(dppe)_2Re=C=CHPh$ from HC≡CPh and $Cl(dppe)_2Re(N_2)$.[39]

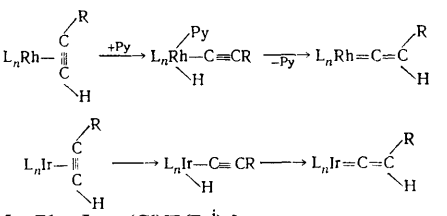
Two alternative mechanisms of the conversion of a π-alkyne complex into a vinylidene complex are most probable:

(1) a two-stage process involving the conversion of the alkyne into a metal-stabilised vinyl cation and the subsequent 1,2-shift of an H atom;[33]

(2) oxidative addition of the alkyne to the metal with formation of a hydride–acetylide intermediate with subsequent dissociation of the M–H bond and protonation (intra- or inter-molecular) of the C_β atom:[7,33]



According to calculations,[33] the mechanism (1) is energetically more favourable but it does not take into account the active role of the metallic centre in the reaction. Although the oxidative addition of alkynes to a metal[168] and the protonation reactions of σ-alkynyl complexes with formation of vinylidene complexes (see below) have been thoroughly investigated, experimental confirmation of the mechanism (2) has been obtained only recently. It has been shown[15] that the reactions involving the conversion of the π-acetylene complexes of rhodium and iridium into the vinylidene complexes proceed via intermediate hydride-acetylide compounds:



R = H, Me, Ph; $L_n = (Cl)[P(Pr^i)_3]_2$.

The ease of the AVR increases with increasing basicity of the metallic centre. The spontaneous isomerisation of π-acetylene complexes to vinylidene is observed more often for sixth-Period transition metals (W, Re, Os, Ir) than for their lighter analogues. The rearrangement is promoted by the presence of donor ligands in the coordination sphere of the metal atom. When the basicity of the metallic centre is insufficient, the presence of bases is required for the occurrence of the AVR.

Thus the isomerisation of the π-complexes of iridium quoted above takes place spontaneously, but the rearrangement of the analogous rhodium complexes requires the presence of pyridine, which participates in the formation of the hydride-acetylide intermediate.[15] The vinylidene complexes $[(C_5Me_5)(PPh_3)(CO)Os=C=CHR]^+$ are obtained in quantitative yields in the reactions of the alkynes HC≡CR (R = Bu^t, Ph) with $(C_5Me_5)(PPh_3)(CO)OsI$ in the presence of $AgBF_4$ (CH_2Cl_2, 22 °C), but a vinylidene complex is not formed under these conditions from $(C_5Me_5)(CO)_2OsI$.[46] The complex $Cp(CO)_2Re(\eta^2\text{-}HC\equiv CPh)$ is converted into $Cp(CO)_2Re=C=CHPh$ in a neutral medium,[35] while the isomerisation of $Cp(CO)_2Mn(\eta^2\text{-}HC\equiv CPh)$ to $Cp(CO)_2Mn=C=CHPh$ takes place either on a column with Al_2O_3 at pH 9–10 [7] or in the presence of catalytic amounts of hexamethylenetetramine.[110] On passing to alkynes HC≡CR with substituents R having more pronounced electron-accepting properties than Ph, the rearrangement of the π-complexes of Mn requires stronger bases: PhLi (for $HC\equiv C\text{–}C_6H_4\text{–}C\equiv CH$-4) and Bu^{t}Li or KOH (for HC≡CCOOMe).[10,45] The role of the bases in these reactions apparently consists in increasing the basicity of the metallic centre, which can be achieved by their interaction either directly with the metal atom or with the CO ligands.

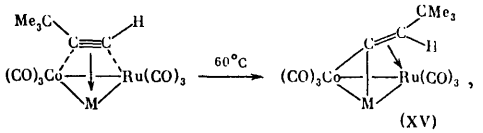
The rearrangement to vinylidene complexes is unknown for π-acetylene complexes of transition metals at the beginning of the Period, in which the metal atom has an unfilled 16-electron shell, for example, $Cp(CO)Nb(\eta^2\text{-}PhC\equiv CEPh_3)_2$ (E = Si, Ge, Sn)[169] or $Br_2(PPh_3)_2M(\eta^2\text{-}HC\equiv CR)$ (M = Mo, W; R = Bu, Ph).[170] On the other hand, the 18-electron complex $(dppe)(CO)_3W(\eta^2\text{-}HC\equiv CPh)$ isomerises spontaneously to the vinylidene complex at 20 °C.[108] The spontaneous conversion of the 18-electron Mn,[7] Re,[111] and Ru[114,115] complexes with the η^2-ligands $PhC\equiv CEPh_3$ (E = Si, Ge, Sn) or $RC\equiv CSiMe_3$ (R = H, Ph) into compounds with the vinylidene groups C=CHR is preceded by the elimination of the EPh_3 or $SiMe_3$ substituents; the solvent serves as the source of the H atom in such cases.

On the basis of the foregoing, one can postulate that the endeavour of the electron-rich metal atom to reduce its electron density is in fact responsible for the rearrangement of the η^2-alkyne to the vinylidene with more marked electron-accepting properties.

Apart from the energy gain, the AVR is also favourable for steric reasons, since the vinylidene incorporated in the metallallene system creates a much smaller steric hindrance in the ligand environment of the metal than the η^2-coordinated alkyne.

The AVR has been less thoroughly investigated for polynuclear systems than for mononuclear systems. The conversion of the halogenoalkynes RC≡CX (R = Bu, Ph, Br, I; X = Cl, Br, I) in reactions with dinuclear cobalt complexes into the vinylidene ligands μ_2-C=CXR as a result of a 1,2-shift of the halogen atom has been reported.[117]

The ready isomerisation of the μ_3-alkyne clusters $RuCO_2$,[84,88,113] MoRuCo,[171] and WRuCo [109] into the μ_3-vinylidene clusters has been observed:

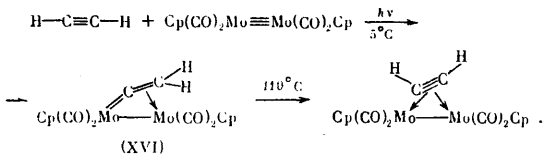


(XV)

where M = $Co(CO)_3$, $Mo(CO)_2Cp$ (XV), or $W(CO)_2Cp$.

The phenylvinylidene clusters (XIV),[101] $Os_6(CO)_{20}(\mu_3$-C=CHPh), and $Os_5(CO)_{15}(\mu_4$-C=CHPh) have been obtained by the interaction of PhC≡CH with $Os_4(CO)_{12}(\mu_3$-S) and $Os_6(CO)_{20}$(MeCN).[102]

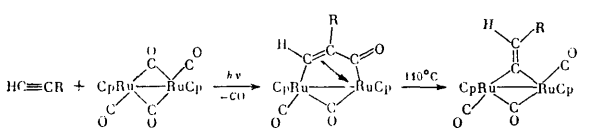
The first type (C) complex with the lateral coordination of vinylidene has been obtained by the photochemical reaction of acetylene with an unsaturated Mo_2 complex:[17]



(XVI)

The reverse isomerisation of the vinylidene to the alkyne is possible for the complexes (XV) and (XVI) with the η^2-coordination of the C=C fragment to the metal: on treatment with the $Cp(CO)_3Mo^-$ anion in boiling tetrahydrofuran (THF)[171] for compound (XV) and on boiling in toluene for compound (XVI).[17]

The reaction



R = H, Ph

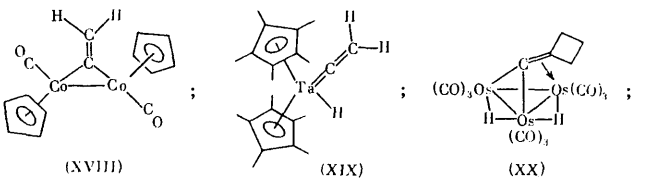
(XVIIa): R=H,
(XVIIb): R=Ph,

as a result of which the alkyne is initially inserted into the Ru–CO bond and the intermediate then isomerises with formation of the complex (XVII),[64,172,173] is a special case of the conversion of an alkyne into a vinylidene.

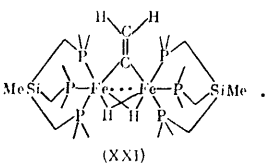
(b) The synthesis of vinylidene complexes from alkenes

Not only 1,1-dihalogenoalkenes and vinyl halides—the traditional precursors of vinylidene species,[1] but also ethylene and its homologues can serve as sources of the vinylidene ligands.

The complexes $Cp_2(CO)_3Fe_2[\mu$-C=C$(CN)_2]$[10,122] and $Cp_2(CO)_2$.$Co_2[\mu$-C=$CH_2]$ (XVIII),[66,126] have been obtained by the reaction of 1,1-dihalogenoalkenes with carbonylmetallate anions. An example of the dehalogenation of 1,1-dihalogenoalkenes by neutral complexes involving the transfer of Cl atoms to the metal is provided by the formation of $Cl_2(\mu$-dppm$)_2Pd_2(\mu$-C=$CH_2)$ from $H_2C=CCl_2$ and $Pd(PPh_3)_4$ in the presence of dppm:[14]



(XVIII) (XIX) (XX)

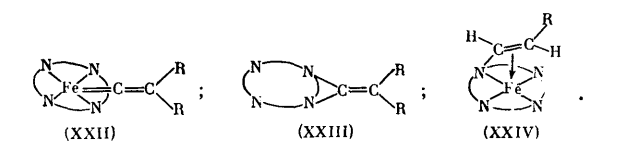


(XXI)

The migration of the vinyl hydrogen atom to the metal during the reaction of $H_2C=CHMgBr$ with $(C_5Me_5)_2TaCl_2$ leads to the complex (XIX).[16]

Processes involving the transfer of two alkene hydrogen atoms to the metallic centre are characteristic of polynuclear systems. A series of complexes $H_2(CO)_9M_3(\mu_3$-C=CRR′) (M = Ru, Os) of type (D) have been obtained by reactions of $H_2C=CRR'$ with $M_3(CO)_{12}$.[10,123] The cluster (XX) has been synthesised recently from methylenecyclobutane and $Os_3(CO)_{12}$ by a similar procedure.[124,125] The unusual complex (XXI) has been obtained by treating (tmps)Fe(μ^4-C_6H_6) [tmps = $MeSi(CH_2PMe_2)_3$; 7 atm, 50 °C] or $[(tmps)_2Fe_2Cl_2]^+$ (1.5 atm, Na/Hg, 20 °C) with $H_2C=CH_2$.[67,68] The formation of the μ-vinylidene and μ-hydride ligands from $H_2C=CH_2$ can be regarded as a model of the first stage in the chemisorption of ethylene on the surfaces of metals.

The report by Mansuy[174,175] that the products of the reactions of $Cl_3CCH(C_6H_4Cl$-4$)_2$ (the insecticide DDT) with Fe-porphyrins (*in vitro*) and with cytochrome P-450 (*in vivo*) are vinylidene complexes of the type (TPP)Fe=C=CR_2 (XXII) aroused much interest:[10]



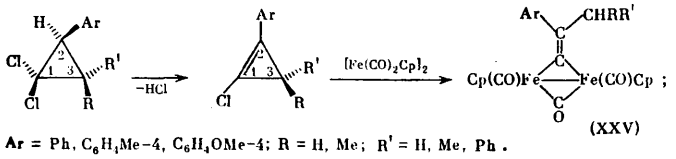
(XXII) (XXIII) (XXIV)

Similar products have been obtained by the reaction of $M_3(CO)_{12}$ (M = Fe, Ru) with *NN′*-vinylideneporphin (XXIII).[176] Later Castro and Wade[177] concluded from the results of an NMR spectroscopic study of the reactions of DDT with Fe-porphyrins that the compounds formed are not the vinylidene complexes (XXII) but the π-alkene complexes (XXIV). However, a recent X-ray diffraction study[178] of the tetraphenylporphyrin derivative of DDT, i.e. the complex (TPP)Fe=C=$C(C_6H_4Cl$-4$)_2$, confirmed that Mansuy's original hypothesis[174,175] was correct.

(c) The synthesis of vinylidene complexes from cyclopropanes and cyclopropenes

The vinylidene complexes (XXV) are readily formed in heterophase reactions of 2-aryl-1,1-dichlorocyclopropanes with $[Cp(CO)_2$.$Fe]_2$ (NaOH, $NBu_4^+HSO_4^-$, THF/H_2O, 20 °C).[127] The cycloalkanes are dehydrochlorinated in the first stage in these reactions, with

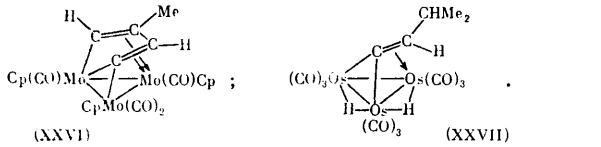
formation of chlorocyclopropenes, which then react with the bimetallic centre, this being accompanied by the selective cleavage of the C(1)–C(3) bond:



(XXV)

Ar = Ph, C_6H_4Me-4, C_6H_4OMe-4; R = H, Me; R' = H, Me, Ph.

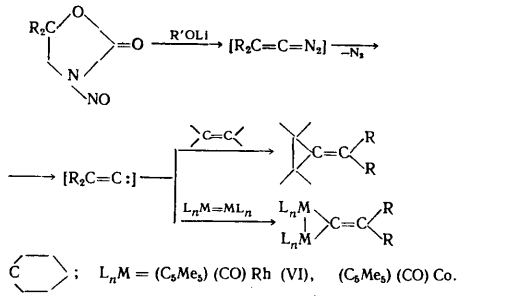
3,3-Dimethylcyclopropene adds at 20 °C with ring opening to the complexes $Cp_2Mo_2(CO)_4$ and $H_2Os_3(CO)_{10}$ containing multiple metal–metal bonds; thermolysis of the adducts leads to the μ_3-vinylidene clusters (XXVI)[87] and (XXVII)[128] respectively:



(XXVI) (XXVII)

(d) The synthesis of vinylidene complexes from *NN'*-nitrosooxazolidinones

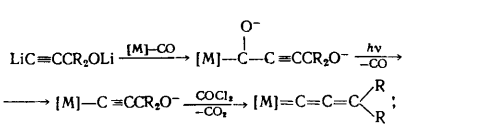
The successful use of the isolobal analogy between the C=C and M=M double bonds enabled Herrmann et al.[65,69] to develop a novel method of synthesis of vinylidene complexes with the aid of diazo-compounds formed when cyclic *N*-nitrosourethanes are treated with Bu^{t}OLi:



CR_2 = CMe_2, ; L_nM = (C_5Me_5) (CO) Rh (VI), (C_6Me_6) (CO) Co.

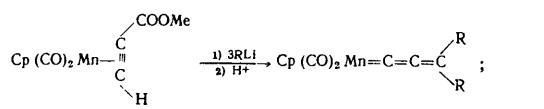
(e) The synthesis of cumulenylidene complexes

t-Propargyl alcohols and their dilithio-derivatives are widely used for the synthesis of the allenylidene complexes of Cr, W, Mn, Re, Fe, and Ru:[10,48,50,53,77,106]



R = Alk, Ar.

The salts and esters of propiolic acid are also used for this purpose:[8,10,57]



R = Bu^t (II), C_6H_{11}, CH_2Ph, Ph.

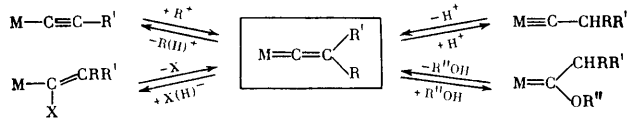
Together with simple dialkyl- or diaryl-allenylidene complexes, more complex products, for example compound (IV), are formed in these reactions.[50]

The oxapropatrienylidene complex $(CO)_5Cr=C=C=C=O$ has been obtained from $[ICr(CO)_5]^-$ and $AgC\equiv CCOONa$ in the presence of $AgBF_4$ and $CSCl_2$.[61]

2. The synthesis of unsaturated carbene complexes from complexes with σ-organic ligands

The general approach to the synthesis of vinylidene complexes from complexes with σ-alkynyl, vinyl, carbyne, and carbene ligands (Scheme 2) is based on the conversion of these ligands into vinylidenes on treatment with acid and bases. Scheme 2 also illustrates the possibility of the interconversion of complexes of these types proceeding via vinylidene complexes and determining the chemical behaviour of the latter (see Section IV):

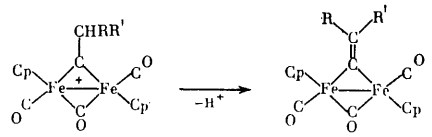
Scheme 2



R = H, Alk; X = H, Hal; R'' = Me, Et.

The addition of cations to the nucleophilic C_β atom in complexes with the M–C≡CR group is a general method of synthesis of mononuclear vinylidene complexes of W, Fe, Ru, and Os. The acetylide complexes can be protonated by acids[9,10,116] and alkylated with the aid of R_3O^+ (R = Me, Et),[9,131] $MeSO_3F$,[130,132] or RX (R = Me, Et, Ph, CH_2; X = halogen).[44,58,131] Tropylium[41] and arenediazonium[41,133] cations and halogen atoms[42,47] add to the C_β atom. On treatment of $H(CO)_9Os_3(\mu_3\text{-}C\equiv CCPh_2OH)$ with CF_3COOH, the OH group migrates from the C_γ atom to the Os_3 ring, which results in the formation of the μ_3-allenylidene cluster (XI).[83]

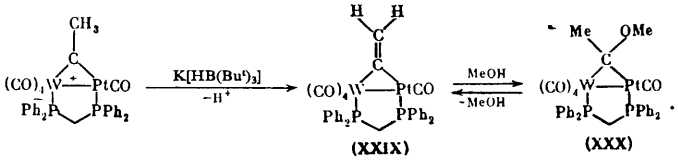
A second general method of synthesis of vinylidene complexes consists in the deprotonation of carbyne complexes, which proceeds under mild conditions on treatment with a wide variety of reagents. A proton is eliminated from $Cp[P(OMe)_3]_2Mo\equiv C\text{–}CH_2Bu^t$ in the reactions with BuLi, CF_3I, and PhN_2^+.[144,145] The methylcarbyne complex $[Cp_2(CO)_2(\mu\text{-}CMe_2)Ru_2(\mu\text{-}CCMe)]^+$ is converted into $Cp_2(CO)_2(\mu\text{-}CMe_2)Ru_2(\mu\text{-}C=CH_2)$ in the presence of water.[153] A series of vinylidene complexes (XXVIII) have been obtained by treating μ-carbyneiron cationic complexes with MeLi, NH_4OH, or $NaHCO_3/H_2O$:[146–149]



(XXVIII)

R and R' = H, Alk, $-(CH_2)_n-$; n = 4, 5.

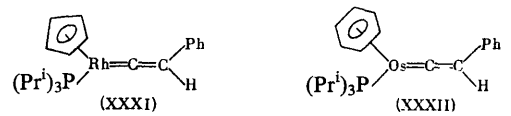
The heterometallic vinylidene complex (XXIX) has been obtained by a similar procedure:[12]



(XXIX) (XXX)

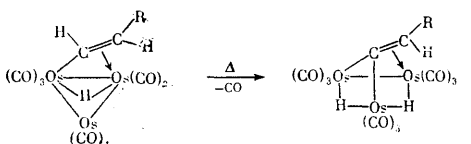
It has also been synthesised from the μ-carbene complex (XXX) as a result of the elimination of MeOH on Al_2O_3 at pH 9–10; the last reaction is reversible.[12]

The allenylidene compounds $(CO)_5M=C=C=C(Ph)(NEt_2)$ are formed as a result of the elimination of EtOH on treatment of the carbene complexes $(CO)_5M=C(OEt)CH=C(Ph)(NEt_2)$ (M = Cr, W) with BF_3 or $AlEt_3$.[49] The vinylidenerhodium complex (XXXI) and the vinylideneosmium complex (XXXII) have been obtained by eliminating HCl in reactions of $L_n(Cl)M-CH=CHR$ with NEt_3 and Bu^tLi respectively:[142]



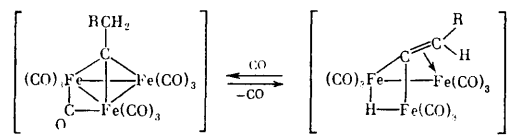
(XXXI) (XXXII)

In the synthesis of type (D) vinylidene complexes from carbonyl clusters with μ-vinyl ligands [compounds (XXXIII)][10,139–141] or μ-carbyne ligands [compounds (XXXV)],[150–152] a hydrogen atom migrates from the ligand to the metallocycle, which precedes the elimination of a CO group from the metal:



(XXXIII) (XXXIV)

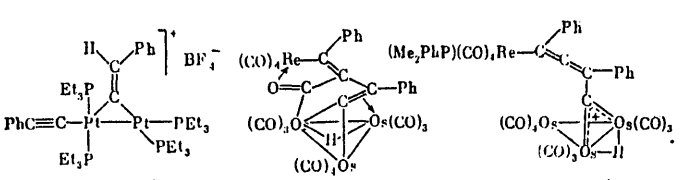
R = H, Alk, Ph, C_5H_4FeCp;



(XXXV) (XXXVI)

R = H, Pr, Ph, C(O)Me, COOMe.

A series of polynuclear vinylidene complexes have been synthesised by adding metal-containing fragments or molecules to σ-alkynyl complexes. Thus the complex (XXXVII) has been synthesised by the interaction of $(PEt_3)_2Pt(C\equiv CPh)_2$ with $[HPt(PEt_3)_2.(Me_2CO)]BF_4$.[13] The combination of alkynyl ligands in $(CO)_5.Re-C\equiv CPh$ and $H(CO)_{10}Os_3(\mu-C\equiv CPh)$ led to the unusual μ_3-vinylidene complex (XXXVIII), which rearranges to the complex (XXXIX) with an allenyl-substituted μ_2-carbyne ligand on treatment with PMe_3Ph:[85,135,136]



(XXXVII) (XXXVIII) (XXXIX)

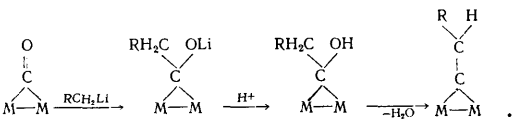
Heating of the complex $H(CO)_9Ru_3(\mu_3-C\equiv CR)$ (R = Pr^i, Bu^t) with $[CpNiCO]_2$ in the presence of H_2 leads to the complexes (XII).[21,22] The pentanuclear vinylidene cluster $(Ph_3P)_2Au_2Ru_3(\mu_3-C=CHBu^t).(CO)_9$ is formed in the reaction of $[(CO)_9Ru_3(\mu_3-C\equiv CBu^t)]^-$ with $[(Ph_3PAu)_3O]BF_4$.[24]

The heteronuclear vinylidene complex (X) has been obtained by the reaction of the two carbyne complexes $Cp(CO)_2W\equiv CMe$ and $CpWFe_2(\mu_3-CC_6H_4Me\text{-}4)(CO)_9$ at 80 °C.[82]

3. The formation of vinylidene ligands from CO, CH_2, and CH

In view of the growing interest in the synthesis of organic products from CO and H_2,[179] the possibility of the formation of unsaturated carbenes as a result of the reduction of CO at metallic centres merits special attention.

The conversion of CO groups into $C=CH_2$ was first noted in the reaction of $Ru_3(CO)_{12}$ with $NaBH_4$.[10,166] Stone and co-workers[157] developed a preparative method of synthesis of $Cp_2(CO)_3Fe_2.(\mu-C=CH_2)$ (XXVIII) (yield 80%) by the successive treatment of $Cp_2(CO)_2Fe_2(\mu-CO)_2$ with MeLi and CF_3COOH at –60–0 °C. The synthesis of compound (XVII) and of its FeRu analogue has been achieved similarly.[153,164,165] It has been shown for $(CO)_8(\mu_4-PPh)_2.Co(\mu-CO)_2$ that complexes with monosubstituted vinylidene can be obtained by this method: using BuLi as the alkylating agent, $(CO)_8(\mu_4-PPh)_2(\mu-CO)Co_4(\mu_2-C=CHPr)$ has been synthesised.[74] It is suggested that the process proceeds via the formation of a μ-methyl-(hydroxy)carbene intermediate, whose dehydration leads to the vinylidene complex:

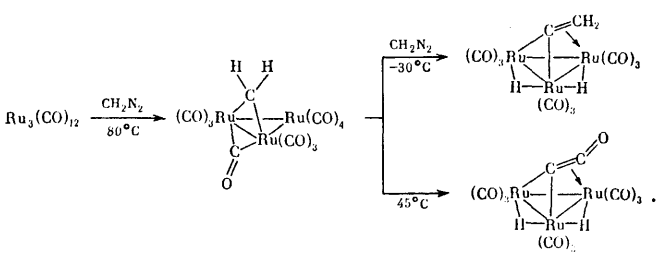


The conversion of the terminal CO group into $C=CH_2$ takes place in the reaction[143]

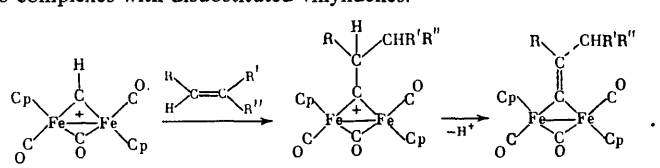
$$CpMn(CO)_3 \xrightarrow[2)(CF_3SO_2)_2O]{1)\,MeLi} [Cp(CO)_2Mn{=}C{=}CH_2] \longrightarrow [Cp(CO)_2Mn]_2(\mu\text{-}C{=}CH_2).$$

The formation of the complex $Cp_2(CO)_2Fe_2(\mu-C=CH_2)_2$ on treatment of $Cp_2(CO)_2Fe_2(\mu-CO)_2$ with the Wittig reagent $Ph_3P=CH_2$ has been reported.[158]

Ruthenium and osmium clusters with the μ-methylene ligand, which readily combines with CO or with a second CH_2 fragment with transfer of two H atoms to the metallocycle and the formation of new C–C bonds, may be key compounds in the synthesis of UCC:[167]



The μ-methylidyne complex $[Cp_2(CO)_3Fe_2(\mu-CH)]^+$ readily combines with alkenes, including cycloalkenes, via the C–H bond, being converted into compounds with more complex μ-carbyne ligands, whose deprotonation on treatment with $NaHCO_3/H_2O$ leads to complexes with disubstituted vinylidenes:[147–149,159–163]



Processes involving the growth of the carbon chain with formation of C=C double bonds, similar to the reactions illustrated above, can probably occur in the surface reduction of metal-containing catalysts with CO.

IV. The reactivity of the complexes

The complexes of unsaturated carbenes are usually crystalline brightly coloured substances, many of which are stable in air at 20 °C. Their thermal stability increases with increase in the number of metal atoms in the molecule on passing from type (A) to type (E). Neutral UCC are soluble in aliphatic hydrocarbons, while the ionic complexes are soluble in polar organic solvents. In solutions, the UCC as a rule gradually decompose.

The UCC exhibit a high and varied reactivity due to the presence of several reaction centres in their molecules. Reactions involving the cleavage of the M–C_α, C=C, and C–H bonds are known for the type (A), (B), and (D) complexes. Cyclo-addition reactions via the electron-rich M=C and C=C bonds and reactions involving insertion in a C–H bond are characteristic of the type (A) complexes. By virtue of the clear-cut charge distribution in the metallacumulene chains $M=\overset{+}{C}_\alpha=\overline{C}$ and $M=\overset{+}{C}_\alpha=\overline{C}_\beta=\overset{+}{C}_\gamma$ (see Section II), the reactions of type (A) UCC with electrophiles and nucleophiles are distinguished by a high regioselectivity.

1. The cleavage of the M–C_α and $C_\alpha=C_\beta$ bonds

The study of the mass spectra of the carbonyl complexes $[(CO)_4Fe]_2(\mu\text{-}C=CPh_2)$,[4] $[Cp(CO)_2M]_n(C=CHPh)$ (M = Mn, Re; n = 1, 2),[180] and $Cp(CO)_2Mn=C=C=CR_2$ (R = Bu^t, C_6H_{11})[8,57] indicates a greater strength of the M–C_α bonds compared with M=CO. The $[C=CPh_2]^+$ fragments recombine with formation of the butatriene $[C_4Ph_4]^+$ and the radialene $[C_6Ph_6]^+$,[4] while the $[C=C=CR_2]^+$ fragments recombine into the hexapentaene $[C_6R_4]^+$.[8,57]

The high strength of the M–C_α bonds in the UCC prevents the use of the latter as the sources of unsaturated carbenes. The formation of the hexapentaenes $R_2C=C=C=C=C=CR_2$ (R = Bu^t, C_6H_{11}, CH_2Ph) on thermolysis of the complexes $Cp(CO)_2Mn=C=C=CR_2$ is known.[8,57] The complex $(CO)_5Cr=C=C=C=O$ eliminates the C_2 species in hexane at 0 °C and is converted into $Cr(CO)_6$, whose treatment with Me_2SO/MeOH leads to dimethyl malonate.[61]

Ethylene is evolved on hydrolysis and methanolysis of $(C_5Me_5)_2$.$(H)Ta=C=CH_2$ (XIX).[16] Treatment of $Cp_2(CO)_3Fe_2(\mu\text{-}C=CH_2)$ (XXVIII) with H_2 lead to the evolution of ethane.[146] Cp_2Fe, $Cp_2Fe_2(CO)_4$, and $Cp_3(\mu\text{-}CO)_3Fe_3(\mu_3\text{-}CMe)$ are formed when compound (XXVIII) is refluxed in Bu_2O.[99]

The cleavage of the C=C bond on photolysis of compound (XVII) leads to $Cp_2(CO)_3Ru_2(\mu\text{-}CH_2)$.[165,173] Treatment of $[(\eta^5\text{-}C_9H_7)(PPh_3)_2Ru=C=CHPh]^+$ with O_2 affords $[(\eta^5\text{-}C_9H_7)$.$(PPh_3)_2Ru\text{–}CO]^+$,[43] while after the oxidation of $[Cp(PPh_3)(L)Ru=C=CHPh]^+$ (L = PPh_3, CO) (CH_2Cl_2, 25 °C), PhCHO and PhCOOH were isolated in addition to the carbonyl complexes.[181]

The possibility of the involvement of type (E) vinylidene complexes in metathetical reactions of alkenes has been demonstrated: when the complex (XII) was heated with $D_2C=CD_2$ (toluene, 70 °C), the formation of $D_2C=CHBu^t$ was detected.[182]

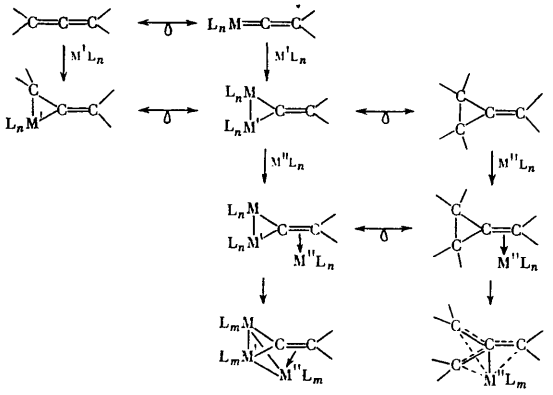
The cleavage of the ketenylidene ligand into C and CO takes place in the reaction of $H_2(CO)_9Os_3(\mu_3\text{-}C=C=O)$ with $(C_2H_4)_2PtL$ [L = $P(C_6H_{11})_3$] in toluene at 20 °C, which leads to the carbonyl-carbide clusters $H_2(CO)_9Os_3Pt(\mu_4\text{-}C)(CO)L$ and $H_2(CO)_9Os_3Pt_2$.$(\mu_5\text{-}C)(\mu\text{-}CO)L_2$.[183]

2. Addition to the M=C_α, C=C, and C–H bonds

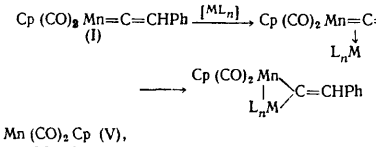
(a) Metallation of the M=C=C system

The metallallene system-containing type (A) complexes $L_nM=C=CR_2$, the character of the bond in which was examined in Section II, are isolobal with the organic allenes $R_2C=C=CR_2$, because the L_nM and R_2C fragments are in isolobal correspondence with one another.[25] The ability of allenes to coordinate transition metal atoms with formation of π-complexes is widely known. The fact that the type (A) complexes are isolobal with allenes is manifested by their ability to combine with coordinatively unsaturated and electron-unsaturated species $[L_nM]$ at the M=C_α bond. The type (A) complexes are then converted into type (B) compounds with bridging unsaturated carbenes (Scheme 3):

Scheme 3



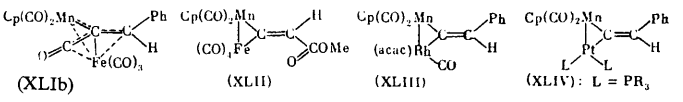
The possibility of the metallation of the M=C=C system was first demonstrated in relation to reactions of a vinylidene derivative of cymantrene (I):[7,20,184]



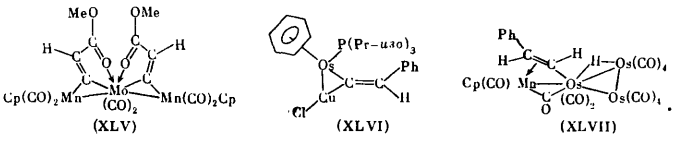
ML_n = Mn(CO)$_2$Cp (V), Re(CO)$_2$Cp (XL), Fe(CO)$_4$ (XLIa).

By virtue of the tendency of certain neutral type (A) vinylidene and allenylidene complexes to be converted into a more stable type (B) compound, such reactions sometimes proceed spontaneously.[7,53,57,77,118,143]

A series of dinuclear vinylidene complexes with Mn–Mo,[71,185] Mn–W,[71,185] Mn–Mn,[7,186] Mn–Re (XL),[20] Mn–Fe (XLII),[63,187] Mn–Rh (XLIII),[75] and Mn–Pt (XLIV),[11,79,188] bonds as well as the trinuclear bisvinylidene complex (XLV)[71] have been obtained from $Cp(CO)_2Mn=C=CHR$ [R = Ph (I) or COOMe]. The unusual dinuclear complex (XLIb) with an organometallic ligand of the trimethylene-methane type is formed as a result of the isomerisation of compound (XLIa) via the intramolecular carbonylation of the C_α atom:[184]



(XLIb) (XLII) (XLIII) (XLIV): L = PR_3

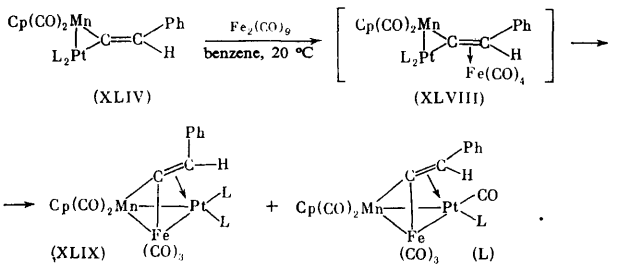


(XLV) (XLVI) (XLVII)

μ-Vinylidene compounds with Rh–Cr, Rh–Mn, Rh–Fe, and Rh–Cu bonds[70,189] have been obtained by the metallation of the Rh=C=C system in compound (XXXI), while the addition of CuCl to compound (XXXII) led to the synthesis of the complex (XLVI) with an Os–Cu bond.[142] The possibility of the addition of unsaturated cluster molecules to type (A) vinylidene complexes has been demonstrated in the formation of compound (XLVII) from the complex (I) and $H_2Os_3(CO)_{10}$.[190,191]

The allenylidene complexes $L_nM=C=C=CR_2$ combine with the $[M'L_n]$ fragment at the $M=C_\alpha$ bond with formation of type (B) μ-allenylidene compounds; compounds with W–W,[77] Mn–Mn,[62,63] Fe–Fe,[53] and Mn–Fe[63] bonds have been obtained in this way.

The type (B) complexes, incorporating the planar $\overline{MM'}(\mu\text{-}C=CR_2)$ system (see Section II), are isolobal with methylenecyclopropanes and, like the latter, can combine with yet another metal-containing fragment (see Section 3). The reaction of compound (XLIV) [L = PPh_3 or $P(OR)_3$] with $Fe_2(CO)_9$ results in the formation of the type (D) complexes (XLIX) and (L), whose molecules contain Mn, Pt, and Fe atoms:[104,192,193]



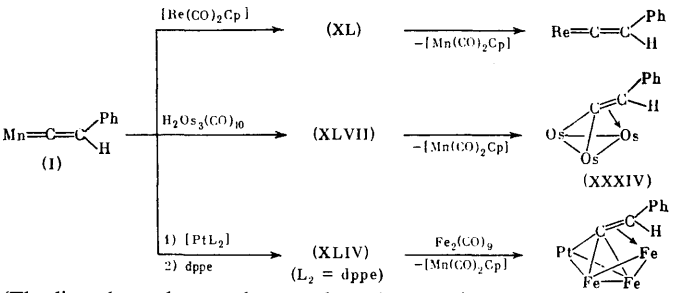
The metallation of type (B) vinylidene complexes with the aid of transition metal carbonyl hydrides involves the hydrogenation of the C_β atom of the vinylidene and the formation of μ_3-carbyne complexes. The cluster $Cp_2(CO)_6MnFe_2(\mu_3\text{-}CMe)$ has been obtained by treating the complex (XXVIII) with $H_2Mn_3(CO)_{12}$.[98,99] The trinuclear clusters $Cp_3(CO)_3MoCo_2(\mu_3\text{-}CMe)$ and $Cp_2(CO)_5MnCo_2(\mu_3\text{-}CMe)$ are formed in the reactions of $HMo(CO)_3Cp$ and $HMn(CO)_5$ respectively with $Cp_2(CO)_2Co_2(\mu\text{-}C=CH_2)$ (XVIII).[66,126]

An example of the metallation of type (D) μ_3-vinylidene clusters is the synthesis of $H(CO)_{11}Fe_3Rh(\mu_4\text{-}C=CHR)$ (R = H, Ph) from $[H(CO)_9Fe_3(\mu_3\text{-}C=CHR)]^-$ and $[ClRhCO]_2$ in the presence of $TlBF_4$.[194]

In a number of instances, the stabilisation of heterometallic intermediates similar to compound (XLVIII) is achieved as a result of the elimination of one of the metallic fragments and its substitution by new groups $[M'L_n]$. The reaction of a vinylidene complex of type (XLIV), where L_2 = dppe, with $Fe_2(CO)_9$ results in the formation of $(dppe)PtFe_3(\mu_4\text{-}C=CHPh)(CO)_9$ (XIII).[104] The tetranuclear complex $Cp(CO)_9FeCo_3(\mu_4\text{-}C=CH_2)$ has been obtained by heating compound (XXVIII) with $Co_2(CO)_8$ or $Co_4(CO)_{12}$.[98,99] The interaction of $(CO)_9Co_2Ru(\mu_3\text{-}C=CHBu^t)$ with $NaMo(CO)_3Cp$ leads to the formation of the complex (XV) as a result of the exchange of one of the $Co(CO)_3$ groups for $Mo(CO)_2Cp$.[109,171]

The possibility of the transfer of an unsaturated carbyne from one metal atom to another is of special interest. In the transfer of the C=CHPh ligand from the Mn to the Re atom,[20] to the Os_3 metallocycle,[190,191] and to the "butterfly" type cluster $PtFe_3$ [104] (Scheme 4), the cleavage of the $Mn=C_\alpha$ bond is preceded by the stage involving the formation of new metal–carbon and metal–metal bonds:

Scheme 4

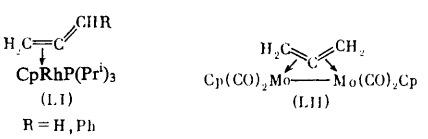


(The ligands at the metal atoms have been omitted.)

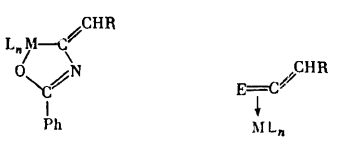
The transmetallation reactions can be used to synthesise UCC for which convenient direct methods of synthesis are not available.

(b) The addition of unsaturated organic compounds

The type (A) compounds (XXXI) and the type (C) compounds (XVI) combine with methylene at the electron-rich $M=C_\alpha$ bond, being converted into the corresponding allene π-complexes (LI) [195] and (LII):[17]

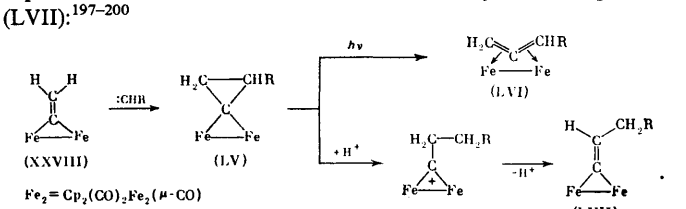


The [2 + 3]cycloaddition of benzoylnitrene to the $M=C_\alpha$ bond, which occurs in the reactions of compounds (XXXI) and (XXXII) with benzoyl azide at –78 °C, affords in 70–80% yield the complexes (LIII) with five-membered heterocycles, whose acidification leads to the corresponding immonium salts.[196] The π-complexes of thio-, seleno-, and telluro-ketens (LIV) have been obtained in the reactions of compound (XXXI) and (XXXII) with chalcogens:[119,120,142]



$L_nM = Cp[P(Pr^i)_3]Rh$, $(\eta^6\text{-}C_6H_6)[P(Pr^i)_3]Os$;
R = H, Ph; E = S, Se, Te.

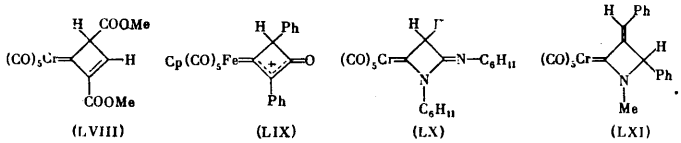
The carbenes :CHR (R = H, COOEt) add to the type (B) complex (XXVIII) at the $C_\alpha=C_\beta$ bond with formation of the cyclopropylidene compounds (LV), which isomerise on UV irradiation to the π-allene complexes (LVI) and the subsequent protonation and deprotonation reactions convert them into the vinylidene complexes (LVII):[197–200]



The structures of compounds (LV) and (LVI) have been confirmed by X-ray diffraction.[197,199]

The photochemical reaction of $Cp_2(CO)_3Ru_2(\mu\text{-}C=CH_2)$ (XVIIa) with ethylene leads to the μ-carbene complex $Cp_2(CO)_3Ru_2[\mu\text{-}C(Me).CH=CH_2]$.[165,173]

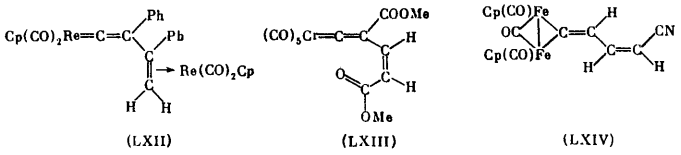
A wide variety of complexes with cyclic carbenes have been obtained by the [2 + 2]cycloaddition to the vinylidene ligand of alkynes, σ-acetylide complexes, carbodiimides, and imines—for example, compounds (LVIII),[106] (LIX),[201] (LX),[202] (LXI),[203] and others:[10]



(LVIII) (LIX) (LX) (LXI)

The complex (III) is formed as a result of the [3 + 3]cycloaddition of $Cp(PPh_3)_2Ru^+=C=CHC(Me)=CH_2$ to $Cp(PPh_3)_2.Ru^+=C=C=CMe_2$.[48]

The insertion of alkynes in the C–H bond of the C=CHR ligands led to the butadienylidene complexes (LXII),[35] (LXIII),[106] and (LXIV):[204]



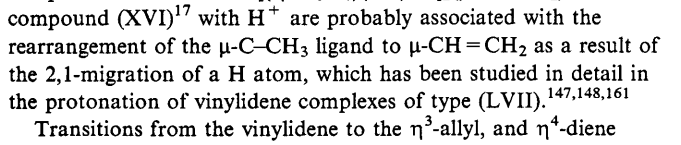
(LXII) (LXIII) (LXIV)

3. The reactions of unsaturated carbene complexes with electrophiles and nucleophiles

(a) The addition of electrophiles to the C_β atom in type (A) and (B) complexes

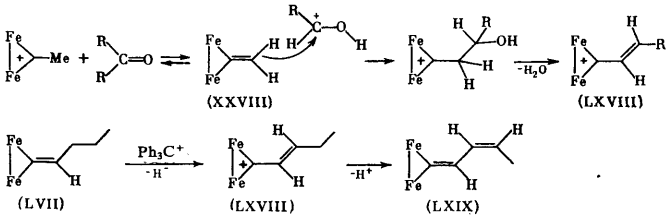
In conformity with the nucleophilic character of the C_β atom in type (A) and (B) UCC (see Section II), the protonation of these compounds leads to mononuclear[36,37,56,108,130,205] and dinuclear[10,12,56,64,66,126,146,147,149,160–163,204] carbyne complexes respectively (see Scheme 2). The instances of the formation of σ,π-vinyl complexes on treatment of $[(\eta^5\text{-}C_9H_7)(CO)Rh]_2(\mu\text{-}C=CH_2)$[118] and compound (XVI)[17] with H^+ are probably associated with the rearrangement of the μ-C–CH_3 ligand to μ-$CH=CH_2$ as a result of the 2,1-migration of a H atom, which has been studied in detail in the protonation of vinylidene complexes of type (LVII).[147,148,161]

Transitions from the vinylidene to the η^3-allyl, and η^4-diene complexes of molybdenum have been achieved by adding carbonium ions to the C_β atom and by subsequent reactions of the carbyne ligands.[144] The complexes (LXV) (M = Fe, R = H;[206] M = Ru, R = Me[73,207]), (LXVI),[73] and (LXVII)[207] with highly unsaturated bridges have been obtained by the electrophilic addition of $[Cp_2(CO)_3M_2(\mu\text{-}CR)]^+$ (M = Fe, Ru; R = H, Me) to the complexes (XXVIII) with R = R′ = H and (XVIIa) with subsequent shifts of the H atom along the chain or the loss of H_2:



(LXV) (LXVI) (LXVII)

The condensation of the μ-methylcarbyne with the aldehydes RCHO (R = Bu^t, C_6H_4Me-4, CH=CHPh), leading to the vinylcarbynes (LXVIII), proceeds via the intermediate formation of compound (XXVIII) and the electrophilic attack by the protonated aldehydes on its C_β atom:[208]



(XXVIII) (LXVIII)

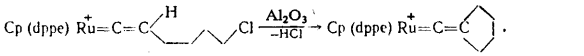
(LVII) (LXVIII) (LXIX)

On the other hand, treatment of a vinylidene complex of type (LVII) with Ph_3C^+ induces the dehydrogenation of the vinylidene side chain, which makes it possible to achieve a conversion to the vinylvinylidenes (LXIX) via the vinylcarbynes (LXVIII).[15]

(b) Deprotonation of the vinylidene ligand

A general reaction of type (A) complexes with the C=CHR ligands is deprotonation on treatment with various bases, which leads to σ-acetylide compounds[10,43,46,58,107,116,143] (see Scheme 2).

In a number of instances, the deprotonation is accompanied by the simultaneous elimination of a substitutent from the vinylidene side chain, for example:[58]



The dehydration of the γ-vinylidene alcohols $L_nM=C=CHC.(OH)R_2$ is a general method of synthesis of the allenylidene complexes $L_nM=C=C=CR_2$ (M = Mn,[109,110] Fe, Ru [48,52]).

The formation of the η^2-keten ligand $CH_2=C=O$ from $\mu\text{-}C=CH_2$ at a diruthenium centre, which occurs on hydrolysis of the product of the deprotonation of the vinylidene complex (XVII) on Al_2O_3, is of interest.[209]

(c) The reactions of vinylidene ligands at polynuclear centres

In contrast to the type (A) and (D) UCC, the metallic centre is actively involved in the reactions of type (D) vinylidene complexes and the mode of their reactions with electrophiles and nucleophiles depends on the charge on the cluster.

The neutral complex (XXXIV) (R = H) reacts with CF_2COOD, combining with D^+ at the Os–Os bond and being converted into $[(\mu\text{-}H)_2(\mu\text{-}D)(CO)_9Os_3(\mu_3\text{-}C=CH_2)]^+$;[210] the analogous reaction of compound (XXXIV) (R = C_5H_4FeCp) proceeds via the intermediate formation at –30 °C of the unstable σ,π-vinyl complex $(\mu\text{-}H)_2(CO)_8(\mu\text{-}CO)(CF_3COO)Os_3(\mu\text{-}CD=CHR)$.[140]

Treatment of the anionic complex (XXXVI) (R = H) with D^+ in the presence of H_2 leads to $(\mu\text{-}H)_3(CO)_9Fe_3(\mu_3\text{-}C\text{–}CH_2D)$, whereupon the H_2 molecule adds to the metallic core with formation of hydride bridges.[211] On the other hand, the cation $[(C_5Me_5)_3(\mu\text{-}CO)_3Ru_3.(\mu_3\text{-}C=CH_2)]^+$ is converted into the μ_3-carbyne clusters $(C_5Me_5)_3.(\mu\text{-}CO)_3Ru_3(\mu_3\text{-}C\text{–}CH_2R)$ (R = H, Me) on treatment with $NaBH_4$ or MeLi.[154]

The reactions of the vinylidene complexes (XV) [171] and (XXXIV)[105,212] with H_2 (60–100 °C) entail the selective addition of one H atom to the C_β atom and of the other to the metal–metal bond. It has been shown recently[100] that the hydrogenation of $(CO)_{13}(\mu\text{-}PPh_2)Ru_5(\mu_5\text{-}C\equiv CPPh_2)$ (1 atm, 80 °C), leading to the cleavage of the C≡C bond, takes place stepwise with absorption of

three H_2 molecules and the successive formation of clusters with μ_4-vinylidene, μ_4-carbyne, and μ_5-carbide ligands and at each stage of this process one H atom adds to the C_β atom of the ligand, while the other becomes a bridge at the Ru–Ru bond:

$$[M](C{\equiv}CPPh_2) \xrightarrow{H_2} [HM](C{=}CHPPh_2) \xrightarrow{H_2} \longrightarrow [H_2M](C{-}CH_2PPh_2) \xrightarrow[-2CO]{H_2} [H_3M'](\mu_5\text{-}C)(CH_3PPh_3),$$

$$[M] = (CO)_{13}(\mu\text{-}PPh_2)Ru_5, \quad [M'] = (CO)_{11}(\mu\text{-}PPh_2)Ru_5.$$

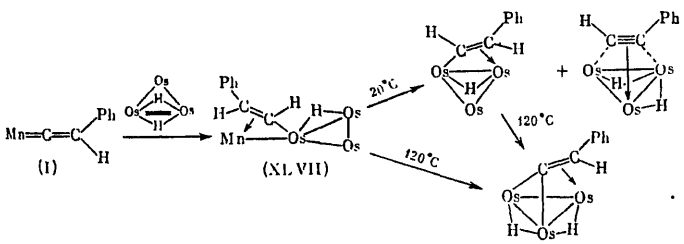
There is no doubt that in the interconversions of the vinylidene, carbyne, and other ligands at polynuclear centres, the metallic core of the cluster functions as a "hydrogen sponge", combining with hydrogen from outside and then transferring it to the ligand and also participating in processes involving H transfer from one part of the molecule to the other.

The migration of an H atom from the metallic core to the C_β atom of vinylidene has been observed in the conversion of the vinylidene complexes (XXXVI) into the carbyne complexes (XXXV) on treatment with CO at 20 °C[150–152] (see above).

The formation of the formylcarbyne cluster $(\mu\text{-}H)_3(CO)_9Os_3(\mu_3\text{-}C\text{-}CHO)$ in the reaction of $[(\mu\text{-}H)_2(CO)_9Os_3(\mu_3\text{-}C{\equiv}CH)]^+$ with H_2O at 0 °C proceeds via a stage involving the isomerisation of the unstable hydroxyvinylidene complex $(\mu\text{-}H)_2(CO)_9Os_3[\mu_3\text{-}C{=}CH(OH)]$ via the intramolecular transfer of a H atom from the hydroxyl to the Os_3 ring.[134]

An example illustrating the migration of a H atom from the Os_3 ring to the organic ligand and in the reverse direction is provided by the reactions of phenylvinylidene in the presence of the $MnOs_3$ system illustrated in the scheme below:[190,191]

Scheme 5

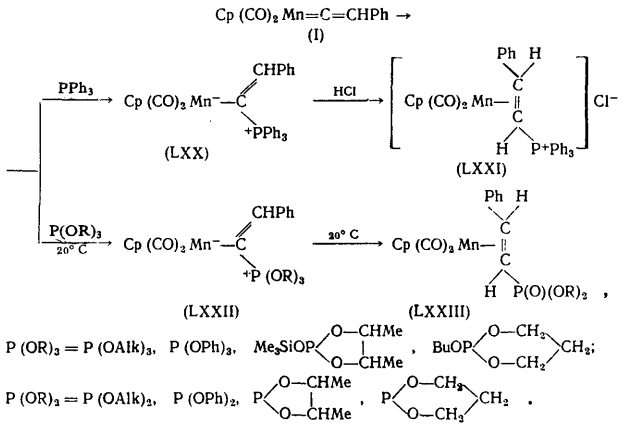


(d) The addition of nucleophiles to the C_α atom

Reactions involving the addition of nucleophiles are most characteristic of the type (A) UCC $L_nM{=}C{=}CRR'$, which have a very markedly electrophilic C_α centre (see section II). The hydrogenation of vinylidene complexes leads to σ-vinyl complexes (see Scheme 2).[10] When vinylidene complexes are acted upon by alcohols, thiols, ammonia, and primary and secondary amines, the nucleophilic species (OR^-, SR^-, NH_2^-, NHR^-, NR_2^-) adds selectively to the C_α atom, while a hydrogen atom adds to a C_β atom and Fischer carbene complexes are formed.[10,12,116,143,213] A direct method of synthesis of alkoxycarbene complexes from $W(CO)_6$, alkynes, and alcohols via vinylidene intermediates has been proposed recently:[214]

$$W(CO)_6 \xrightarrow{RC{\equiv}CH} (CO)_5W(HC{\equiv}CR) \longrightarrow (CO)_5W{=}C{=}CHR \xrightarrow{R'OH} (CO)_5W{=}C\begin{matrix}CH_2R\\OR'\end{matrix}.$$

Pyridine[143] and tertiary phosphines,[10,45,215–217] none of which contain an active H atom, add to the C_α atom of the vinylidene complexes of Mn, Re, and Fe with formation of zwitter-ionic complexes, for example, (LXX):[215]



$P(OR)_3 = P(OAlk)_3$, $P(OPh)_3$, Me_3SiOP (O–CHMe / O–CHMe), $BuOP$ (O–CH_2 / O–CH_2 / CH_2);

$P(OR)_3 = P(OAlk)_2$, $P(OPh)_2$, P (O–CHMe / O–CHMe), P (O–CH_2 / O–CH_2 / CH_2).

The ionic π-alkene complex (LXXI) is formed from compound (LXX) on treatment with HCl.[218] The products of the addition of phosphites to compound (I)—the zwitter-ionic complexes (LXXII)—are spontaneously converted into the neutral vinylphosphonate π-complexes (LXXIII) as a result of the Arbuzov reaction.[219–221]

The allenylidene complexes $L_nM{=}C{=}C{=}CR_2$, having two electrophilic centres, combine with electrophiles (OR^-, SR^-, NR_2^-, PR_3) at either the C_α atom or the Cγ atom depending on their electron-donating capacity.[10,51,106,216]

V. Prospects for the utilisation of unsaturated carbene complexes

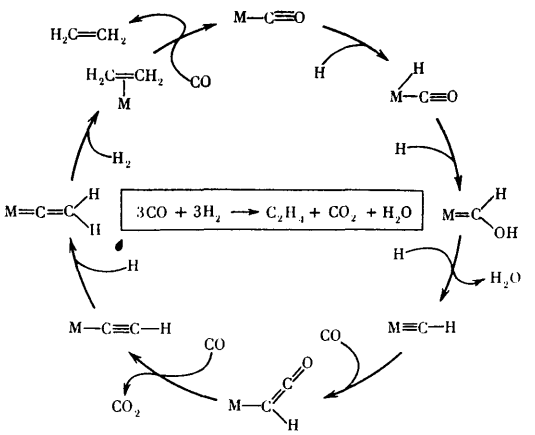
The vigorous development of the chemistry of the UCC during the last decade has led to a better understanding of the rules governing the formation, structure, and chemical behaviour of compounds of this new class. By virtue of the development of convenient preparative methods of synthesis (see Section III), not only individual UCC but also a series of related complexes have become available. Reactions involving the successive metallation of unsaturated carbenes, in which mono-, di-, and tri-nuclear UCC are used as "building blocks" as well as transmetallation reactions have led to the possibility of the specific synthesis of compounds whose molecules incorporate the atoms of several transition metals in definite combinations and proportions, for example, MnFe, MnRh, MnPt, RhCu, OsCu, $MoCo_2$, $MnCo_2$, Co_2Ru, MoCoRu, MnFePt, $MnOs_3$, $FeCo_3$, Fe_3Rh, Fe_3Pt, etc. There is no doubt that such compounds can find applications both directly (in catalysis) and for the preparation on their basis of new polymetallic materials (powders, coatings, films, ceramics, etc.).

The examples of the formation of unsaturated carbene ligands from a wide variety of sources, including single-carbon sources, presented in Section III, permit the conclusion that the UCC or the unsaturated carbene species present on the surface of the catalyst can participate in many catalytic processes. The ketenylidene Fe, Ru, and Os clusters are regarded as model compounds in the study of the reactions of CO on the surfaces of metals. It has been reported[222] that the synthesis of methyl acetate from CO, H_2, and

MeOH in the presence of $[Fe_6(CO)_{16}C]^{2-}$ proceeds via the intermediate $[(CO)_{12}Fe_4(\mu_4\text{-}C{=}C{=}O)]^{2-}$. The observed proportions of linear and branched hydrocarbons in Fischer–Tropsch processes have been explained by the formation of surface vinylidene species and their subsequent reactions.[223]

On the basis of the latest advances in the chemistry of organic compounds of transition metals, a model has been proposed for the mechanism of the catalytic synthesis of alkenes from CO and H_2 at a metallic centre, including vinylidene intermediates (Scheme 6).[224] The known reactions of complexes of Group VI–VIII transition metals, occurring with high degrees of conversion under mild conditions, serve as prototypes of each stage in this cycle.

Scheme 6

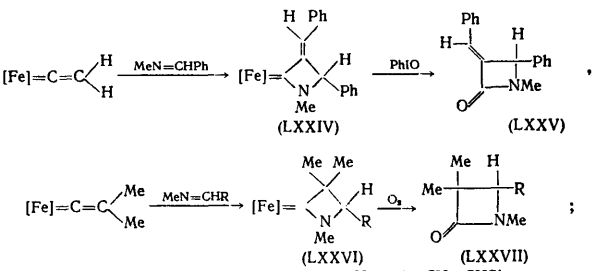


The selective formation of the butatriene *trans*-$(Bu^t)HC{=}C{=}C{=}CH(Bu^t)$ in the catalytic dimerisation of $HC{\equiv}CBu^t$ in the presence of the complex $H_2Ru(CO)(PPh_3)_3$ (50 cycles per Ru atom) proceeds via the AVR stage and the subsequent combination of two butylvinylidene species in the coordination sphere of Ru.[225]

The "small-scale chemistry"—the synthesis of organic substances necessary for modern medicine, agriculture, the special polymer industry, the food and perfume industry, etc.—have nowadays assumed increasing current interest. The new approaches to the synthesis of these substances should satisfy criteria such as high selectivity, productivity, low cost, low energy consumption by the processes, and their ecological safety.[226,227]

The reactions of unsaturated carbenes at metallic centres, examined in Section IV, include processes involving the hydrogenation, dehydrogenation, carbonylation, phosphorylation, and isomerisation of unsaturated organic groups, the growth of the carbon chain, and the formation of C_3–C_6 carbocyclic and heterocyclic compounds. As a rule, these processes proceed at 20–60 °C and atmospheric pressure. The high regioselectivity and stereoselectivity of the majority of the reactions are striking. Many organometallic compounds are formed in nearly quantitative yields. These complexes contain as the ligand an organic molecule capable of existing in a free state (alkene, allene, keten) or an organic group which constitutes a synthon prepared for further processes. The removal of the metal-containing fragment and the isolation of the organic product from these complexes do not usually present special difficulties. All these factors make the synthesis of a wide variety of organic substances with the aid of UCC extremely attractive.

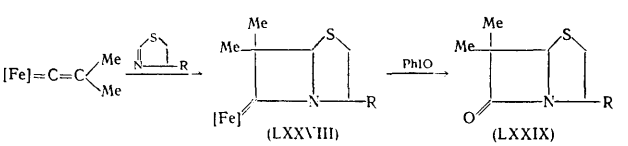
The synthesis of a series of β-lactams (LXXV) and (LXXVII) from imines and the available vinylidene iron complexes via [2 + 2]cycloaddition stages (–78–+25 °C) with formation of the azetidinylidene complexes (LXXIV) and (LXXVI) and their subsequent oxidation can serve as an example:[228]



[Fe] = Cp (CO) (PPh_3) Fe^+; R = Ph, C_6H_4Me-3, C_6H_4Me-4, CH=CHPh.

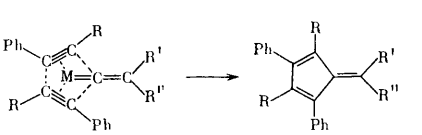
α-Benzylidene-β-lactam (LXXV) has been obtained similarly from the chromium complex (LXI).[203]

The interaction of the complex $\{Cp(CO)[P(OMe)_3].Fe{=}C{=}CMe_2\}^+$ and 2-thiazoline derivatives with subsequent oxidation of the carbene intermediate (LXXVIII) leads to bicyclic β-lactams with the penicillin structure (LXXIX):[229]



[Fe] = Cp (CO) $[P(OMe)_3]$ Fe^+; R = H, COOEt.

The possibility of obtaining unsaturated cyclic compounds involving vinylidene complexes is illustrated by the "assembly" of fulvenes from two alkyne molecules and a vinylidene ligand in the coordination spheres of palladium[230] and molybdenum:[231]



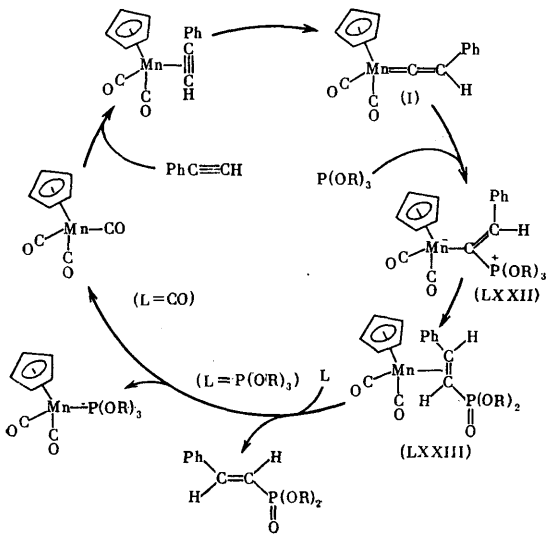
M = Pd, R = R'' = H, R' = Ph; M = Mo, R = Ph, R' = R'' = CN.

A fundamentally new approach to the synthesis of vinylphosphonic acid esters (usually obtained by the esterification of the chlorides of phosphonic acids or by the reactions of alkyl phosphites with alkynes or halogenoalkenes at 150–170 °C) is based on the interaction of phosphites with an unsaturated carbene in the coordination sphere of a transition metal atom.[219–221, 232]

The cyclic Scheme 7 illustrates the successive stoichiometric reactions: the formation of $Cp(CO)_2Mn{=}C{=}CHPh$ (I) from $CpMn(CO)_3$ and $PhC{\equiv}CH$, the conversion of the complex (I) into

the phosphonium complex (LXXII) and the styrylphosphonate complex (LXXIII), and the isolation from the latter of a phosphorus-containing alkene on treatment with $P(OR)_3$ or CO.

Scheme 7



In practice, styrylphosphonates are synthesised in one stage, without the isolation of the intermediate complexes (LXXII) and (LXXIII), in aliphatic or aromatic hydrocarbons:

$$Cp(CO)_2Mn{=}C{=}CHPh + 2P(OR)_3 \xrightarrow[4\text{–}6\ h]{20\text{–}80^\circ C} \longrightarrow \begin{matrix} Ph \\ H \end{matrix}\!\!>\!C{=}C\!<\!\begin{matrix} H \\ P(O)(OR)_2 \end{matrix} + Cp(CO)_2MnP(OR)_3.$$

The reaction is rigorously stereoselective and the styrylphosphonates formed in quantitative yields have exclusively the trans-configuration.[221,232] With the aid of this method, it is possible to obtain not only dialkyl but also the diaryl and cyclic esters of styrylphosphonic acids which are otherwise difficult to obtain.

It is to be expected that the number of examples of the use of UCC in the syntheses of organic compounds will increase. Since many UCC are prochiral or incorporate a chiral metallic centre, they will probably find applications in the asymmetric synthesis of biologically active substances and preparations.

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The enhancement of interest in the chemistry of UCC and the expansion of studies on these lines in many countries have been reflected in a sharp increase in the number of publications during the last 2–3 years†. Information has been published about the improvement of the methods of synthesis and the discovery of new useful properties of these compounds, and new possible applications of such substances are being vigorously sought. All these factors permit an optimistic prediction of the development of the chemistry of UCC and of the realisation of its potential practical possibilities in the immediate future.

†During the preparation of the review for the press, new communications appeared on this topic.[233–280]

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