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Carbene complexes in catalysis

I I Moiseev
Institute of Petrochemical Synthesis, USSR Academy of Sciences, Moscow

ABSTRACT. The methods for forming carbene complexes in catalysis are analysed in the case of the catalytic conversions of hydrocarbons, acids, carbonyl compounds, carbon monoxide, and methanol.

The bibliography includes 85 references.

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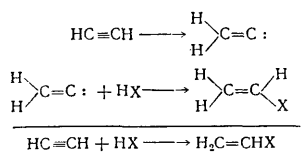
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I. Introduction

When the role of coordination compounds that contain carbene ligands is considered, most attention is usually given in catalysis[1–10] to the interaction between the carbene complex and substrate. Questions relating to the formation of such complexes have been examined to a considerably lesser extent. The present review is devoted mainly to examining those reactions, including model reactions, that result in the formation of carbene molecules and their complexes during the catalytic conversions of the main classes of organic compounds that are most frequently used in industrial and laboratory synthesis.

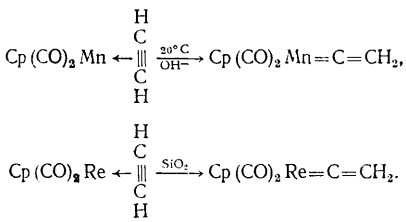
II. Alkynes

The idea that carbene molecules participate in the intermediate stages of catalytic processes was first suggested by Neff.[11] According to this hypothesis, addition reactions to acetylene such as those of hydrogen halides include the isomerisation of acetylene to the so-called "isoacetylene", which is free vinylidene, and reaction of the latter with hydrogen halides:



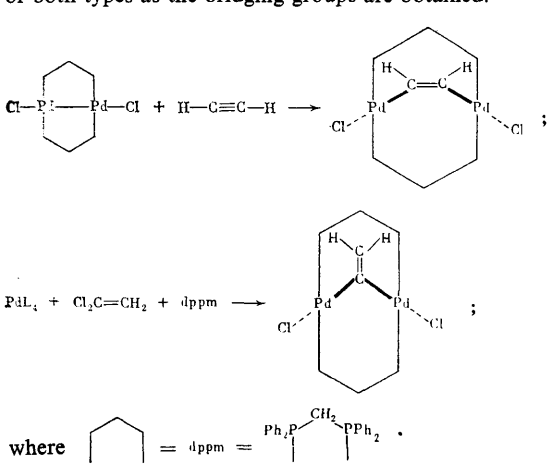
Neff did not elucidate the role of the catalyst, usually Hg^{2+} salts, in these reactions. This hypothesis was later contradicted by other ideas, according to which the reaction of acetylene with hydrogen halides takes place via an intermediate π-complex of Hg^{2+} with an acetylene molecule.[12,13] as well as a complex of a nucleophile with acetylene,[14] the so-called "reverse π-complex", in which bonding between the attacking reagent and the unsaturated ligand only occurs as a result of dative interaction.

However, it should be noted that when the central atom is a good electron donor, acetylene π-complexes and acetylides can be converted to vinylidene derivatives:[15–17]



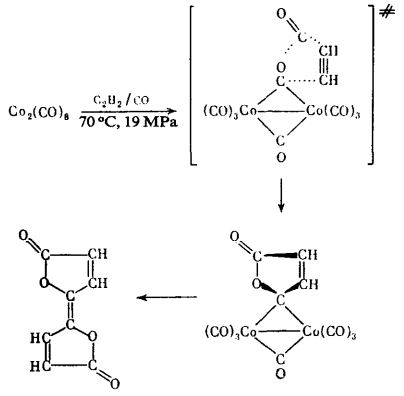
Thus as a result of the stabilisation of the vinylidene ligand in the internal coordination sphere of the transition metal complex, the reaction, which in the case of free acetylene and vinylidene requires the expenditure of about 167 kJ mol^{-1} of energy,[18] becomes possible. Quantum-chemical analysis of the interaction between the Cu^{1+} ion and acetylene and vinylidene indicates that there is stronger bonding of the latter with the central atom.[19] The relative stability of these types of complexes must depend to a considerable extent on the nature of the central atom. It cannot be ruled out that in time addition reactions to alkynes that take place with the involvement of carbene complexes as key intermediates will be discovered.

Reactions of alkynes in the presence of polynuclear systems are complicated by the possible formation of complexes with 1,2-vinylidene in addition to a symmetrical π-complex and a complex with a 1,1-vinylidene ligand.[20] Thus, for $Pd_2(\mu\text{-}Q)_2Cl_2$, where Q is bis(diphenylphosphino)methane, derivatives containing vinylidene ligands of both types as the bridging groups are obtained:[21]

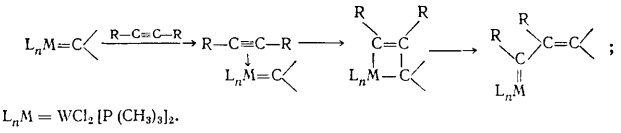


A number of cyclisation processes of alkynes which take place via intermediate complexes with bridging carbene ligands are known.[21]

Scheme 1



It is believed that the polymerisation of alkynes by carbene complexes of transition metals takes place via the cycloaddition of the alkyne to a carbene complex to form a metallocyclobutene followed by conversion of the latter to a complex with a new carbene ligand:[22]

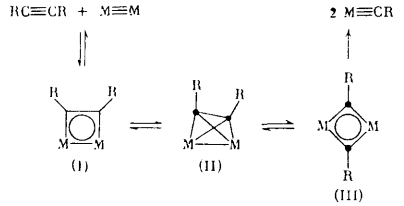


$L_nM = WCl_2[P(CH_3)_3]_2$.

Reaction of alkynes with ditungsten (3+) alkoxides that contain a W≡W bond gives carbyne complexes[23]

$$W_2(OBu\text{-}t)_6 + RC{\equiv}CR \rightarrow 2RC{\equiv}W(OBu\text{-}t)_3.$$

The W≡C bond is apparently so strong that the energy released on forming it compensates that expended on cleavage of the C≡C bond (~830 kJ mol^{-1}) and the reaction takes place in benzene at 25 °C. It is assumed that in this reaction the alkyne first adds on to the W≡W multiple bond to form the dimetallocyclobutadiene (I). The latter isomerises to complex (II), and both the electrons of the π-bonds of the initial ligand and the electrons of the π-bonds of the initial complex take part in formation of bonds between the metal atoms and the organic ligand. Isomerisation of this complex to the symmetrical dimetallocyclobutadiene (III) and dissociation of the latter result in formation of the observed and carbyne complex.

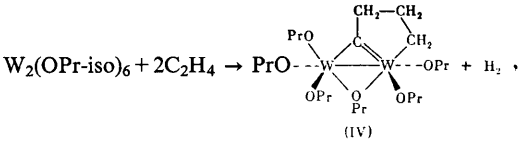


The isolated carbyne complexes catalyse the disproportionation of alkynes.

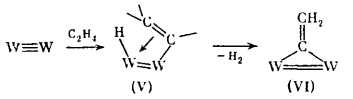
III. Alkenes

In the reaction of ditungsten hexa-alkoxides with alkynes the oxidation state of the metal atom increases as a result of oxidative addition. Oxidation of the metal is probably one of the driving forces for cleavage of the alkyne and formation of a carbyne complex. In the analogous reaction with an alkene the oxidation state of the metal would change to a lesser extent, which is evidently the explanation for the reaction of alkenes with ditungsten hexa-alkoxide not giving carbene analogues of the carbyne complexes.

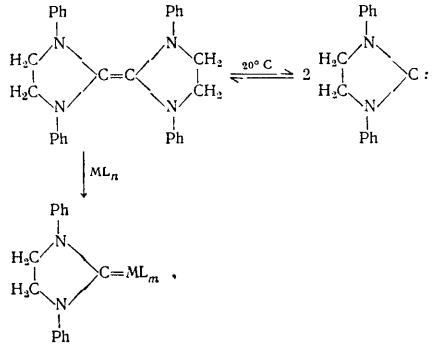
When $W_2(OPr\text{-}iso)_6$ is reacted with ethylene, complex (IV) containing a 5-membered metallocycle is formed:[24]



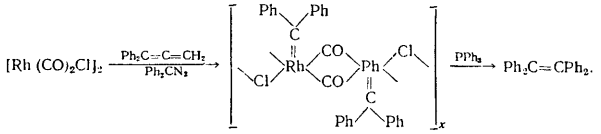
The driving force of this process is also oxidation of the metal atoms of the initial tungsten compound with the alkene. This process is believed to involve the intermediate formation of complexes with vinyl (V) and vinylidene (VI) ligands:



Cleavage of the C=C bond with formation of carbene complexes occurs comparatively rarely under mild conditions. Thus, it was possible to obtain a number of Pd(II), Pt(II), Au(I), Rh(I), Cr(0), and Re(0) complexes from electron-rich unsaturated compounds that can partially decompose to free carbenes even at 20 °C:[25–27]

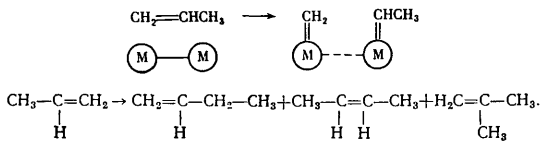


In the reaction of a Rh(I) complex with 1,1-diphenylallene (*o*-xylene, 4 h), which probably undergoes cleavage within the coordination sphere of the central atom to diphenylcarbene and vinylidene ligands, a polymeric complex of rhodium with diphenylcarbene was obtained. The same complex was synthesised by treating the initial rhodium complex with diphenyldiazomethane. Treatment of the carbene complex generated with PPh_3 gave tetraphenylethylene:[28]

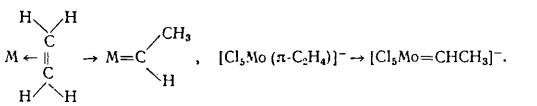


The cleavage of lower alkenes to give carbene complexes of transition metals appears to be a fairly general phenomenon only under relatively severe conditions. Thus, comparison of the

behaviour of CH_2N_2/H_2 and CO/H_2 mixtures, reaction of which with metals very probably leads to the formation of carbene intermediates, with the behaviour of a $CH_2=CHCH_3/H_2$ mixture showed that in all cases the distribution of products conforms to the same rule. This observation led to the conclusion that on Ru, Fe, Rh, and Os deposited on silica gel, alkenes dissociate at 1 atm and 250–300 °C to form carbene ligands, and the resulting complexes catalyse the homologisation of olefins:[29]

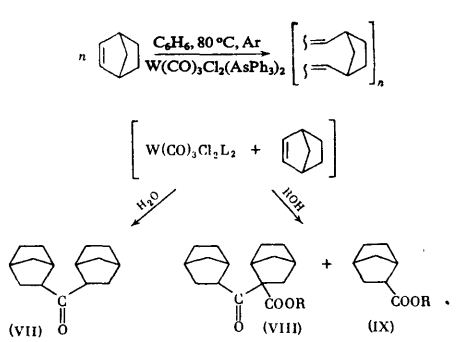


Another possible general method for the formation of carbene complexes from olefins assumes the internal isomerisation of a π-coordinated olefin to a carbene ligand. Quantum-chemical analysis showed that this type of isomerisation was energetically unfavourable for Pd(II) complexes but was practicable for Mo(IV) complexes:[30]

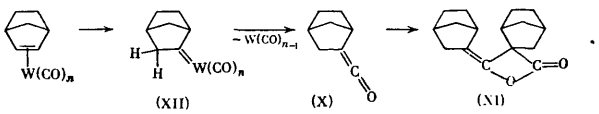


The theory concerning the mutual interconversion of alkyl- or dialkyl-carbene ⇄ alkene has been repeatedly discussed in the literature. Before the publication of the first X-ray diffraction studies devoted to an analysis of Zeise salt,[31] it was proposed[32] that this first known alkene π-complex was in fact a complex with methylcarbene. It transpired subsequently, however, that this view was incorrect and that even the isomerisation of alkenes in solutions of palladium and platinum salts takes place by routes that do not involve intermediate carbene complexes.[33] Nevertheless, it was not ruled out that in Mo(0) and W(0) carbonyl complexes the conversion of an alkene or alkadiene to a carbene ligand is possible. This is suggested by the results obtained from a study of the reaction between diphenylcarbenepentacarbonyltungsten and conjugated dienes.[34] Metathesis of lower olefins by contact with photoreduced molybdenum silicate catalysts that contain Mo(IV) ions is assumed to take place by a chain mechanism involving carbene intermediates that are generated by isomerisation of a π-coordinated alkene by means of an intramolecular 1,2-shift of an H atom.[35]

Chemical confirmation that such mechanisms occur was first obtained during a study of the reaction between norbornene and a tungsten(II) complex[36–38]

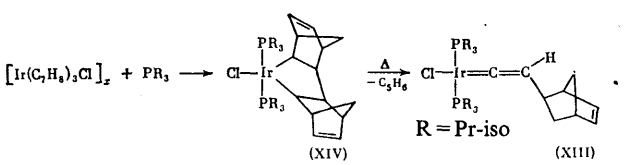


The composition of the observed products derived from alcoholysis and hydrolysis of the reaction mixture [compounds (VII), (VIII), and (IX)] clearly indicates that there is isomerisation of coordinated norbornene to the corresponding carbene ligand, which on reacting with coordinated CO is converted to ketene (X), giving the dimer (XI):[36–38]



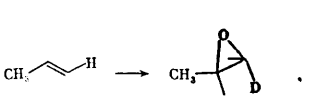
Ketone (VII) and ketocarboxylate ester (VII) are formed by the reaction of (XI) with water or alcohol, while the formation of (IX) results from the addition of alcohol to ketene (X). 2-Norbornylidene-phenylmethane was detected in the products resulting from interaction of the reaction mixture with benzaldehyde, which suggests that carbene complex (XII) is present in the mixture.

It is not ruled out that the 1,2-shift of an H atom, as detected by Bensze and Kraut-Vass,[38] which results in isomerisation of the π-coordinated alkene to the corresponding coordinated carbene is quite a general route for forming carbene intermediates. Another route which is apparently specific to norbornadiene occurred during a study of the behaviour of iridium complexes with this diene.[39] It was found that when polymeric tris(norbornadiene)iridium chloride was reacted with triisopropylphosphine in benzene at 50 °C, the square-planar vinylidene complex (XIII) was readily formed. At lower temperatures there is the formation of the polycyclic product (XIV), which is a precursor of the final vinylidene complex:



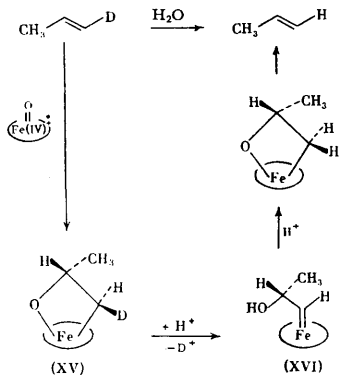
It is likely that in the first stage of this reaction during displacement of norbornadiene ligands by trialkylphosphine, the former undergo oxidative addition to the central atom, culminating in the formation of intermediate complex (XIV), which contains a substituted iridocyclopentane ring. This process is probably assisted by an increase in electron density on the iridium atom as a result of the initial addition of the strong donor ligand—triisopropylphosphine. Thermal elimination of cyclopentadiene from (XIV) should result in the formation of an intermediate with an iridocyclopentene residue. However, this intermediate probably isomerises to the more stable vinylidene complex (XIII) even as it is being formed.

In the epoxidation of propylene in D_2O containing cytochrome R-450, regiospecific and stereospecific substitution of the H atom situated *trans* to the CH_3 group occurs with replacement by a D atom:[40]



Under these conditions H/D exchange takes place between propylene and the solvent. It has been suggested that the reaction of the alkene with the active centre of cytochrome [$Fe^{4+}=O$] takes place

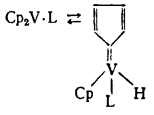
via the intermediate (XV) containing a four-membered metallocycle. Deprotonation of (XV) gives the carbene complex (XVI):



(XV) (XVI)

The process of protonation and deprotonation permits isotope exchange. The simultaneous cleavage of the Fe—O and Fe—C bonds in a complex of the type (XV), accompanied by elimination of epoxide, results in the formation of an alkene oxidation product.

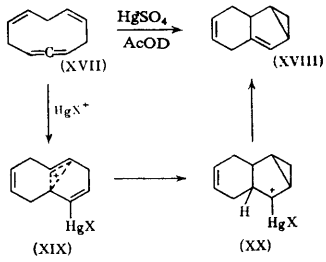
Isotope exchange between ethylene and deuterobenzene in the presence of bis(cyclopentadienyl)vanadium occurs by a mechanism that involves the conversion of a cyclopentadienyl complex to a complex containing a cyclopentadienylidene ligand and hydride:[41]



$L = C_2H_4,\ C_6D_6.$

The reversible insertion and elimination of ligand L on the V—H bond accounts for the observed deuterium exchange.

According to Thies et al.[42] cyclisation of the allene derivatives (XVII) to (XVIII) when treated with mercuric sulphate in acetic acid

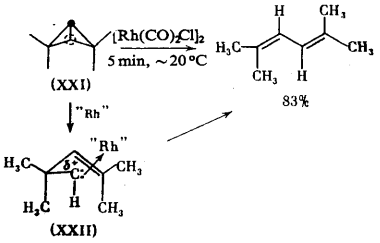


(XVII) (XVIII) (XIX) (XX)

involves attack by the mercury cation on the allene group. Then, after migration of the double bonds, the organomercury derivative (XIX) with delocalisation of the positive charge is formed. This non-classical cation is stabilised on being converted to carbene complex (XX), in which the C carbene atom has a positive charge. Elimination of the HgX^+ cation accompanied by a 1,2-shift of the H atom lead to the formation of the observed product (XVIII).[42]

IV. Alkanes and their derivatives. Activation of C—H, C—C, and C—Cl bonds

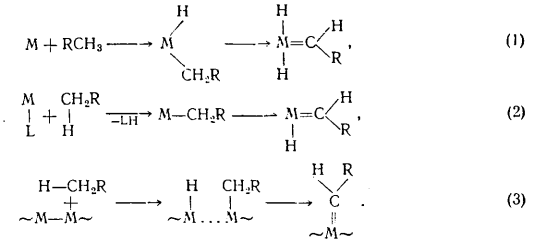
The cleavage of C—C bonds in reactions of alkanes with metal complexes under mild conditions is a rare phenomenon. However, if the compound contains strained rings, cleavage of these bonds is considerably facilitated. Examples are known of the isomerisation of derivatives of cyclopropane, bicyclobutanes, and related hydrocarbons by treatment with silver, platinum, palladium, rhodium compounds, etc. It is thought that these reactions can take place via carbene intermediates. For example, 2,2,4,4-tetramethylbicyclo[1.1.0]butane (XXI) when treated with dimeric rhodium carbonyl chloride isomerises to 1,1,4,4-tetramethylbutadiene.



(XXI) (XXII) 83%

It appears that at the first stage oxidative addition of the initial hydrocarbon (XXI) to the Rh(I) atom takes place with cleavage of the weakest C—C bond (that common to both rings) and a compound containing two Rh—C σ-bonds is formed. As a result of the cleavage of one of the Rh—C bonds and one of the neighbouring C—C bonds, this complex is converted to a carbene—olefin complex (XXII, which isomerises to the final product.[43]

H/D exchange reactions of alkanes that are catalysed by metals or their coordinate compounds[44,45] are often represented by schemes involving oxidative addition of the alkane to a metal atom [reaction (1)] or replacement of ligand L by an alkyl within the coordination sphere of the complex [reaction (2)] followed by elimination of an α-hydrogen atom to form a carbene derivative:



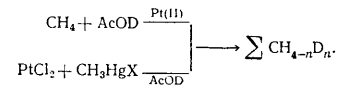
(1)

(2)

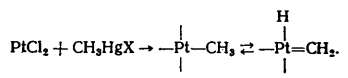
(3)

Oxidative addition of the alkane to a metal or polynuclear compound with cleavage of the metal—metal bond is probably much more energetically favourable than reaction (1) [reaction (3)].

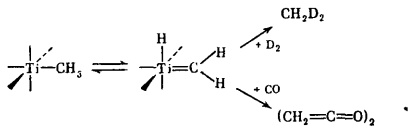
In the alkylation of $PtCl_2$ with methylmercury derivatives in the presence of deuteroacetic acid, the same series of deuteromethanes was detected[46] as in experiments on exchange between CH_4 and CH_3COOD in solutions containing Pt(II) chloride complexes:[46]



This phenomenon can be regarded as confirmation of the intermediate formation of methylplatinum complexes in H/D exchange between CH_4 and CH_3COOD. The simultaneous occurrence of not only monodeuterated products but also multiple exchange products in the reaction mixture indicates that there is an equilibrium between methyl and carbene

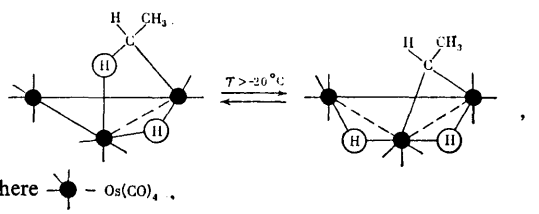


It appears that interconversions of alkyl and carbene hydride complexes occur quite widely in the chemistry of organic derivatives of transition metals. Thus, the simultaneous formation of all the deutero derivatives of methane with di- and tri-deuteromethanes predominating when the system $TiCl_4$ + $AlClMe_2$ is reacted with deuterium suggests[45] the following equilibrium is taking place:



Formaldehyde and ketene dimer were found amongst the products of the reaction between carbon monoxide and the $TiCl_4$ + $AlClMe_2$ mixture. The formation of ketene conforms well with the proposal that titanium carbene complexes are present during the experiments.[47]

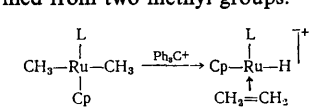
Not only methyl but also other alkyl derivatives display a tendency towards α-elimination of an H atom and formation of a complex containing both a carbene group and a coordinated hydride.[1-6,48] Analysis of PMR spectra of solutions of $HOs_3(CO)_{10}C_2H_5$ showed that above –20 °C this complex, which contains an ethyl group, is converted to a methylcarbene complex:[49]



where .

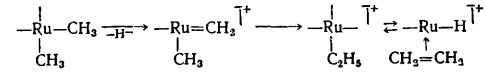
The process of α-elimination is assisted since in the initial complex one of the α-hydrogen atoms of the coordinated ethyl group converges with an Os atom as if ready for transposition to a bridging hydride ion.

The process in which a coordinated alkyl group is converted to a carbene ligand as a result of the elimination of a hydride ion is widely used in preparative work. Carbocations and other electrophiles are used as the H^- acceptor. Similar processes probably occur in catalysis, such as during oxidative dehydrogenation of hydrocarbons where a suitable oxidising agent can accept H^-. These types of processes may be responsible for the formation of new carbon–carbon bonds. A particular indication of this is given by the model reaction of a dimethylruthenium complex with triphenylcarbocation (hydride ion acceptor), as a result of which coordinated ethylene is formed from two methyl groups:[50]



Cp = η^5 cyclopentadienyl.

It appears that the complex formed after elimination of the hydride ion, containing both a coordinated methyl group and a carbene ligand, isomerises to a complex with an ethyl group as a result of insertion of coordinated carbene into the ruthenium–methyl bond. Elimination of a β-hydrogen atom from the ethyl group gives the observed final product:



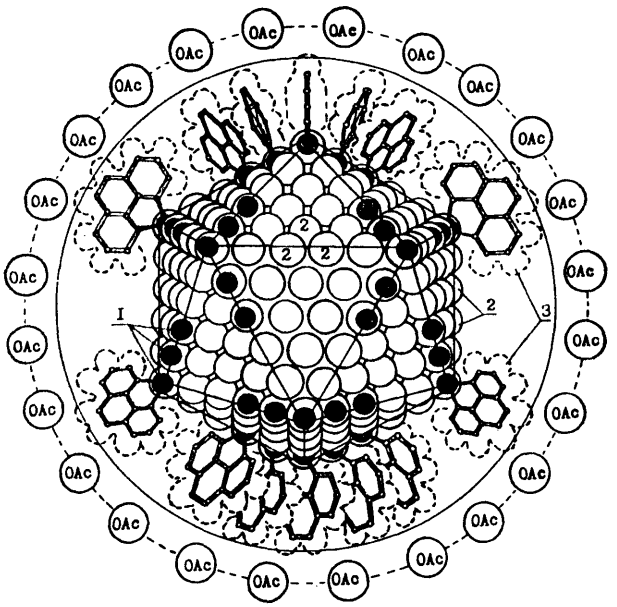
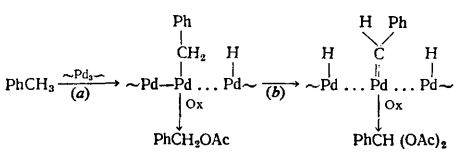


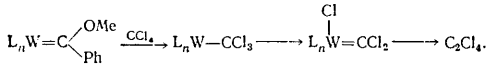
Figure 1. Hypothetical structural scheme of the very large cluster $Pd_{561}Phen_{60}(OAc)_{180}$: *1*, Pd atoms on the edges of the icosahedron that are available for coordination with phenanthroline molecules; *2*, Pd atoms that are available for coordination with substrate; *3*, coordinated phenanthroline molecules.[51,52]

Palladium clusters with the hypothetical formula $Pd_{561}Phen_mO_nX_l$ (m = 60, n = 0, X = OAc, l = 180; m = 80, n = 60, X = PF_6, l = 60) [51,52] catalyse the oxidative acetoxylation of alkenes and arylalkanes. Analysis of molecular models (Fig. 1) shows that out of 252 palladium atoms of the external layer of the compact metal core of these compounds only 30–40 are sterically accessible to substrate molecules. The results of determining the number of active sites in the cluster by an inhibition method [53] are consistent with this conclusion. It follows also from molecular models that the active sites of such clusters contain three palladium atoms. This makes it possible to simplify the discussion of the mechanism of the interaction between substrate and cluster by considering only three out of all the palladium atoms. In the acetoxylation of toluene appreciable quantities of benzylidene diacetate are formed together with benzyl acetate.[54] Since benzyl acetate is not oxidised to benzylidene diacetate under the experimental conditions, this indicates that when the route responsible for the formation of benzylidene diacetate occurs, a toluene molecule does not leave the surface of the cluster until two hydrogen atoms have separated from it. This condition is met by a scheme involving the oxidative addition of toluene to a group of three palladium atoms [stage (*a*)] and also elimination of an H atom from a coordinated phenylmethyl group to give a coordinated phenylcarbene [stage (*b*)].



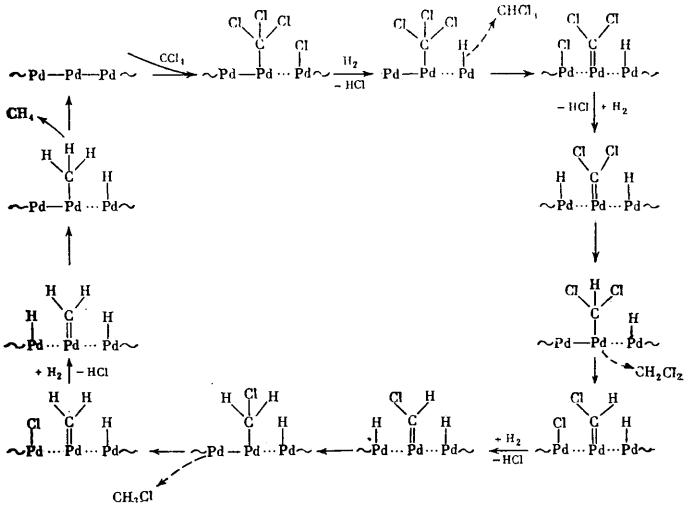
The reaction products, as in the acetoxylation of alkenes, are formed by transfer of electrons from the coordinated organic ligands and H atoms to the oxidising agent (Ox).

Processes related to α-elimination apparently occur during the conversion of haloalkanes using transition metal compounds. Thus, tetrachloroethylene is amongst the products from the reaction between CCl_4 and pentacarbonylphenylmethoxycarbenotungsten, in addition to CO, HCl, CH_2Cl_2, and $CHCl_3$. The occurrence of tetrachloroethylene may be due to the formation of a trichloromethyltungsten derivative and its conversion by α-elimination of a chlorine atom from the CCl_3 group to a dichlorocarbene complex.[55] The latter is the source of tetrachloroethylene:

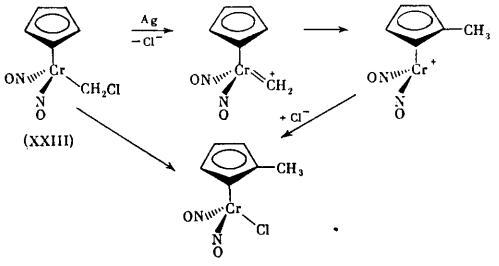


In the reactions of CCl_4 with hydrogen on palladium catalysts obtained by reduction of palladium(II) compounds in the presence of alcohols, $CHCl_3$, CH_3Cl, and CH_4 are all formed at the same time.[56] The simultaneous formation of these products indicates that a substrate molecule can, without leaving the surface of the catalysts, replace more than one Cl atom with H. In the same way as for the oxidative acetoxylation of toluene, these phenomena can be accounted for by a scheme that involves the oxidative addition of CCl_4 to two atoms of the "triplet" of Pd atoms with alternating stages for replacement of Cl atoms on palladium by H atoms and α-elimination of Cl atoms to form a carbene ligand. Addition of H atoms to the latter results in regeneration of a coordinated halomethyl group. According to this scheme, the observed reaction products are formed by reductive elimination of a methyl or halomethyl radical and H or Cl atoms. The yield of reaction products is determined by the ratio of rates for reductive elimination and α-elimination:

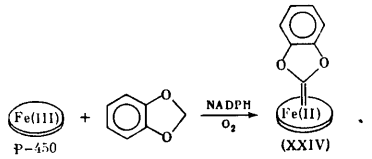
Scheme 2



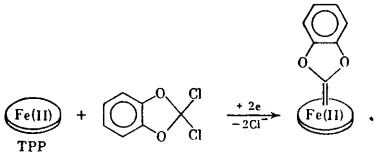
Elimination of the Cl^- ion from the chloromethyl group bonded to the chromium atom and formation of an intermediate chromium carbene complex are responsible for the silver-catalysed migration of the CH_2 group in the chloromethyl residue to the cyclopentadienyl ring of complex (XXIII):[57]



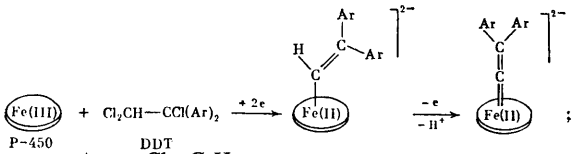
The formation of carbene complexes from compounds containing C–H and C–Hal bonds plays an important part in redox processes which take place in living organisms.[58] Thus, it is thought that during oxidative metabolism of 1,3-benzodioxole, a powerful insecticide synergist, a complex is formed in which the iron atom of cytochrome P-450 is bonded to a carbene ligand that is generated after the removal of two H atoms from the methylene group of 1,3-benzodioxole:[58]



An analogue of complex (XXIV) was obtained from tetraphenylporphyrin (TPP) and 2,2-dichloro-1,3-benzodioxole:



It is thought that carbene complexes also occur during the reductive metabolism of a number of inhalation anaesthetics by cytochrome P-450. When the insecticide 2,2-bis(*p*-chlorophenyl)-1,1,2-trichloroethane (DDT) is reacted with the cytochrome P-450 analogue, iron(II) tetraphenylporphyrinate, a very stable arylvinylidene complex is obtained:[58]



Results which suggest that σ-alkyl and carbene complexes of iron undergo interconversion during the oxidation or reduction of a number of substrates with cytochrome P-450 have been obtained.[59–61]

V. Alcohols

In recent years the reactions of methanol on high-temperature zeolite catalysts of the type ZSM-5 have stimulated considerable interest.[62] At 300–500 °C a mixture of hydrocarbons—alkanes, alkenes, arenes, etc.—is formed from methanol. In practical terms

those reactions of the greatest interest are selective conversions of methanol, such as:

$$2CH_3OH \longrightarrow CH_2{=}CH_2 + 2H_2O,$$
$$3CH_3OH \longrightarrow CH_3CH{=}CH_2 + 3H_2O,$$
$$3CH_3OH \longrightarrow \underset{\diagdown\,\diagup}{CH_2 - CH_2} + 3H_2O,$$
$$\qquad\qquad\quad CH_2$$
$$CH_3OH + H^+ \xrightarrow{-H_2O} CH_3^+ .$$

It is not difficult to see that the formation of the organic products can occur via schemes that involve the elimination of water units from methanol and the reaction of the resulting carbene. However, with acid catalysis, protonation of the alcohol and reactions of the alkoxonium ion are mainly to be expected, giving dimethyl ether, the trimethyloxonium ion, etc. In schemes that depict the results of acid-catalysed reactions of methanol, there is a frequent occurrence of the methyl cation, which, however, should only be regarded as a residue from correspondingly more complex structures[63] or part of a transition state. In actual fact the carbocation CH_3^+, which is a complex between a proton and methylene,[63] or its solvated forms such as methoxonium ion ($CH_3O^+H_2$), trimethyloxonium ion ($(CH_3)_3O^+$, and similar species could act as methylene donors, but the bond between the proton and CH_2 is quite strong[64] (proton affinity of methylene is ~8.65 eV). Consequently, in order to generate carbene from CH_3^+ a fairly strong base would be needed, at any rate one stronger than water, whose proton affinity is estimated to be 7.3–8.2 eV. In fact, when trimethyloxonium hexafluoroantimonate or tetrafluoroborate undergo thermolysis (350 °C), hydrocarbons are not formed.[65,66] This result can be readily understood when the low proton-accepting capacity of these anions is taken into account. It should be noted that the formation of carbenes by the elimination of protons from carbocations using stronger bases is well-known. Thus, the cation $(MeS)_2CH^+$ reacts with tertiary amines to give tetraethylmercaptoethylene, which is the expected product from the dimerisation of dimethylmercaptocarbene:[67]

$$(MeS)_2CH^+ \xrightarrow[CH_2Cl_2,\ -10°C]{(iso\text{-}Pr)_2NEt} (MeS)_2C: \longrightarrow (MeS)_2C{=}C(SMe)_2.$$

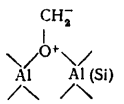
During the reactions of methanol on zeolites, it appears that deprotonated Brønsted sites can act as a base that adds on a proton from trimethyloxonium, which is the most probable form of existence for CH_3^+ in the dehydration of CH_3OH or $(CH_3)_2O$. Consequently, the products that occur products that occur during dehydration of methanol could be formed by generation of carbene-type intermediates [CH_2, $CH_2^- - O^+(CH_3)_2$] and their subsequent reactions. This conclusion is consistent with the formation under identical conditions on an HZSM-5 catalyst of the same series of products from both methanol and the known carbene source—diazomethane.[65]

At the same time there is evidence that the synthesis of hydrocarbons from methanol is a more complex process. Thus, when dimethyl ether was dehydrated on an HZSM-5 catalyst at 240 °C in the presence of a free-radical trap, the characteristic EPR spectrum of a stable *N*-oxyl radical was observed.[68] This could result from the participation of free radicals in the process, for example,

$$CH_3OCH_3 \xrightarrow[-H^\cdot]{HZSM\text{-}5} {}^\cdot CH_2OCH_3 \xrightarrow{CH_3OCH_3} \begin{cases} \rightarrow CH_3CH_2OCH_3 + CH_3O^\cdot \\ \rightarrow CH_3OCH_2CH_2OCH_3 + H^\cdot \end{cases}$$

$$PhCH{=}N^+(Bu\text{-}t){-}O^- \xrightarrow{R^\cdot} Ph(R)CYHN(t\text{-}Bu)O.$$

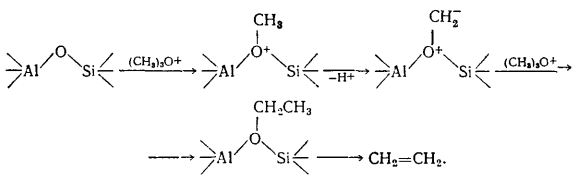
or from a more complex scheme involving trimethyloxonium, an ylide complex of carbene with dimethyl ether ($CH_2^- - O^+Me_2$), and carbene-type surface complexes,



and others. However, the behaviour of dimethyl ether during thermolysis of the free radical source benzoyl peroxide is evidence against the participation of free radicals in the dehydration of methanol. Neither methyl ethyl ether (a possible source of ethylene in the acid-catalysed dehydration of MeOH) nor hydrocarbons were detected amongst the reaction products. 1,2-Dimethoxyethane that is formed also does not give hydrocarbons.[69]

These findings are consistent with the results of Hunter et al.,[70] who investigated the effect of radical traps such as NO on the dehydration of dimethyl ether on HZSM-5. It transpired that addition of 1–3% NO had no effect on either the activity of the catalyst or the yield of even such a product as methane. In addition, oxygen probably deactivates the catalyst by oxidising the ylide $^-CH_2 - O^+(CH_3)_2$ to formaldehyde, which when added reduces the activity of the catalyst, as shown in separate experiments.

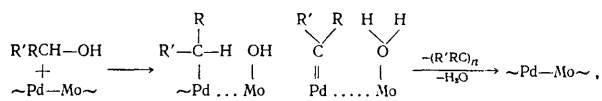
It is thought that in the reaction between trimethyloxonium and HZSM-5, CH_3^+ is transferred to the O atom of the aluminosilicate with subsequent deprotonation to form an ylide which is alkylated by a second trimethyloxonium ion.[71] The ethyl group formed in this process is the source of ethylene:



The kinetic data suggest, however, that the actual process is more complex. Thus, as the bulk rates (500–5000 $cm^3\ min^{-1}\ g^{-1}$ at a pressure of 1–100 mm Hg, 400 °C) increase, the yield of ethylene from the dehydration of methanol decreases and propylene is mainly formed,[69] which is at variance with schemes in which its formation is attributed to attack by carbene on ethylene. The problem concerning the detailed mechanism of this reaction is quite complex and it would appear that the structure of the zeolites and the interaction of their surface with the carbon-containing intermediates that are formed must be taken into account. Quantum-chemical analysis indicates that coordinated methoxyl groups display considerable readiness to eliminate carbene because of the presence of an intramolecular hydrogen bond between one of the H atoms of a CH_3 group and the neighbouring basic oxygen atom of an AlO_4 residue bonded to this methyl group.[63] Reaction between a carbene-donor intermediate of this type and a free or coordinated methanol molecule can result in formation of the observed products. It cannot be ruled out that the decisive role in the formation of hydrocarbons is played by sections of the surface that are adjacent to each other and on which such intermediates are stabilised as well as by species such as CH, CH_2, CH_3, etc.

There was a recent synthesis[73] of a palladium–molybdenum cluster (XXV) (Fig. 2), in alcohol solutions of which slow dehydration of aliphatic and arylaliphatic alcohols occurs.[74] Dimethyl ether is absent from the reaction products from the dehydration of methanol, while in the dehydration of ethanol neither

diethyl ether nor ethylene is formed. This suggests that the elimination of water is not catalysed by either protons or Lewis acids. In the dehydration of benzyl alcohol, approximately equal quantities of *trans*-stilbene and water are formed. These findings may be interpreted by assuming that an H atom and hydroxyl radical are eliminated from the same carbon atom of the alcohol molecule to form a carbene ligand that is stabilised through coordination. It should be noted that homonuclear palladium clusters such as $Pd_4(CO)_4(OAc)_4$ and mononuclear molybdenum carbonyl complexes do not catalyse this reaction. It is probable that the Pd–Mo bond which occurs in complex (XXV) is absolutely essential for catalysis. It is possible that the alcohol, when introduced on to this bond in the Pd_4Mo_4 group, alkylates the Pd atom and oxidises the Mo atom, to which a hydroxyl group is added. After transfer of a proton from the coordinated alkyl to the coordinated hydroxyl on the reaction site, an H_2O molecule bonded to the Mo atom and a carbene ligand coordinated with the Pd atom are formed.



$$PhCH_2OH \xrightarrow[80^\circ C]{«Pd_4Mo_4»} PhCH{=}CHPh + 2H_2O.$$

Elimination of these ligands and restoration of the palladium–molybdenum bond complete the catalytic cycle.

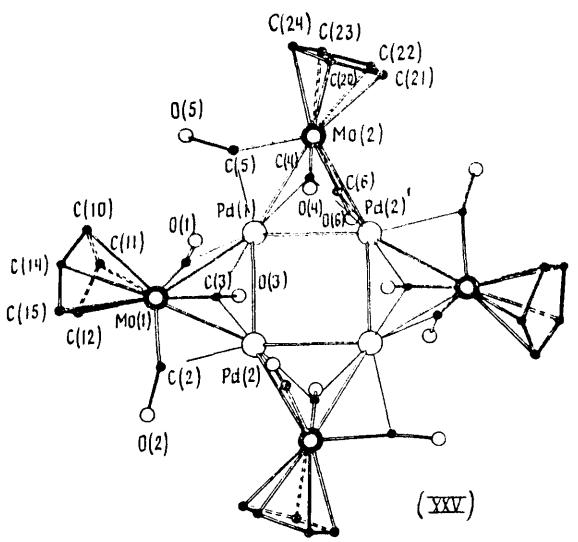


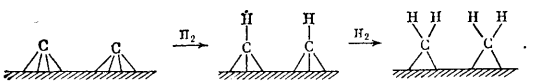
Figure 2. Structure of the anion of the palladium–molybdenum cluster with the composition $Na_2\{Pd_4[CpMo(CO)_3]_4\}.2THF$.[70]

VI. Carbon monoxide

The theory concerning the formation of intermediate carbene complexes has been widely applied in discussions of the mechanism of the hydrogenation of carbon monoxide (Fischer–Tropsch reaction) on both solid catalysts and in solution.[75] It is thought that both coordinated (adsorbed) carbonyl groups and carbide carbon, i.e. C atoms actually coordinated, participate in reduction processes. Thus, for the most general case the reduction of CO is based on the reaction:

$$M(CO)_n + M^1 \xrightarrow[-M^1O]{} (CO)_{n-1}MC.$$

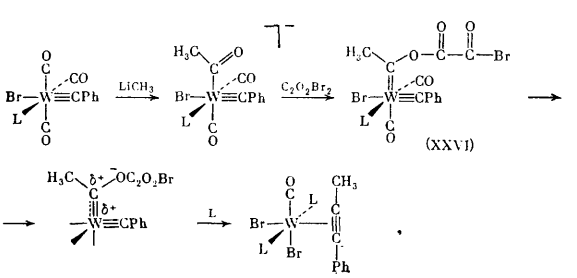
It may be assumed that M^1O subsequently reacts with CO or H_2, resulting in regeneration of the catalyst. Depending on the nature of the catalyst, it appears that routes involving hydrogen and $M(CO)_n$ or $(CO)_{n-1}MC$ or both compounds together take place. It is thought, however, that intermediate carbene species are formed in all these reactions. Thus, carbene complexes play a key role in the initiation of this process, which has the kinetic characteristics of a chain process (primary reactions of coordinated carbonyl, conversions of the carbide atom to carbyne and carbene groups), in chain growth, in reactions of metal acyl derivatives, and others.[73] For example, reduction of carbide complexes by heterogeneous catalysis is depicted by a scheme that involves the formation of intermediate carbyne and carbene compounds (without specifying the nature of the groups bonded to the C atom)



Carbene complexes constitute a source of alkenes and alkanes. It would appear that alkynes could be formed from carbyne complexes, but the synthesis of acetylene in the gas phase according to the reaction

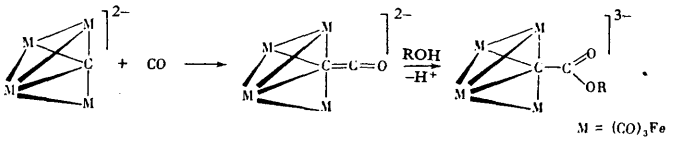
$$2CO + 3H_2 = HC{\equiv}CH + 2H_2O$$

is fairly improbable thermodynamically (ΔG^0_{298} = + 26.5 kJ mol^{-1}) and is not feasible under mild conditions. There has only been one report[76] about the synthesis of acetylene from CO and H_2 at 1 atm and 100 °C in the presence of graphite intercalation compounds with $FeCl_3$ (composition C_9FeCl_3) activated with potassium naphthalide. The nature of the processes taking place in this system is unclear. It should be noted, however, that the synthesis of acetylene from CO to H_2 will probably occur if it is interlinked with any exoergic process. Thus, for example, in the model reaction in which LiMe serves as the reducing agent instead of H_2 while one of the oxygen atoms of a carbonyl group is removed using oxalyl bromide, the carbyne group PhC≡ is included in the composition of the final alkyne PhC≡CMe:[77]



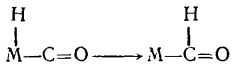
In this case not only is phenylacetylene formed but an exoergic process also takes place—the partial hydrolysis of oxalyl bromide. It is of considerable importance that this synthesis takes place via an intermediate carbene-carbyne complex (XXVI).

Another route for converting carbide complexes assumes the formation of intermediate ketenides—analogues of transition metal vinylidene derivatives—by a scheme[78] such as

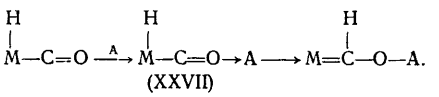


M = $(CO)_3Fe$

Hydroxycarbene groups play a key role during the reduction of coordinated CO groups. Migration of a coordinated H atom to coordinated CO

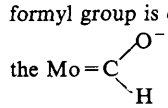


is somewhat unfavourable thermodynamically and difficult kinetically.[79] For this process $\Delta G^0_{298} > 0$ and $E_\alpha > 167$ kJ mol^{-1}. Analysis[79] of the experimental data indicated that in all cases isomerisation of the carbonyl hydride complex to a formyl derivative only takes place when there is a proton or aprotic acid A in the system which is capable of forming an adduct with the carbonyl hydride complex (XXVII):



(XXVII)

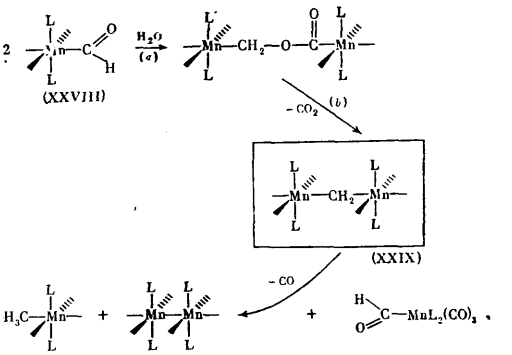
Apart from a proton, cations of alkali and alkaline earth metals as well as complexes of virtually all transition metals can act as electrophile A. It appears that because of the increase in effective positive charge on the carbon atom of the carbonyl group in adduct (XXVII), transfer of the coordinated hydride from the metal to carbon is facilitated. The final product is hydroxycarbene complex in which the H atom has been replaced by electrophile A. It is probable that the higher the stability of such a hydroxycarbene complex, the stronger is the influence of thermodynamic factors that assist this transfer of the H atom. Addition of two hydrogen atoms to this hydroxycarbene complex results in the formation of a complex with a hydroxymethyl ligand MCH_2OH, which on reaction with synthesis gas can give methanol, oxygenated products with a longer chain, and other products.

It should be noted that in the formyl derivative of molybdenum $C_5Me_5(CO)_2(PPh)_3MoCHO$, the vibration frequently ν_{CO} of the formyl group is only 1602 cm^{-1}, which suggests that a structure with the  bond predominates. In fact, this and related complexes are readily protonated or methylated to form cationic hydroxycarbene complexes with the composition

$$[(\eta^5\text{-}C_5Me_5)(CO)_2(PPh_3)Mo{=}C(H)OR^-]^+X^-,$$

R = H or Me, $X^- + CF_3COO^-$ or PF_6^- (Ref.80).

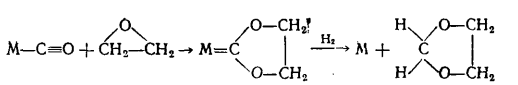
However, there are examples which suggest that conversion of the CHO group to CH_3 can occur by a more complex route[81] than that discussed above:



(XXVIII) (XXIX)

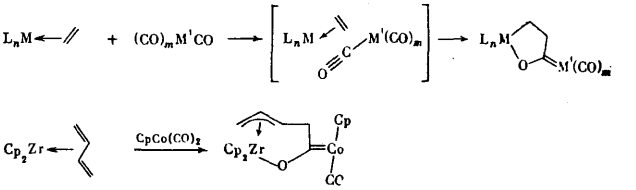
In fact, reduction of the manganese formyl complex (XXVIII) incorporates a redox disproportionation involving a water molecule [stage (*a*)], elimination of CO_2 from the complex with a bridging ester group [stage (*b*)] and finally the formation of a binuclear complex (XXIX) with a bridging carbene. Reduction of this methylene derivative with a third molecule of formyl complex (XXVIII) gives a methyl derivative and a dimeric derivative with a Mn–Mn bond.

In the schemes reviewed in the literature, the reactions of carbonyl complexes with reagents which are present in the system other than H_2 and hydride complexes are not usually taken into account. It is possible that the inclusion of oxygenated compounds as potential reagents would considerably extend our ideas about possible routes for reducing CO. Thus, it was shown[82] that carbonyl complexes of Fe, Ru, Mn, and Re can react with ethylene oxide to form dioxocarbene complexes that are potential sources of cyclic formaldehyde acetal:



M = $CpFe(CO)_2^+$, $CpRu(CO)_2$, $CpMn(CO)(NO)^-$, $Re(CO)_4Cl$, $Ru_3(CO)_{11}$, $Re_2(CO)_9$.

In a similar manner the condensation of a π-coordinated alkene or diene with a coordinated carbonyl leads to carbene complexes[83] which can be hydrogenated to obtain oxygenated compounds in a Fischer–Tropsch synthesis:



Reactions of this type are to be expected for Group IV elements, which can apparently form fairly strong bonds with the oxygen atom of the coordinated carbonyl group. Probably this "double" coordination of CO assists the cycloaddition of carbon monoxide and the coordinated alkene or alkadiene as depicted in the scheme shown here.

VII. Carbonyl compounds and carboxylic acids

Information about reactions in which a carbonyl compound acts as a donor of a carbene ligand is extremely limited. This is not surprising if we consider the strength of the C=O bond and the need to use a very powerful reducing agent to bond to the O atom being removed from this group. Amongst reactions of this type, in which the formation of intermediate carbene complexes may be presumed, should be included the reduction of benzophenone to tetraphenylethylene:[84]

$$2Ph_2C{=}O \xrightarrow[97\%]{\text{Red, } TiCl_3/THF} Ph_2C{=}CPh_2,$$

Red = Zn, $LiAlH_4$, Li, K.

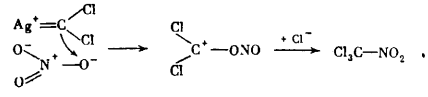
The titanium complex present in the system evidently has different functions compared to the reducing agents used. It cannot be excluded that the Ti atom first coordinates ketone molecules and then—after the removal of O atoms on treatment with the reducing agent—forms a complex with diphenylcarbene, which undergoes conversions to give tetraphenylethylene:

$$Ph_2C{=}O \xrightarrow{\text{Red, } TiX_n} Ph_2C{=}TiX_n \xrightarrow[-TiX_n]{} Ph_2C{=}CPh_2.$$

The thermolysis of anions of trihalo-substituted carboxylic acids is one of the oldest methods for generating carbenes.[85] However, the effect of transition metals on this process and on the reactions of dihalocarbenes formed in the system has hardly been studied at all. One of the few known reactions is the synthesis of chloropicrin[85] by thermolysis of trichloroacetate in the presence of silver nitrate:

$$Cl_3CC(O^-)(=O) \xrightarrow{AgNO_3} Cl_3C{-}NO_2.$$

It cannot be excluded that the dichlorocarbene formed in the system is stabilised by coordinating with the silver ion, and then acting as a fairly strong electrophile it attacks the nitrate ion according to the scheme



From the examples given in this review it follows that in principle the generation of carbene complexes is to be expected from elements of virtually all Groups of the Period Table in their reactions with the most important examples of organic substrates. It is probable that structural factors which enhance the strength of the metal–ligand bond must assist the formation of intermediate carbene complexes. Identification of these factors constitutes a problem of theoretical chemistry and undoubtedly plays an important part in determining the mechanism of many catalytic processes and predicting the activity of catalyst complexes. It would not be an exaggeration to say that carbenes and coordinated compounds that contain them as ligands should be regarded as just as important and as widely occurring intermediates as carbocations and *C*-centred free radicals were traditionally considered to be. The genetic bond which exists between these intermediate species and their complexes is responsible for the interconversions of these intermediates.

References

1. B A Dolgoplosk *Kinet. Katal.*, 1977, **18** 1146
2. B A Dolgoplosk *Kinet. Katal.*, 1981, **22** 807
3. B A Dolgoplosk *Kinetika i Kataliz* (Kinetics and Catalysis), Vol. 13 (Results in Science and Technology), Moscow, VINITI, 1984, p. 70
4. B A Dolgoplosk, K L Makovetskii, Yu V Korshak, et al *Vysokomol. Soedin.*, 1977, **19** 2464
5. K L Makovetskii, B A Dolgoplosk, Yu V Korshak, et al. *Zh. Vses. Khim. Ova. im D. I Mendeleeva*, 1979, **24** 513
6. B A Dolgoplosk, I A Oreshkin, E I Tinyakova *Kinet. Katal.*, 1984, **25** 306
7. M Regits, G Maas *Diazo Compounds: Properties and Synthesis*, Academic Press, New York, 1986, 75 pp
8. M P Doyle *Chem. Rev.*, 1986, **86** 919
9. M Brookhart, W B Studabaker *Chem. Rev.*, 1987, **87** 411
10. R Taube, K Sayfert *Rev. Inorg. Chem.*, 1986, **8** 31
11. J A Nieuwland, R R Vogt *The Chemistry of Acetylene* (Translated into Russian), Izd. Inostr. Lit., Moscow, 1947, 325 pp
12. R M Flid, I I Moiseev, E M Kalmykova *Zh. Fiz. Khim.*, 1957, **31** 904
13. I I Moiseev, Candidate's Thesis in Chemical Sciences, Lomonosov Institute of Fine Chemical Technology, Moscow, 1958
14. E A Shilov *Problemy Mekhanizma Organicheskikh Reaktsii* (Problems Concerning the Mechanism of Organic Reactions), Izd. AN UKrSSR, 1954, p. 14
15. A B Antonova, N E Kolobova, P V Petrovsky, et al. *J. Organomet. Chem.*, 1977, **137** 55
16. N E Kolobova, L L Ivanov, O S Zhvanko, et al. *J. Organomet. Chem.*, 1984, **265** 271
17. A Hohn, H Otto, M Dziallas, H Wernen *J. Chem. Soc., Chem. Commun.*, 1987, 852
18. C Dykstra, H F Shaefer *J. Am. Chem. Soc.*, 1978, **100** 1378
19. N M Vitkovskaja, V G Bernshtein, F K Schmidt *React. Kinet. Catal. Lett.*, 1986, **31** 167
20. B L Shaw *J. Chem. Soc., Chem. Commun.*, 1986, 1629
21. R S Dickson, P J Frazer *Adv. Organomet. Chem.*, 1974, **12** 812
22. A Mayr, K S Lee, M A Kjelsberg, D V Engen *J. Am. Chem. Soc.*, 1986, **108** 6079
23. M L Listemann, R R Schrock *Organometallics*, 1985, **4** 74
24. M H Chisholm, M Hampden-Smith *J. Am. Chem. Soc.*, 1987, **109** 5871
25. D J Cardin, M J Doyle, M F Lappert *J. Chem. Soc., Chem. Commun.*, 1975, 907
26. B Cetinkaya, P Dixneuf, M F Lappert *J. Chem. Soc., Chem. Commun.*, 1973, 206
27. D J Cardin, B Cetinkaya, M F Lappert *J. Chem. Soc., Dalton Trans.*, 1973, 515
28. P Hong, N Nishii, K Sonogashira, N Nagihara *J. Chem. Soc., Chem. Commun.*, 1972, 993
29. M Leconte, A Theoller, D Rojas, J M Basset *J. Am. Chem. Soc.*, 1984, **106** 1141
30. O V Gritsenko, M I Mitkov, A A Bagatur'yants, V B Kazanskii *IV Mezhdunarodnyi Simpozium po Gomogennomy Katalizy: Tezisy Dokladov* (Abstracts of Reports at the IVth International Symposium on Homogeneous Catalysis), Vol. 1, Chernogolovka, 1984, p. 78
31. G B Bokii, G A Kukina *Kristallografiya* (Crystallography), Vol. 2, Izd. Nauka, Moscow, p. 400
32. J Chatt *Cationic Polymerisation and Related Complexes* (Edited by P H Plesh), Heffer, Cambridge, 1953, p. 40

33. I I Moiseev *π-Kompleksy v Zhidkofaznom Okislenii Olefinov* (π-Complexes in the Liquid-phase Oxidation of Olefins), Izd. Nauka, Moscow, 1970, 240 pp
34. S P Kolesnikov, N I Okhrimenko, O M Nefedov *Dokl. Akad. Nauk SSSR*, 1978, **243** 1193
35. I V Elev, B N Shelemov, V B Kazanskii *Kinet. Katal.*, 1987, **28** 409
36. L Bensze, A Kraut-Vass, L Prokai *J. Chem. Soc., Chem. Commun.*, 1985, 911
37. L Bensze, L Prokai *J. Organomet. Chem.*, 1985, **294** C5
38. L Bensze, V Kraust-Vass *J. Organomet. Chem.*, 1985, **280** C14
39. M Dziallas, H Werner *J. Organomet. Chem.*, 1987, **333** C29
40. J T Groves, G V Avaria-Neisser, K M Fish, et al. *J. Am. Chem. Soc.*, 1986, **108** 3837
41. E A Grigoryan *Usp. Khim.*, 1984, **53**(2) 347 [English translation in *Russ. Chem. Rev.*, 1984(2)]
42. R W Thies, P K Hong, R Buswell *J. Chem. Soc., Chem. Commun.*, 1972, 1091
43. P G Gassman, T J Atkins, F J Williams *J. Am. Chem. Soc.*, 1971, **93** 1812
44. N F Gol'dshleger, M B Tyabin, A E Shilov, A A Shteinman *Zh. Fiz. Khim.*, 1969, **43** 2174
45. A E Shilov, A A Shteinman *Kinet. Kataliz.*, 1977, **18** 1129
46. E A Grigoryan, Kh R Gyulumyan, F S D'yakovskii, I R Mullagaliev *Kompleksnye Metalloorganicheskie Katalizatory Polimerizatsii Olefinov* (Organometallic Complex Catalysts for the Polymerisation of Olefins), Vol. 4, Chernogolovka, 1977, p. 6
47. E A Grigoryan, Kh R Gyulumyan *Kompleksnyeni Metalloorganicheskie Katalizatory Polimerizatsii Olefinov* (Organometallic Complex Catalysts for the Polymerisation of Olefins), Vol. 8, Chernogolovka, 1980, p. 74
48. V A Yakovlev, I A Oreshkin, B A Dolgoplosk *Zh. Metalloorg. Khim.*, 1989, **2** 93
49. M Gree-Uchijima, J R Shapley, G M St. George *J. Am. Chem. Soc.*, 1986, **108** 1316
50. H Kletzin, H Werner, O Serhadli, M L Ziegler *Angew. Chem.*, 1983, **95** 49
51. M N Vargaftik, V P Zagorodnikov, I P Stolyarov, et al. *Dokl. Akad. Nauk SSSR*, 1985, **284** 896
52. M N Vargaftik, V P Zagorodnikov, I P Stolarov, et al. *J. Chem. Soc., Chem. Commun.*, 1985, 937
53. V P Zagorodnikov, M N Vargaftik *Kinet. Katal.*, 1986, **27** 851
54. M K Starchevskii, M N Vargaftik, O M Nefetov, I I Moiseev *Izv. Akad. Nauk, SSSR, Ser. Khim.*, 1980, 2427
55. S P Kolesnikov, T L Mitenina, O M Nefedov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 2303
56. G S Dosaeva, S M Velichko, Yu A Treger, I I Moiseev *IV Vsesoyuznaya Konferentsiya "Sovremennoe Sostoyanie i Perspektivy Razvitiya Teoreticheskikh Osnov Proizvodstva Khlororganicheskikh Productov" Tezisy Dokladov* (Abstracts of Reports at the IVth All-Union Conference "The Present State and Future Prospects for the Development of Theoretical Principles for the Production of Organochlorine Products"), Part 1, Baku, 1985, p. 179
57. J L Hubbard, W R McVicar *J. Am. Chem. Soc.*, 1986, **108** 6422
58. J-I Setsune, D Dolphin *Can. J. Chem.*, 1987, **65** 459
59. D Mansuy *Pure Appl. Chem.*, 1987, **59** 759
60. P J Brothers, J P Collman *Acc. Chem. Res.*, 1986, **19** 209
61. I Artand, N Gregoire, J-PBattioni, D Dupre, D Mansuy *J. Am. Chem. Soc.*, 1986, **110** 8714
62. Kh M Minachev, D A Kondrat'ev *Usp. Khim.*, 1983, **52**(12) 1921 [English translation in *Russ. Chem. Rev.*, 1983(12)]
63. V B Kazanskii *Kinet. Katal.*, 1987, **27** 47
64. V I Kondrat'ev (Editor) *Energii Razryva Khimicheskikh Svyazei. Potentsialy Ionizatsii i Srodstvo k Elektronu: Spravochnik* (Chemical Bond Energies. Ionisation Potentials and Electron Affinity: Handbook), Izd. Nauka, Moscow, 1974, 351 pp
65. G A Olah *J. Chem. Soc., Chem. Commun.*, 1986, 9
66. J Sommer *J. Chem. Soc., Chem. Commun.*, 1986, 1497
67. R A Olofson, S W Walinsky, J P Marino, J L Jernow *J. Am. Chem. Soc.*, 1968, **90** 6554
68. J Rooney, J K A Clarke, R Darcy, et al. *J. Chem. Soc., Chem. Commun.*, 1986, 425
69. R Hunter, G J Hutchings, W Pickl *J. Chem. Soc., Chem. Commun.*, 1987, 843
70. R Hunter, G J Hutchings, W Pickl *J. Chem. Soc., Chem. Commun.*, 1987, 1369
71. S D Hellring, K D Schwitt, C D Chang *J. Chem. Soc., Chem. Commun.*, 1987, 1320
72. R M Dessau *J. Catal.*, 1986, **99** 111
73. T A Stromnova, I N Busygina, S B Katser, et al. *Dokl. Akad. Nauk SSSR*, 1987, **295** 890
74. T A Stromnova, I N Busygina, S B Katser, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 1435
75. V Chime (Editor) *Catalysis in C_1 Chemistry* (Translated into Russian from English) (Edited by I I Moiseev), Izd. Khimiya, Leningrad, 1987
76. W Jones, R Schlogl, J M Thomas *J. Chem. Soc., Chem. Commun.*, 1984, 464
77. G A McDermott, A Mayr *J Am. Chem. Soc.*, 1987, **109** 580
78. M A Beno, J M Williams, M Tachikawa, E L Muetterties *J. Am. Chem. Soc.*, 1981, **103** 1485
79. I I Moiseev *Zh. Vses. Khim. Ova im D. I. Mendeleeva* 1982, **27** 309
80. A Asdar, C Lapinte *J. Organomet. Chem.*, 1987, **327** C33
81. H Berke, G Weller *Angew. Chem.*, 1982, **94** 135
82. G L Missler, S Kim, R G Angelici, R A Jacobson *Inorg. Chem.*, 1987, **26** 1690
83. G Erker, R Lecht, J L Petersen, H Bönnemann *Organometallics*, 1987, **6** 1962
84. H M Colquhour et al. (Editors) *New Pathways for Organic Synthesis*, Pergamon, New York–London, 1985, 431 pp
85. V Kirmse *The Chemistry of Carbenes* (Translated into Russian), Izd. Mir, Moscow, 1966, 320 pp