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The Reactions of Carbene Complexes of Transition Metals with Unsaturated Hydrocarbons

A.I.Syatkovskii and B.D.Babitskii

The influence of the structure of individual carbene complexes of transition metals on the rates and stereoselectivities of their reactions with unsaturated hydrocarbons are examined.
The bibliography includes 114 references.

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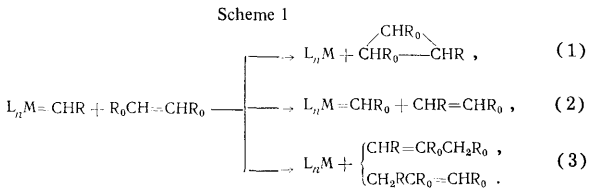
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I. INTRODUCTION

The carbene complexes of transition metals play a decisive role in complex catalytic processes involving the transformation of unsaturated hydrocarbons, such as the metathesis of cyclic and acyclic olefins,[1-6] the cometathesis of olefins with cyclopropanes,[7,8] and the polymerisation of alkynes,[9-11] and also in the formation of cyclopropanes from olefins on decomposition of aliphatic diazo-compound by transition metal salts.[12-15] The catalysts of these processes are as a rule multicomponent systems in which it is extremely difficult to determine the specific parameters of the active centres formed (the degree of oxidation of the metal, its ligand environment, the characteristics of the carbene ligand, etc.). The lack of such information significantly hinders the study of the reaction mechanism and hence prevents a purposeful search for more effective and stereoselective catalytic systems. On the other hand, the considerable progress achieved in the synthesis of a whole series of individual carbene complexes of transition metals, capable of reacting with unsaturated hydrocarbons or cyclopropanes, makes it possible to regard them as adequate models of the active centres in the catalytic processes enumerated above.

Depending on the nucleophilicity or the electrophilicity of the carbene ligand, the reactions of the carbene complexes with olefins can proceed via the following pathways; the conversion of the olefin into a cyclopropane derivative (1), the exchange of alkylidene fragments between the olefin molecule and the carbene complexes (2), and the addition of the carbene ligand to the olefin with formation of a set of new olefins (3):

Scheme 1



The aim of the present review is to discuss the influence of the structures of different carbene complexes on the rates and stereoselectivities of their reactions with olefins. We believe that it is useful to carry out such a survey because the existing reviews on the chemistry of carbene complexes of transition metals are devoted either to electrophilic[16-22] or nucleophilic[23] complexes which naturally precludes the analysis of reactions (1)-(3) from a single standpoint. Furthermore, in the communications enumerated above attention was concentrated on relatively stable carbene complexes for which reactions with unsaturated hydrocarbons are in general uncharacteristic.

This review deals with the reactions of only individual carbene complexes of transition metals and is not concerned with the problems associated with the possible mechanisms of the generation and role of such complexes in catalytic processes.

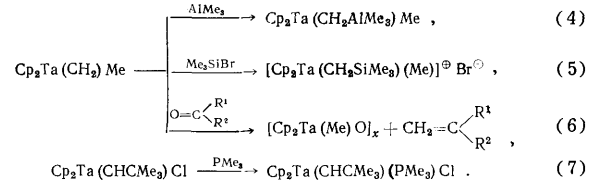
II. THE METAL–CARBON BOND IN ELECTROPHILIC AND NUCLEOPHILIC CARBENE COMPLEXES OF TRANSITION METALS

X-Ray diffraction and spectroscopic data have shown that in mononuclear complexes of the type $L_nM{=}C(X)Y$ (I) the carbene carbon is sp^2-hybridised, while the M, C, X, and Y atoms are usually located in a single plane.[16-23] The conventional subdivision of carbene complexes in terms of their chemical reactions into electrophilic and nucleophilic involves the consideration of a specific molecule in terms of the predominant contribution of the three possible resonance structures (II)-(IV):



(II) (III) (IV)

For example, the carbene ligand in the tantalum and niobium complexes enters into typical nucleophilic reactions and such complexes have come to be described in terms of the resonance structures (III) and (IV):[23-26]



Here



In the chemical reactions represented by Eqns.(4)–(6) the nucleophilic carbene complexes behave as analogues of ylides, such as, for example, the phosphonium ylides $R_3\overset{+}{P}-\overset{-}{C}H_2$ (where R = alkyl or aryl). Indeed reactions (4) to (6) can be compared with the analogous reactions of phosphonium ylides (the formation of adducts with electron-deficient boron and aluminium compounds, alkylation of ylides with formation of phosphonium salts, and the Wittig reaction respectively).[27]

In contrast to the tantalum complexes examined above, the pentacarbonylcarbene complexes of chromium, molybdenum, tungsten and also certain complexes of iron and rhenium react in conformity with the resonance structures (II) and (III).[28–31]

In electrophilic carbene complexes the attack by nucleophiles is on the carbene carbon atom and reactions (8)–(11) are to some extent similar to the reactions known for individual singlet carbenes†: the formation of ylides in the reactions with phosphines and amines, insertion in the metal–carbon bond, and the carbene–olefin isomerisation:[12,32,33]

$$(CO)_5W[C(OMe)Ph] \xrightarrow{LiPh} Li^{\oplus}\{(CO)_5W^{\ominus}-[C(Ph)_2OMe]\}, \quad (8)$$

$$(CO)_5W(CHPh) \xrightarrow{PPh_3} (CO)_5W[\overset{\oplus}{C}(H)(Ph)(\overset{\oplus}{P}Ph_3)], \quad (9)$$

$$[Cp(PPh_3)(NO)Re(CH_3)]^{\oplus} \xrightarrow{C_5H_5N} [Cp(PPh_3)(NO)Re(CH_2\cdot C_5H_5N)]^{\oplus}, \quad (10)$$

$$(CO)_5W[C(Me)Ph] \xrightarrow{\Delta} (CO)_5W[CH_2{=}CHPh]. \quad (11)$$

The phenomenological approach to the reactions of carbene complexes examined above is in many instances inapplicable despite its attractive simplicity. For example, it is obscure within the framework of this approach why the carbene ligand linked to an 18-electron centre in the complexes $(CO)_5W(CHPh)$, $(CO)_5Cr[C(OMe)Me]$, or $[Cp(CO)_2Fe(CH_2)]^+$ undergoes electrophilic reactions, while in the electron-deficient complexes of tantalum $Cl_2CpTa(CHCMe_3)$ and $Cp(PMe_3)_2(C_2H_4)Ta.(CHCMe_3)$ containing 14 and 16 electrons respectively in the valence shell of the transition metal the carbene species enters into nucleophilic reactions.[34] The treatment of nucleophilic carbene complexes as analogues of phosphonium ylides is particularly unsatisfactory, because these compounds react similarly only with fairly polar reagents (see Section IV). Furthermore, the representation of the carbene complexes by formulae (II)–(IV) makes it impossible to infer the strength with which the carbene is bound to the transition metal, which is one of the most important factors in the determination of the reaction pathway. For a correct interpretation of the reactivity of carbene complexes, it is necessary to analyse the nature of the bond between the transition metal and the carbene species.

The results of quantum-chemical calculations on carbene complexes by non-empirical[35,36] and semi-empirical[34,37,38] methods have shown that the carbene ligand is bound in the complex mainly as a result of the transfer of electrons from the σ orbital of the carbene carbon to the metal (σ-binding) and the reverse transfer of electron density from the highest occupied molecular orbital (HOMO) of the metal with the corresponding symmetry to the unoccupied $2p_z$ orbital of the carbene (π-binding).

In conformity with the perturbation theory, one can predict that the efficiency of the π-binding is determined by two factors. It is directly proportional to the square of the overlap integral between the HOMO of the metal and $2p_z$ orbital of the carbene and is inversely proportional to the difference between the energies of these orbitals.[34] Calculations for model methylene complexes of chromium, iron, and tantalum have shown that both factors promote the most effective π-binding in the case of tantalum, for which the highest population of the $2p_z$ orbital of the carbene ligand has been obtained.[34]

On the other hand, a semiempirical calculation for the $(CO)_5Cr[C(Me)OMe]$ molecule[37] and the experimental study of the EPR spectra of the radical-anions obtained on chemical reduction of this and similar complexes[39] show that in these compounds the lowest unoccupied molecular orbital (LUMO) of the complexes is almost entirely the $2p_z$ orbital of the carbene fragment, i.e. the π-binding in these complexes is minimal.

Thus the increase of the effectiveness of the π-binding increases the population of the $2p_z$ orbital of the carbene ligand and hence increases its nucleophilicity. Furthermore, an increase of the effectiveness of the π-binding is equivalent to an increase of the amount of double bond character of the linkage between the metal and the carbene carbon and should therefore be reflected in parameters such as the metal–carbon bond strength and the energy barrier to the rotation of the carbene around this bond in the complex. Experimental data permitting a comparison of the strengths of the metal–carbon bonds in electrophilic and nucleophilic carbene complexes are unfortunately lacking but nevertheless attention should be drawn to the fact that nucleophilic methylene, benzylidene, and neopentylidene complexes of tantalum are more stable in reactions involving the transfer of the carbene ligand than the corresponding electrophilic complexes of tungsten or iron. The possibility of the rotation of the carbene species around the metal–carbon bond in the complex has been studied experimentally[40–46] and with the aid of quantum-chemical calculations.[36,38,47,48] Apparently an increase of the nucleophilicity of the carbene ligand does indeed lead to an increase of the activation energy for rotation although even a semiquantitative estimate of the relative contributions of the electronic and steric interactions to the rotation barrier involves enormous difficulties.

The electron distribution in the carbene ligand and hence its reactivity depend also on the substituents attached to the carbene carbon. For electrophilic complexes, the influence of the nature of α-substituents at the carbene carbon atom on its reactivity can be illustrated by comparing different pentacarbonyl carbene Fischer complexes:

$$(CO)_5M{=}C\begin{matrix}ZR\\ \diagdown\\ R'\end{matrix} \quad (V)$$

where Z = O, N, or S, M = Cr, Mo, or W, and R, R' = alkyl or aryl.

In complexes (V) the presence of substituents capable of behaving as π-donors in the α-position relative to the carbene carbon leads to the transfer of electron density from the ZR group to the $2p_z$ orbital of the carbene, which is responsible for the appearance of partial double bond character in the linkage between the C_{carb} and Z atoms.[16–22] {An analogous effect has been observed also for the compound $[Cp(CO)_2Fe(CHPh)]^+$ and the existence of conjugation between the benzene ring and the carbene carbon in this complex has been demonstrated.[49]} The carbene ligand in the Fischer complexes remains an electrophilic centre, although the capacity of such complexes for reactions with nucleophiles is lower than that of the complexes $(CO)_5W(CHPh)$ and $(CO)_5W(CPh_2)$ which have a similar structure.[19,21,30,50,51]

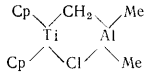
†The term singlet carbene is used to designate carbene species with zero spin regardless of whether in terms of free energy this is the ground state (CF_2; CCl_2) or the first excited state (CH_2; CHCOOMe).

The transfer of electron density to the carbene carbon in the complex $\{Cp(CO)(PPh_3)Fe[C(Me)OEt]\}^+$ is so great that the complex can react with nucleophiles as a carboxonium salt:[52]

$$\left[Cp(CO)(PPh_3)Fe{-}C(Me)(\overset{\oplus}{O}Et)\right] + I^{\ominus} \rightarrow EtI + Cp(CO)(PPh_3)Fe{-}C(Me)(O)$$

There are very few data concerning the influence of the substituents at the carbene carbon atom on the reactions of nucleophilic carbene complexes. It has been established[53,54] that, for a fixed ligand environment, the methylene, neopentylidene, and benzylidene complexes of tantalum and niobium differ only in the rate of addition of the carbene ligand to olefins, while the replacement of the ligands in the coordination sphere of the metal is reflected both in the rate of the reaction and in its regioselectivity (Section IV).

In discussing the influence of the substituents at the carbene carbon atom on the reactivity of the carbene complexes, it is necessary to note the existence of a group of nucleophilic complexes in which a kind of stabilisation of the carbene ligand is achieved as a result of the formation of adducts with organoaluminium compounds.[55-58] Among compounds of this kind, the methylene complex of titanium having the structure



(VI)

was studied in greatest detail.[55-57] The carbene ligand in these dinuclear complexes is of the bridge type and manifests nucleophilic properties in its reactions.[55,56] Complexes of type (VI) will be considered in Section IV.

The data described indicate that the nature of the transition metal and its ligand environment determine mainly the nucleophilic or electrophilic character of the chemical reactions of the carbene ligand in the complex, while the substituents in the α-position relative to the carbon atom influence only the relative reactivity without altering as a rule the overall reaction pathway.

In conclusion of this Section we shall return to the question of the legitimacy of representing the carbene complexes of transition metals by the resonance formulae (II)–(IV). The low barrier to rotation about the metal–carbon bond and the considerable polarisation of the latter as a result of the effective transfer of electron density to the metal atom (σ-binding) make it possible to describe fairly correctly the electrophilic carbene complexes by the resonance structure (II). In the nucleophilic carbene complexes the metal–carbon bond is formed as a result of two processes: the transfer of electron density to the metal (σ-binding) and the reverse transfer of electron density to the $2p_z$ orbital of the carbene ligand (π-binding). One can therefore assume that the distribution of electron density in the carbene ligand resembles that in a triplet carbene with a partly filled $2p_z$ orbital rather than distribution in a carbanion (as in phosphonium ylides[59,60]). Such biphilicity is manifested, in particular, in the ability of the carbene ligand in nucleophilic carbene complexes to interact effectively with the π-electron system in olefins (Section IV). Thus the description of nucleophilic complexes by formula (IV) is not entirely correct.

III. THE REACTIONS OF ELECTROPHILIC CARBENE COMPLEXES

Conversion into cyclopropane derivatives is the most typical reaction of the electrophilic carbene complexes with olefins. Like the reactions of free singlet carbenes with olefins, the process proceeds *cis*-stereospecifically.[18-21,29,61,62] Scheme 2 presents the products of the reactions of the benzylidene complexes of iron[62] and tungsten[29,61] with *cis*- and *trans*-but-2-enes and α-olefins;

Scheme 2

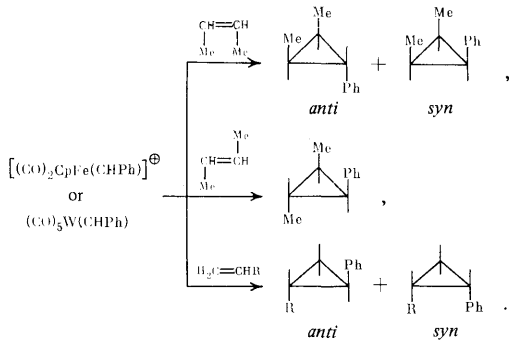


Table 1. The ratio of the *syn*- and *anti*-isomers of cyclopropanes produced in the reactions of $(CO)_5W(CHPh)$ [61] and $[Cp(CO)_2Fe(CHPh)]^+$ [62] with various olefins.

Olefins	$(CO)_5W(CHPh)$	$[Cp(CO)_2Fe(CHPh)]^{\oplus}$
Propene	1.8	7.8
But-1-ene	0.9	6.5
3-Methylbut-1-ene	0.36	4.6
Styrene	9.7	⩾100
cis-But-2-ene	41	>100
Cyclopentene	2.6	⩾200
2-Methylbut-2-ene	94	>50

During the process, there is no preliminary "ejection" of the carbene from the complex and, at least in the stage determining the stereoselectivity of the addition, the carbene remains bound to the transition metal.[18,21,63] The reactivity of the complexes, determined by the electrophilicity of the carbene ligand, varies within wide limits for different compounds. The most reactive complexes are those in which the carbene ligand contains no heteroatoms in the α-position relative to the carbene carbon: $(CO)_5W(CHPh)$, $[Cp(CO).(PPh_3)Fe(CHMe)]^+$, $[Cp(CO)_2Fe(CHPh)]^+$, $[Cp(CO)_2.Fe(CH_2)]^+$, etc. Even at −70 °C these complexes enable the corresponding cyclopropanes to be obtained from olefins in high yields.

The study of the reactions of the complex $[Cp(CO)_2.Fe(CH_2)]^+$ with olefins showed that olefins containing an electron-rich double bond of the type of that in ethyl vinyl ether are more reactive than but-1-ene or cyclohexene.[41] The relative reactivity series for olefins in the reaction with the complex $(CO)_5W(CHPh)$ has been obtained[61] and a satisfactory correlation has been observed with the analogous series for the reaction involving the formation of cyclopropane by free carbenes in the singlet state:[64,65]

$$\underset{\sim 0}{CH_2{=}CH_2} \ll \underset{1.0}{CH_2{=}CHCMe_3} < \underset{10.9}{CH_2{=}CHMe} \sim \underset{7.6}{MeCH{-}CHMe} \ll \underset{850}{MeCH{=}CMe_2} \ll \underset{3500}{CH_2{=}CMe_2} \quad (12)$$

The observed reactivity series for olefins shows that the rate of addition of the carbene ligand is determined in the first place by the charge on the most substituted carbon atom

in the olefin. This suggests that, in the transition state arising during the conversion of olefins into cyclopropanes by complexes of the type $(CO)_5W(CHPh)$, charge separation should take place, the excess positive charge being stabilised by the alkyl substituents at the most substituted carbon atom.[61] All these results not only emphasise the electrophilic character of the carbene ligand in the cyclopropane formation reaction but also reveal the similarity of the mechanisms of the reactions of electrophilic carbene complexes and free singlet carbenes with olefins.

When there are no coordination vacancies in the electrophilic complex at the metal atom, the LUMO of the complex is localised at the carbene ligand. The interaction of this complex with an olefin apparently proceeds analogously to the interaction of singlet carbenes with olefins—as electrophilic attack by the unoccupied $2p_z$ orbital of the carbene on the π-electron system of the olefin with formation of cyclopropanes.[66,67]

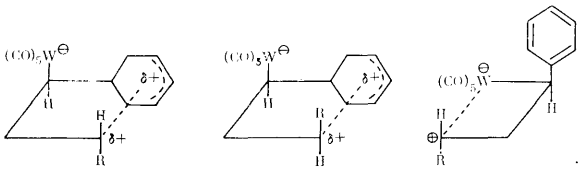
More detailed information about the mechanism of the interaction of the electrophilic complexes with olefins is provided by the study of the influence of the nature of the reactants on the ratio of the *syn*- and *anti*-isomers in cyclopropanes—the reaction products (Scheme 2). Certain results have been taken from the literature[61,62] and are presented in Table 1, which shows that the iron complex gives rise in all cases to higher ratios of the *syn*- and *anti*-isomers of cyclopropanes, but the character of the variation of the stereoselectivity as a function of the structure of the olefin is identical for the two complexes studied. Furthermore, it is possible to identify the following features:

(a) among the products of the interaction of olefins with the above complexes the thermodynamically unfavourable *syn*-isomer is formed predominantly in most cases;

(b) an increase of the steric volume of the alkyl substituents at the double bond in α-olefins decreases the fraction of the *syn*-isomer.

In order to explain the results, a mechanism has been proposed[61] involving the possibility of the stabilisation of the positive charge in the intermediates (VII) and (VIII) by the π-electron system of the benzene ring; the intermediate (VII), leading to the formation of the syn-isomer, is energetically more favourable than the intermediate (VIII), since there is no steric repulsion between the R and $W(CO)_5$ groups in it.

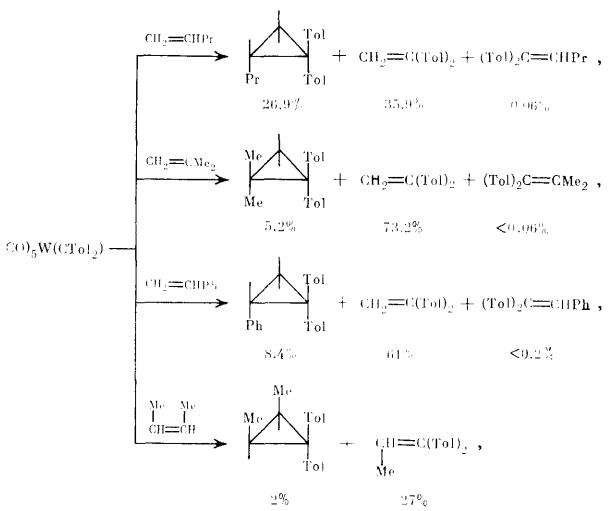
An increase of the steric volume of the substituent R in the olefin decreases the role of the stabilisation by the π-electrons of the benzene ring and the process can proceed via intermediates of type (IX) whose formation is controlled by the difference between the free energies of the reaction products.



(VII) (VIII) (IX)

Experimental confirmation of this hypothesis has been obtained.[62] It has been shown that, on passing from $[Cp(CO)_2Fe(CHPh)]^+$ to the complex $\{Cp(CO)_2Fe[C(H).(p\text{-}CH_3C_6H_4)]\}^+$, which has an electron-donating substituent in the ring, the ratio of the *syn*- and *anti*-isomers in the products of addition to propene increases from 7.8 to 10.0. It is noteworthy that the concept of the stabilisation of the positive charge in the transition state in the cyclopropane formation reaction by the benzene ring had been put forward earlier by Closs and Moss to account for the tendency towards the preferential formation of the *syn*-isomers in the reactions of phenylcarbenes, generated in different ways, with but-1-ene, *cis*-but-2-ene, and 2-methylbut-2-ene.[68-70] Other factors promoting the formation of the *syn*-isomer can probably also exist. It has been established that the reactions of $[Cp(CO)_2Fe(CHMe)]^+$ with styrenes and cyclo-octene result in the formation of cyclopropanes in which the ratios of the *syn*- and *anti*-isomers are 4.7 and >4.5 respectively.[46] On the basis of the analogy with the reactions of free singlet carbenes, one can assume, for example, that the *syn*-disposition of the substituents in the transition state (or the intermediates) favours a more effective charge transfer from the HOMO of the olefin to the LUMO of the carbene.[66,71,72]

If the electrophilicity of the carbene ligand in the complex is reduced as a result of the substituents in the α-position relative to the carbene carbon [this is characteristic, for example, of the Fischer complexes (V)], then its reactivity in relation to olefins diminishes. The dissociation of the metal–carbon bond in such complexes and the transfer of the carbene ligand to the olefin take place at temperatures above 50 °C.[18-21,30,51] However, at the temperatures indicated it is necessary to reckon with the dissociation of the initial compound to form CO and a coordination-unsaturated carbene complex,[19,21,61,73] which leads to a new pathway in the reactions with olefins. Thus ditolylcarbenepentacarbonyltungsten (X) reacts with olefins at ~70 °C to form cyclopropanes and the products of the exchange of the alkylidene fragments.[51,74]



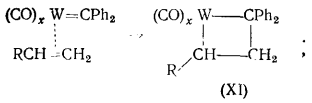
where Tol = *p*-Me–C_6H_4.

The following series of relative reactivities of olefins in relation to complex (X) has been established:[74]

$$\underset{49.5}{CH_2{=}CHPr} > \underset{10.4}{CH_2{=}CMe_2} > \underset{1.0}{MeCH{=}CHMe} > \underset{\sim 0}{MeCH{=}CMe_2}\ .$$

To a first approximation, this series agrees with the relative thermodynamic stabilities of transition metal complexes of olefins[75] but is the reverse of series (12) of the relative reactivities of olefins in the reactions with $(CO)_5W(CHPh)$.

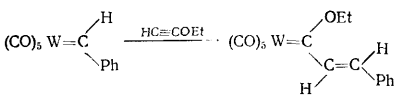
The experimental data obtained agree best with the following scheme: owing to the dissociation of the initial complex during the reaction, a coordination vacancy appears at the metal atom and the reaction with olefins can proceed via a metallacyclobutane intermediate of type (XI):



(XI)

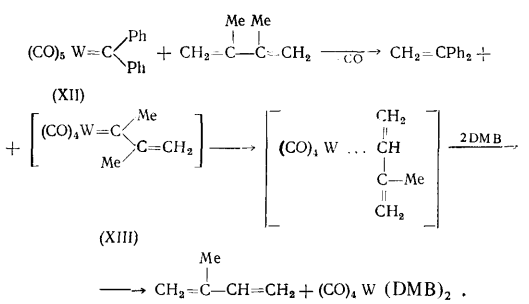
its decomposition in fact leads to the formation of the products of the exchange of alkylidene fragments. Later studies showed that the ratio of the products of the transalkylidenation reaction and the cyclopropanes in the reactions of compound (X) with olefins is independent of the carbon monoxide pressure in the system[73] and cyclopropanes are apparently formed in this instance also via the intermediate (XI). The possibility of the preliminary abstraction of one of the CO groups in the carbene complex apparently arises also in the reactions of the Fischer complexes (V) with olefins containing electron-accepting groups.[21]

Electrophilic carbene complexes can react with acetylenes,[61] dienes,[76,77] and cyclopropanes[78] and the above compounds behave similarly to olefins. For example, the complex $(CO)_5W(CHPh)$ enters into the transalkylidenation reaction with ethoxyacetylene, which behaves as a cyclo-olefin with a ring of "zero" size:[61]



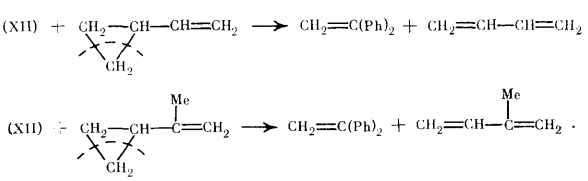
The complexes $(CO)_5W(CPh_2)$ and $(CO)_5W[C(Me)Ph]$ react analogously with ethoxyacetylene.

Diphenylcarbenepentacarbonyltungsten (XII) reacts with 2,3-dimethylbuta-1,3-diene (DMB) in accordance with the following scheme:[76,77]



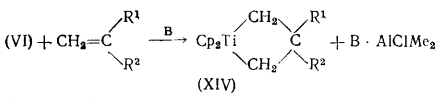
(XIII)

In the first stage the alkylidene fragments are exchanged between complex (XII) and DMB, which results in the formation of 1,1-diphenylethylene and the carbene complex (XIII). The second stage of the reaction consists of the carbene–olefin isomerisation in the intermediate carbene complex (XIII) with formation of an isoprene molecule [cf. Eqn.(11)]. At ~90 °C the same complex (XII) is capable of demethylenating three-membered carbon rings,[78] which can be regarded as a kind of metathesis reaction of cyclopropanes:[7,8,79]



IV. THE REACTIONS OF NUCLEOPHILIC CARBENE COMPLEXES

The difference in the nature of the carbene species in nucleophilic complexes with transition metals and in complexes with phosphines is manifested most clearly in the reactions with olefins having a non-polarised or a weakly polarised double bond. Phosphonium ylides do not react with such olefins, whereas two reaction pathways have been observed for nucleophilic carbene complexes: the exchange of the alkylidene fragments (2) and the addition of the carbene ligand to the olefin with formation of new olefins (3). It has been suggested that both these reactions proceed via a four-centre transition state with formation of intermediates of the metallacyclobutane type. Sometimes it is possible to isolate and characterise such a metallacyclobutane (XIV):[80,81]



(13)

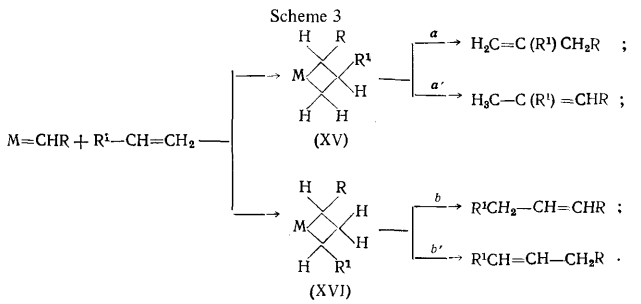
(XIV)

R^1 = t-Bu, R^2 = H; R^1 = iso-Pr, R^2 = H; R^1 = Ph, R^2 = H; $R^1 = R^2$ = H; $R^1 = R^2$ = Me; B = Lewis base.

As a rule, the metallacyclobutane formed decomposes rapidly and its structure can be inferred only on the basis of the reaction products.

Electron-deficient nucleophilic complexes of tantalum and niobium react with α-olefins to form a set of new olefins.[23,53,54,82–84] A reaction of this type has been studied in greatest detail for the tetrahedral complex $CpCl_2Ta(CHCMe_3)$[83,84] and also for several octahedral complexes of tantalum and niobium having the general formulae $L_2Cl_3M(CHCMe_3)$ and $L_2Cl_3M(CHPh)$, where M = Ta or Nb and L = PPh_3, PPh_2Me, or $PPhMe_2$.[53,54] Four different olefins can be formed in the general case as a result of the reaction:

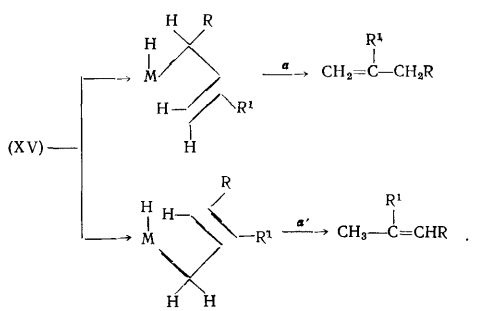
Scheme 3



(XV) (XVI)

The ratios of the olefins depend on the structure of the carbene complex and the olefin (Table 2).

The reaction products *a*, *a'*, *b*, and *b'* are formed as a result of β-elimination in the metallacyclobutanes (XV) and (XVI) with subsequent addition of a proton to the α- or α'-position in the metalla-ring.[54,82–84] For example, products *a* and *a'* are formed as follows in the decomposition of the metallacyclobutane intermediate (XV):



(14)

The ratio of the contributions of the pathways $(a + a')/(b + b')$ depends only slightly on the initial carbene complex and the olefin, which indicates the absence of an explicit preference for the formation of the intermediate (XV) or (XVI). Thus

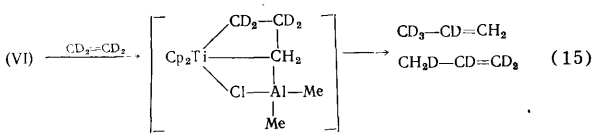
the hypothesis, put forward initially by McLain and co-workers,[82-84] that the polarisation of the metal–carbon bond in the carbene complexes of tantalum and niobium has a decisive influence on the regioselectivity of their reactions with α-olefins has not been confirmed.

Table 2. Composition of the products of the reactions (as percentages) of the neopentylidene and benzylidene complexes of tantalum with ethylene, propene, and styrene.[54]

Olefin	*a*	*a'*	*b*	*b'*
	$(PMe_3)_2Cl_3Ta(CHPh)$			
Ethylene	—	—	73	27
Propene	49	21	4	26
Styrene	5	49	46	
	$(PMe_3)_2Cl_3Ta(CHCMe_3)$			
Ethylene	—	—	7	93
Propene	8	42	7	43
Styrene	6	35	30	29

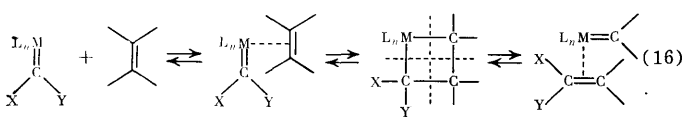
Note. Pathways *a* and *b'* and also pathways *a'* and *b* are equivalent for ethylene.

The reaction involving the transfer of the carbene ligand to ethylene with formation of new olefins has also been observed for complex (VI)[55,56] and the distribution of the deuterium label in the reaction products supports the following reaction mechanism:

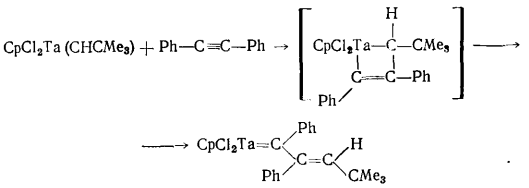


(15)

If the pathway, discussed above, leading to the decomposition of the metallacyclobutane intermediate via β-elimination is ineffective (the simplest case obtains when there are no protons at the β-carbon atom), then the metallacyclobutane formed can again decompose reversibly into a metal–carbene-olefine complex. The decomposition of the metallacyclobutane can proceed in principle in two ways, which leads to the possibility of the exchange of alkylidene fragments between the transition metal and the olefin:


(16)

For example, it has been established that complex (VI), which effects the irreversible transfer of the methylene ligand to ethylene [reaction (15)] on interaction with isobutene or methylene cyclohexane, exchanges the methylene group with these olefins. If a mixture of isobutene and labelled [^{13}C]methylenecyclohexane is used, then in the presence of complex (VI) the label is distributed between both olefins.[56,57] Another example involves the carbene complex $CpCl_2Ta(CHCMe_3)$, which reacts with ethylene or styrene exclusively in accordance with Eqn.(3). On interaction with diphenylacetylene, the complex gives rise to a kind of transalkylidenation reaction, which proceeds via a metallacyclobutane intermediate:[23,84]:



The absence of protons at the β-carbon atom in the metallacyclobutane intermediate is the simplest but not the only factor promoting the transalkylidenation reaction. It is known that, by altering the ligand environment of the metal atom in the complex, it is possible to influence the effectiveness of the β-elimination reaction.[85] It has been shown[54,86] that the relative reactivity in the β-elimination of hydrogen in alkyl compounds of tantalum and niobium is reduced when ligands such as tetrahydrofuran, pyridine, or alkoxy-groups are present in the coordination sphere of the metal, the effect being particularly pronounced in the last instance.

The introduction of the ligands enumerated above into the coordination sphere of the carbene complexes of niobium and tantalum reduces the relative rate of decomposition of the metallacyclobutane intermediate via β-elimination, which increases the yield of the products of the transalkylidenation reaction:[53,54]

$$\underset{\text{(XVII)}}{(PMe_3)_2Cl_3Nb(CHCMe_3)} + CH_2{=}CH_2 \rightarrow \underset{7\%}{CH_2{=}CHCH_2CMe_3} + \underset{93\%}{Me{-}CH{=}CH{-}CMe_3} \quad (17)$$

$$\underset{\text{(XVIII)}}{(THF)_2Cl_3Nb(CHCMe_3)} + CH_2{=}CHEt \rightarrow \underset{73\%}{CH_2{=}CHCMe_3} + \begin{cases} Pr{-}CH{=}CH{-}CMe_3 \\ Et{-}CH{=}CH{-}CH_2CMe_3 \end{cases}\ \underset{17\%}{} \quad (18)$$

$$\underset{\text{(XIX)}}{(PMe_3)(OCMe_3)_2ClNb(CHCMe_3)} + CH_2{=}CHEt \rightarrow \underset{86\%}{CH_2{=}CHCMe_3} + \underset{6\%}{Me_3CCH{=}CHEt} \quad (19)$$

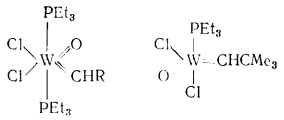
It follows from Eqns.(17)–(19)# that the reaction of complex (XVII)with ethylene proceeds as the transfer of the carbene ligand to the olefin with formation of a set of new olefins, while complex (XIX) undergoes highly selectively the transalkylidenation reaction with t-butoxy-groups: complex (XVIII) is an example of a compound capable of reacting with olefins via both pathways simultaneously. An analogous effect has also been observed for tantalum complexes.[53,54]

The study of the composition of the products of the reactions of neopentylidene complexes of niobium and tantalum with but-1-ene and *cis*-pent-2-ene showed that the relative contribution of the transalkylidenation reaction is greater in the second case.[54] The results obtained suggest that the β-elimination reaction is more probable for α,α'-substituted metallacyclobutanes than for the α,β,α'-substituted derivatives.

Some of the complexes discussed above are capable not only of transferring the initial carbene ligand but also of propagating the kinetic chain in the metathesis reaction. For example, in the metathesis of *cis*-pent-2-ene in the presence of the complex $(PMe_3)Cl(OCMe_3)_2.Nb(CHCMe_3)$, 29 equivalents of but-2-ene and 34 equivalents of hex-3-ene are formed in 24 h per equivalent of the complex. At the same time effective *cis–trans* isomerisation of the initial *cis*-pent-2-ene takes place until the attainment of the composition corresponding to thermodynamic equilibrium.[54]

#Only the main products of the reactions of the initial neopentylidene complexes with olefins are presented in Eqns.(17)–(19).[54]

The formation of the products of the β-elimination of metallacyclobutanes in the course of the reaction with olefins has been observed to some extent for all the carbene complexes of niobium or tantalum (with the exception of the complexes containing the t-butoxy-ligands[53,54]) and for this reason the nucleophilic oxoalkylidene complexes of tungsten (XX) and (XXI), which react with olefins exclusively via the metathesis pathway, are of very great interest:[53,87,88]



(XX) (XXI)

R = H (a); Me (b); Et (c); Ph (d); or CMe_3 (e).

According to the data of Wengrovius et al.,[87] complexes (XX) interact with olefins fairly slowly, but their reactivity in the transalkylidenation reaction can be significantly increased by introducing Lewis acid such as $AlCl_3$, $AlEtCl_2$, $SnCl_2$, etc. as additives to the reaction medium. Complex (XXI) is reactive also in the absence of additives and the initial rate of the transalkylidenation of olefins in the presence of complex (XXI) is equal to the initial rate of the same reaction in the presence of the catalytic system (XXe) + $AlCl_3$.[87] This enabled the authors to postulate that complex (XXI) behaves as an active centre, which effects transalkylidenation also in the (XXe) + $AlCl_3$ binary systems§.

In the reactions of complex (XX) and (XXI) with olefins, it is possible to characterise not only the olefins produced as a result of the transfer of alkylidene fragments but also the carbene complexes formed in the course of the transalkylidenation. For example, the interaction of the neopentylidene complex (XXe) with *cis*-pent-2-ene leads to the formation of approximately equivalent amounts of 2,2′-dimethylhex-3-ene and 4,4′-dimethylpent-2-ene and the corresponding carbene complexes (XXb) and (XXc). On the other hand, in the reaction of complex (XXe) with but-1-ene the only product of the transalkylidenation reaction of the initial complex is 3,3′-dimethylbut-1-ene, while the other possible product, namely 2,2′-dimethylhex-3-ene, was not detected.[87]

The cyclopropane formation reaction, which is most characteristic of electrophilic carbene complexes, has not been observed for nucleophilic carbene complexes of tantalum, niobium, or tungsten. Only one example of the cyclopropane formation reaction is known for the nucleophilic complexes, namely the titanium complex (VI) reacts with isobutene to form 1,1′-dimethylcyclopropane in ~2% yield.[55] It has been established that the fraction of cyclopropanes formed in this reaction increases in the following sequence: ethylene < propene < isobutene; it also increases with the polarity of the solvent employed. A similar reactivity series has been observed for the reactions of electrophilic complexes with olefins [reactions (12)]. It is therefore possible to postulate that the cyclopropane formation reaction involving the titanium complex (VI) proceeds without the formation of a metallocyclobutane intermediate. The fact that the individual compounds $Cp_2\overline{Ti-CH_2-CHR-CH_2}$ (R = t-Bu or iso-Br) do not yield even traces of cyclopropane on decomposition can serve as confirmation of this hypothesis.[80] It is noteworthy that the absence of cyclopropanes from the products of the reactions of nucleophilic carbene complexes with olefins does not imply that this pathway in the decomposition of metallacyclobutanes is in principle impossible (see Section V).

V, THE PATHWAYS IN THE REACTIONS OF CARBENE COMPLEXES OF TRANSITION METALS WITH OLEFINS

Comparison of the reactions of free carbenes and the carbene complexes of transition metals with olefins shows that complex formation not only alters the reactivity of the carbene species but also leads to the appearance of two new reaction pathways: transalkylidenation (2) and the addition of the carbene to the olefin with formation of new olefins (3). The appearance of these specific reactions, which are not characteristic of free carbenes, has been attributed to the ability of the transition metal atom in the carbene complex to coordinate an olefin molecule with subsequent formation of a metallacyclobutane intermediate [reaction (15)].

The results of Hoffmann's semiempirical calculations show that the energy barrier to the formation of metallacyclobutanes¶ from the carbene complex and an olefin is reduced with increase of the positive charge on the metal.[89] This conclusion agrees well with the experimental finding that metallacyclobutane intermediates are formed preferentially precisely in the interaction of nucleophilic carbene complexes with olefins (see Section IV).

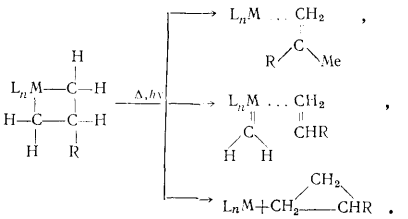
The energy profile of reaction (16) of certain methylene complexes of chromium, molybdenum, tungsten, and titanium with ethylene has been calculated non-empirically.[35,90,91] The free energy of formation of the metallacyclobutane ΔG for the compound $Cl_2Ti(CH_2)$ is -34.5 kcal mol^{-1},[90] which agrees well with the formation of stable metallacyclobutanes (XIV) in the reaction of the titanium complex (VI) with olefins [reaction (13)].[80,81] For the complexes $Cl_4M(CH_2)$, where M = Cr, Mo, or W, $\Delta G > 0$ and diminishes from 25 to 10 kcal mol^{-1} on passing from chromium to tungsten. The results of the calculations show that the free energy of formation of the metallacyclobutane intermediate can depend significantly not only on the nature of the metal but also on its ligand environment. For example, when two chlorine atoms are replaced by the oxo-ligand in the methylene complexes of Group VI metals, the formation of the metallacyclobutane is favoured by energy factors ($\Delta G \cong -20$ kcal mol^{-1}).[35]

The metallacyclobutane intermediate formed can decompose in different ways, which ultimately determines the direction of the entire reaction of the carbene complexes with olefins. The fact that the individual metallacyclobutane complexes of transition metals yield in the general case on photolytic decomposition the same compounds whose formation is to be expected in the reactions of the corresponding carbene complexes with olefins (Schemes 1 and 4) may serve as confirmation of this concept:

§ A possible mechanism of the activating influence of Lewis acids in such systems has been examined by J.Kress, M.Wesolek, J.P.Le Ny, and J.A.Osborn, Chem.Comm., 1981, 1039.

¶ According to Hoffmann's data,[89] the energy minimum corresponds to a four-centre structure with a distorted metallacyclobutane geometry, which is evidently a consequence of the approximation introduced by Rappé and Goddard.[90]

Scheme 4



(20)

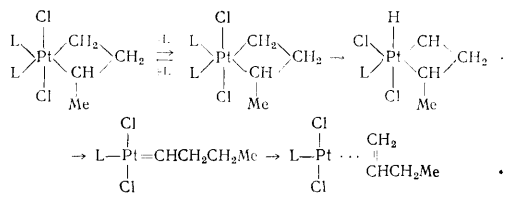
(21)

(22)

In this Section we shall attempt to analyse the factors promoting a particular pathway in the decomposition of metallacyclobutanes presented in Scheme 4.

In the metallacyclobutane intermediates arising in the reactions of nucleophilic carbene complexes of tantalum, niobium, or titanium with olefins, the formation of the products of the decomposition to the metal–olefin complex [reaction (20)] is regarded as a two-stage process involving β-elimination in the metallaring [reaction (14)]. The β-elimination reaction is characteristic to some extent of any mono- or di-alkyl compounds of transition metals[85,92,93] and experimental data confirm the possibility of its occurrence in metallacyclobutanes.[56,94–97]

The mechanism of reaction (20) has been studied in detail for individual metallacyclobutane complexes of platinum(IV).[97–101] It was found that, apart from the decomposition via β-elimination discussed above, this reaction can proceed via α-elimination in the metallacyclobutane with subsequent carbene–olefin isomerisation:[98,100,101]



where L = pyridine, 2-methylpyridine, or 2,6-dimethylpyridine.

Furthermore, the study of the distribution of the deuterium label in the decomposition products

$$(Py)_2Cl_2\overline{Pt[-trans\text{-}CH(Me)-CH(Me)-CD_2]}$$

and

$$(Py)_2Cl_2\overline{Pt-[-CH(Me)CMe_2CD_2]}$$

showed that the decomposition via α-elimination is the dominant process in such cases.[100] At the present time it is difficult to estimate the degree of general validity of the conclusion reached by Ling and Puddephatt,[100] but evidently the possibility of α-elimination must be taken into account in considering the rearrangements of metallacyclobutane intermediates.

The decomposition of the metallacyclobutane to the metal–carbene–olefin complex (21) leads to the formal reduction of the metal atom†, which imposes a limitation on the scope of the process: the metathesis decomposition of 18-electron compounds requires a preliminary change in the electron environment of the metal in the complex.

†The authors used Hoffmann's approach in which the alkylidene ligand is regarded as a neutral species.[34,89]

In the study of the mode of decomposition of 18-electron metallacyclobutane complexes of platinum having the general formula

$$L_2X_2\overline{Pt-CH_2-CH_2-CH_2}$$

(where X = Cl, or Br; L = TMED, bipy, or phen), it was established that the formation of ethylene is due to the possibility of the dissociation of the initial compound at the metal–halogen bond in a sufficiently polar solvent.[102] When the initial platinacyclobutane is a 16-electron complex of the type

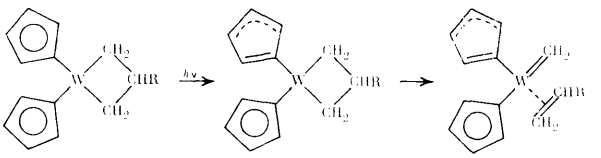
$$L_2\overline{Pt-CH_2-CH_2-CH_2}$$

[where L = PPh_3, $P(Alk)_3$, or bipy], its decomposition in this instance into ethylene and a methylene complex of platinum can be readily achieved in solvents of low polarity.[103]

It has been established that, regardless of the method of decomposition (thermolysis of photolysis), the main products of the reactions of 18-electron metallacyclobutane complexes of tungsten

$$Cp_2\overline{W-CH(R)CH(R)-CH_2}$$

are olefins obtained on decomposition to the metal–olefin complex (20). On the other hand, the decomposition to the metal–carbene–olefin complex takes place only on photolysis of the initial complexes, which is associated with the following chain of transformations via a 16-electron intermediate:[104,105]



(18$\bar{6}$) (16$\bar{6}$) (18$\bar{6}$)

The concerted decomposition of metallacyclobutanes with formation of cyclopropanes [Eqn.(22)] is a typical reductive elimination reaction.[106,107] Analysis of the change in the populations of the frontier orbitals in the decomposition of metallacyclobutanes, carried out by Hoffmann and co-workers, demonstrated the existence of an energy barrier, in terms of symmetry, for reactions (21) and (22): for the d^0–d^4 configurations of the metal in metallacyclobutane, decomposition to the metal–carbene–olefin complex takes place preferentially, while for the d^6 configuration the preferred reaction is reductive elimination with formation of cyclopropanes.[89] This conclusion is in good agreement with experimental data. In the decomposition of the metallacycles

$$Cp_2\overline{W-CH(R^1)CH(R^2)CH_2}$$

(R^1, R^2 = H or Me)[104,105] and

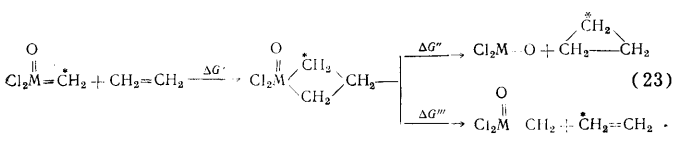
$$Cp_2\overline{Ti-CH_2-CHR-CH_2}$$

(R = iso-Pr or t-Bu),[80] there are virtually no cyclopropanes among the reaction products, while the metallacyclobutane complexes of quadrivalent platinum give rise fairly readily to a compound with a three-membered carbon ring on thermolysis and photolysis. It has been demonstrated[107] in relation to the deuterium-labelled complexes

$$Py_2Cl_2\overline{Pt-CH(R')CH(R^2)\cdot CH(R^2)}$$

(R = H, D, or Alk) that cyclopropanes are formed as a result of the concerted dissociation of the metal–carbon bonds, although the observed influence of solvent polarity on the rate and selectivity of reaction (22) indicate the possibility of a slight charge separation in the transition state.

The mode of decomposition of the metallacyclobutane intermediate depends not only on the characteristics of the electronic structure of the initial complexes examined above but can be determined to a large extent also by the stability of the final reaction products. The thermodynamic assessment of the preference for a particular decomposition pathway involves the determination of the free energies of all the components and it is wrong to the attempt the prediction of the equilibrium ratio of olefins and cyclopropanes on the basis of the free energies of these compounds,[108] as has been justifiably stated by Grubbs.[109] Indeed a non-empirical calculation of the potential surfaces for the cyclopropane formation and transalkylidenation reactions showed that the relative contributions of the two pathways are determined primarily by the transition metal and its ligand environment[35,91] (Table 3).



(23)

Table 3. Calculated free energies of formation and decomposition of the metallacyclobutane intermediates in the transalkylidenation and cyclopropane formation reactions[35] (kcal mol^{-1}).

M	$-\Delta G'$	$\Delta G''$	$\Delta G'''$
Cr	20	−2	20
Mo	24	42	24
W	18	43	18

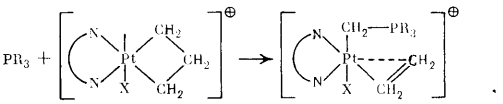
It follows from the data in Table 3 that, on passing from the chromium complex to the molybdenum and tungsten complexes, the metathesis pathway leading to the decomposition of the metallacyclobutane becomes energetically preferable to the decomposition with formation of cyclopropanes, which is associated with the increasing stability of the metal–carbon bond in the carbene complexes of molybdenum and tungsten.

The results of the calculations agree well with the experimental observation of the high strength of the binding of the carbene in the oxoalkylidene complexes of tungsten (XX) and (XXI),[110,111] which undergo the transalkylidenation reaction with olefins with a high degree of selectivity (Section (IV). The occurrence of the transalkylidenation reaction also when Mn^+CH_2 reacts with ethylene propene, and isobutene in the gas phase[113] has been explained by the presence of strong metal–carbon bonds ($E_b \approx 94$ kcal mol^{-1} [112,113]).

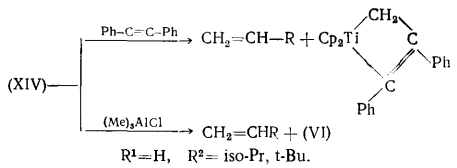
Thus, if there is competition between the two pathways (transalkylidenation and cyclopropane formation) for the carbene complex in the reaction with an olefin, then an increase of the strength of the metal–carbon bond leads to an increasing role of the former. An unusual experimental confirmation of the concept described is provided by data for the decomposition of metallacyclobutanes in the presence of compounds which stabilise the carbene complex in one way or another. For example, the yield of ethylene, the product of the metathesis decomposition of

$$L_2X_2Pt{-}CH_2{-}CH_2CH_2$$

(L = TMED, Py, or bipy; X = Cl, Br, or I), increases sharply in the presence of trialkylphosphines,[102] which is apparently associated with the formation, in the course of the reaction, of ylide-like structures containing a stabilised methylene ligand (the possibility of such stabilisation has been demonstrated[114]):



It has been established[80] that, in the presence of tolane and dimethylaluminium chloride, the complex (XIV) undergoes highly selective metathesis decomposition:



Evidently in this case too the mode of decomposition is determined by the possibility of the formation of stable complexes containing a stabilised carbene ligand.

Examination of the reactions of individual carbene complexes of transition metals with unsaturated hydrocarbons shows that the change in the reaction pathway is caused in the first place by the electron distribution in the carbene ligand in the complex. Strongly electrophilic complexes such as $(CO)_5W(CHPh)$ or $[Cp(CO)_2Fe(CHR)]^+$ (R = H, Me, Ph) react with olefins exclusively with formation of cyclopropanes. The absence of coordination vacancies at the transition metal atom and the presence of the highly electrophilic $2p_z$ orbital in the carbene carbon in the complex gives rise to the similarity of the chemical reactivity of such complexes to those of free singlet carbenes.

Fischer complexes are electrophilic complexes in which the electrophilicity of the carbene ligand has been reduced as a result of the presence of electron-donating substituents in the α-position. The reactivity of such complexes depends significantly on the possibility of the formation of coordination vacancies at the transition metal. If the reaction conditions are such that coordination vacancies are not formed, then the Fischer complexes react with olefins like the complexes $(CO)_5W(CHPh)$ and $[Cp(CO)_2Fe(CHR)]^+$ examined above, although the relative reactivity of the Fischer complexes is much lower.

The possibility of the formation of coordination vacancies at the metal atom leads to the occurrence of a specific transalkylidenation reaction which is uncharacteristic of free carbenes and which reflects the capacity of the carbene complex to react with olefins via a metallacyclobutane intermediate. However, studies of the reaction of $(CO)_5W(CPh_2)$ with olefins have shown that in this case too the transalkylidenation is accompanied by the formation of a fairly large amount of cyclopropanes. Presumably the competition between the two decomposition pathways of the metallacyclobutane intermediate is caused by the impossibility of the formation in the electrophilic carbene complex of a strong metal–carbon bond, which is one of the main factors promoting the metathesis decomposition of the metallacyclobutane.

Nucleophilic carbene complexes react with olefins via the formation of metallacyclobutane intermediates. In the case of typical nucleophilic complexes such as $Cp_2Ta(CH_2)Me$ or $(PMe_3)_2Cl_3Ta(CHR)$ (R = Ph or CMe_3) the main pathway in the decomposition of metallacyclobutane intermediate is

β-elimination of a proton; as a result of reactions of such complexes with olefins, the carbene ligand is transferred to the olefin with formation of a set of new olefins.

When electron-donating ligands are introduced into the coordination spehre of the metal in nucleophilic complexes of tantalum and niobium, a decrease of the polarisation of the metal–carbon bond is to be expected. The relative role of β-elimination in the metallacyclobutane then diminishes and transalkylidenation becomes the main pathway in the reactions with such olefins. The oxoalkylidene complexes of tungsten (XX) and (XXI), which undergo a highly selective transalkylidenation reaction with olefins, also belong to nucleophilic complexes with a comparatively weak polarisation of the metal–carbon bond.

Thus, whereas the cyclopropane formation reaction and the reaction involving the transfer of the carbene ligand with formation of new olefins are characteristic of complexes with an appreciable polarisation of the metal–carbon bond, the transalkylidenation reaction is observed for complexes in which the metal–carbon bond is weakly polar.

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All-Union Lebedev Synthetic
Rubber Institute, Leningrad