

Concerted [2+2] Oxidative-Cycloaddition-Cycloreversion versus Cyclopropanation Reactions at M-carbene Center

Mitan Carmen-Irena^{1, 2}

¹Department of Organic Chemistry, Institute of Organic and Supramolecular Chemistry “C. D. Nenitescu”, Bucharest, Roumania

²Department of Chemistry, University of Illinois at Chicago, Chicago, US

Email address:

cmitan@yahoo.com

To cite this article:

Mitan Carmen-Irena. Concerted [2+2] Oxidative-Cycloaddition-Cycloreversion versus Cyclopropanation Reactions at M-carbene Center. *Science Journal of Chemistry*. Vol. 11, No. 3, 2023, pp. 108-136. doi: 10.11648/j.sjc.20231103.14

Received: May 20, 2023; Accepted: June 13, 2023; Published: June 27, 2023

Abstract: The selectivity of olefin metathesis catalyzed by metal-alkylidene $\text{LnM}=\text{CHR}$, a reversible sequence of concerted [2+2] oxidative-cycloaddition-cycloreversion at metal center, which fits to π -CAM (Complex Assisted Metathesis) principle or π -bond mode, in other words a transalkylidenation reaction through a metallacyclobutane intermediate, as well as the cyclopropanation reactions depends mostly on the structure of the catalysts. Cyclopropane affords as side product in the presence of the Schrock or Grubbs metal carbene complex which alternatively decomposed through β -hydride transfer, or as the major product in the presence of the Fischer carbene complex. The cyclopropanation mechanisms are concerted or stepwise. The insertion of the transition-metal atom into a C-C bond of cyclopropane is predicted to form $\text{MCH}_2 + \text{C}_2\text{H}_4$, through a formal retrocarbene addition, a reverse reaction cyclopropane – metallacyclobutane. Five resonance structures are representative for the metal-carbon bond of alkylidene complexes: 1. ethylene, corresponding to the singlet coupling of a neutral species, 2. π ylide, corresponding to a covalent M-C σ bond and a dative carbon to metal π -back bond, 3. as a dative carbon to metal σ -bond coupled with a dative to carbon π -back bond, corresponding to the singlet-carbene model of bonding, 4. as a four-electron donor corresponding to coordination of the CH_2^{2-} ligand to a LnMq^{+2} fragment in a ionic fashion, and 5. σ ylide, corresponding to a dative M-C σ bond coupled with a covalent M-C π bond. The reactivity of the M-carbene depends on the predominance of one resonance structure over the other, therefore the nucleophilic resonance ($\text{LnM}^{\text{q}+}\text{CH}_2^{\text{q}-}$) contribute approximately 50% to the ground-state wave function, the neutral resonance structures ($\text{LnM}^0\text{CH}_2^0$) 45%, and the electrophilic resonance structures ($\text{LnM}^{\text{q}+}\text{CH}_2^{\text{q}+}$) 5%. The bonding situation, derived from the contribution of the electrostatic and the orbital interaction, the strength of the σ donor and π acceptor bonding, was discussed in terms of well-defined quantum chemical methods.

Keywords: Metathesis Mechanism, Cyclopropanation, Fischer-Carbene, Schrock-Carbene, Grubbs Carbene

1. Introduction

The Herrison-Chauvin mechanism of the alkene metathesis reaction [1] catalyzed by transition metal alkylidenes $\text{LnM}=\text{CHR}$, involves a reversible sequence of concerted [2+2] oxidative-cycloaddition-cycloreversion [2, 3] at metal center, in other words a transalkylidenation reaction [4] through a metallacyclobutane intermediate. The metallacycle cleaves nonproductively to the starting material or in a productive manner to the metathesis product. Two competitive reactions (Figure 1, eq. 1), the metathesis (path. A) or the cyclopropanation (path. B), depends mostly on the structure of the catalysts. Cyclopropane affords as side product in the

presence of the Schrock or Grubbs metal carbene complex, or as the major product in the presence of the Fischer carbene complex. [5, 6] The formal retrocarbene addition, [7] a reverse reaction cyclopropane – metallacyclobutane increases the amount of the metallocarbene $[\text{LnM}=\text{CHR}]$ in the catalytic cycle (Figure 1, eq. 2).

The insertion of the transition-metal atom for second-row ($\text{M} = \text{Y}, \text{Zr}, \text{Nb}, \text{Mo}$) into a C-C bond of cyclopropane is predicted to form $\text{MCH}_2 + \text{C}_2\text{H}_4$ through four members cyclic intermediate which rearrange to a π -complex, whereas the insertion into a C-H bond leads to M-allene or M-propyne (Figure 2). The positive values of the potential energy barrier for C-C and C-H insertion in case of Mo indicate a highly preference for C-C insertion. [8]

2. Nucleophilic Custom Nucleophilic Versus Electrophilic Metal-Carbene Complexes

2.1. Theoretic Consideration on the Reactivity of Metal Carbene

The reactivity of the M-carbene ($\text{LnM}=\text{CHR}$) depends on the oxidation state of the metal, on the nature of the empty and

bonding orbitals, and on the stability of the Lewis base adduct. The Fischer carbene complexes (all of which have metals in low oxidation states and are stabilized by heteroatom or Ph substituents on the carbene carbon) have an electrophilic carbene carbon ($^{\delta-}\text{M}=\text{C}^{\delta+}$), [9-12] in comparison with the Schrock carbene complexes (usually are electron deficient having metals in high oxidation state) where an inverted polarization of the metal carbon bond leads to a nucleophilic carbene carbon ($^{\delta+}\text{M}=\text{C}^{\delta-}$). [9-14]

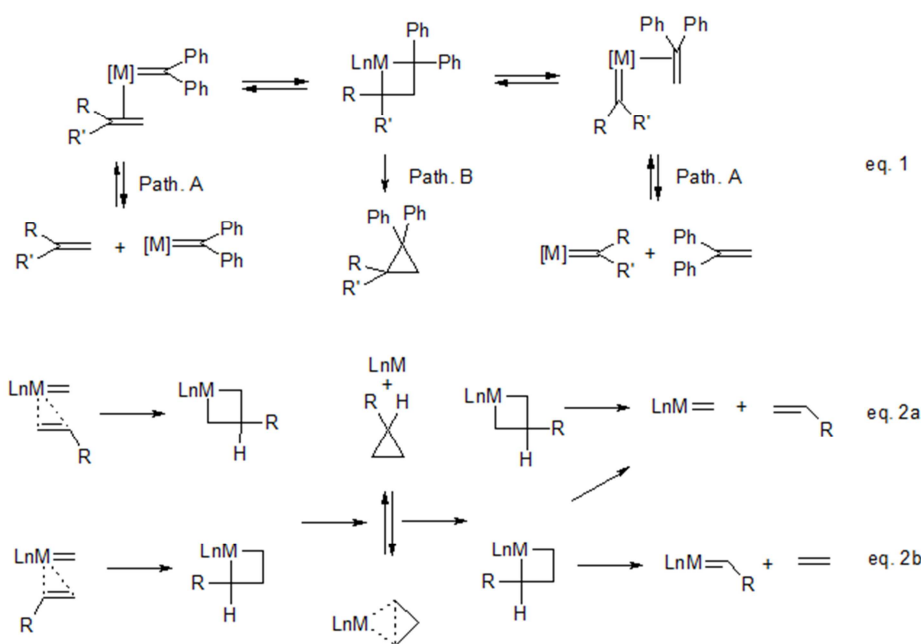


Figure 1. The Metathesis Versus Cyclopropanation.

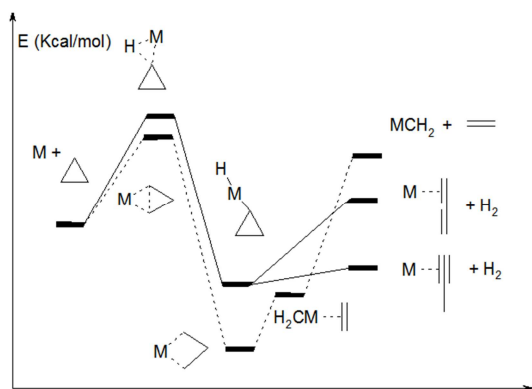


Figure 2. The Potential Energy Diagram for the Reaction of M with Cyclopropane.

Hall and Taylor, using *ab initio* calculations with double ζ basis set in the metal carbene region and limited electron correlation (GMO and CI), define the electrophilic metal carbenes, *e. g.* 18-electron complexes, as singlet-state carbene donating to the metal from its “ sp_2 hybrid” orbital, with a corresponding amount of back-donation from the metal to the empty π orbital, and the nucleophilic metal carbenes, *e. g.* 10 to 16-electron complexes, as triplet state carbene spin-coupled to two electrons on the metal center. [13] In the light of the

Dewar-Chatt-Duncanson (DCD) donor acceptor model the dominant bonding interaction in the Fischer carbenes arises from ligand \rightarrow metal σ donation and metal \rightarrow ligand π back donation, in contradiction to the Schrock carbene complexes. The imidazol-2-ylidenes carbenes represent a particular subclass of Fischer complexes having a little π back donation from the metal. [14] The π -electrons in Fischer type carbene would be polarized toward the metal, and in the Schrock type carbene would be equally distributed, the former binding datively as singlet fragment, whereas the latter binding covalently as triplet fragment (Figure 3). The Hartree-Fock ground state shown that the Fischer-type carbene can be considered as bonding between singlet metal and singlet carbenes fragments, and Schrock-type carbenes as bonding between triplet metal and triplet carbene fragments. Thus, while heteroatoms and phenyl substituents preferentially stabilize the singlet state, alkyl substituents stabilize the triplet state. [13]

The activation energy for ethene addition is reduced by the presence of electron-donating groups on the carbene carbon (*e.g.* methyl substituent) in Schrock complexes. The reaction can be considered as an electrophilic attack of the metal center to the olefin followed by a nucleophilic attack of the carbene carbon to the olefin, the presence of methyl group increasing slightly the nucleophilicity of the carbene center. [15-17]

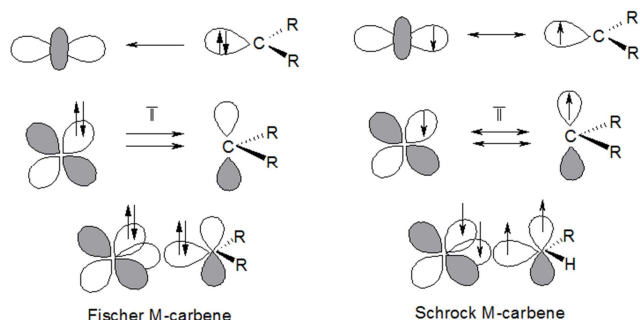


Figure 3. Schematic Representation of the Carbene Bonding to a Transition-Metal Fragment.

Because the metal act as an electron attaching substituent taking a part of π electron density from the unsaturated ligand (olefin) the η^2 -coordinated olefin should be activated toward the nucleophile, but the back-donation from metal to olefin seems to counteract this effect lowering its reactivity, since the π^* orbital of the olefin is occupied and not able to accept an extra electron pair from a nucleophile (Figure 4). The slipping of the ML_n fragment along the olefin from η^2 to η^1 increases the localization of the fragment ligand LUMO ($\pi^*-\lambda b_2$) through its interaction with the olefin π orbital, furthermore increases the overlap population between the nucleophile orbital and the olefin-centered LUMO. [18, 19]

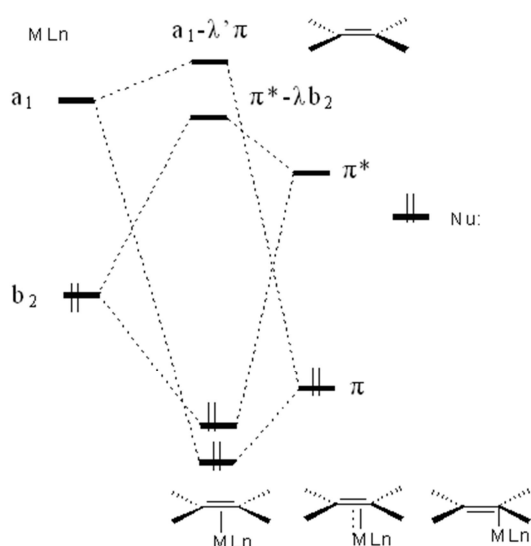


Figure 4. The Diagram of the Frontier Orbitals.

In other words, the formation of the olefin-metal-alkylidene complex should be followed by the slipping of the terminal carbon to form a metallacyclobutane. [20-22] That is in accordance with the Hoffmann prediction, respectively unsymmetrical “non-least-motion” approach of the methylene to ethylene, or with DFT calculation performed by Houk which provide evidence for a nonlinear attack at the unsubstituted carbon of the terminal alkene. [23]

If the metal-ligand bonds are moderately covalent, the addition of C-C π bond across metal-ligand π bond is a thermal 2+2 reaction, predicted to be “forbidden” by a number of rules: Woodward-Hoffmann, Fukui’s frontier orbital, [24] Pearson’s

perturbational overlap, Goddard’s orbital phase continuity principle, [25, 26] and valence-bond approaches by van der Hart, Mulder, and Oosterhoff and by Epiotis. [27-29]

In the metal-free system a mechanism involving a stepwise mechanism through a zwitterion intermediate is preferred, [30-34] but for metal catalyzed cycloaddition processes the symmetry conservation concept [35, 36] highlights the electronic participation of the metal and a pathway through a concerted mechanism. The Lewis acid character of the metal catalysts is expected to alter the orbital coefficients of the reacting atoms and the energy of the frontier orbitals of both reagents. [36-38] In fact Huisgen [39-41] established experimentally that concerted $[\pi 2s + \pi 2s]$ cycloadditions are forbidden by orbital symmetry, but that can be bypassed by reaction occurring via biradicals, zwitterions, or a concerted process $[\pi 2a + \pi 2s]$, whereas Epiotis [42] using quantum mechanical calculations of the restricted Hartree-Fock (RHF) type on model polar 2+2 cycloaddition systems demonstrate that two olefins having substituents with opposite electronic character will approach each other in a *trans* manner. The aromaticity of the transition state can be used for the selection rules of the cycloaddition reactions; the Hückel model *versus* the Möbius model $[\pi 2s + \pi 2a]$.

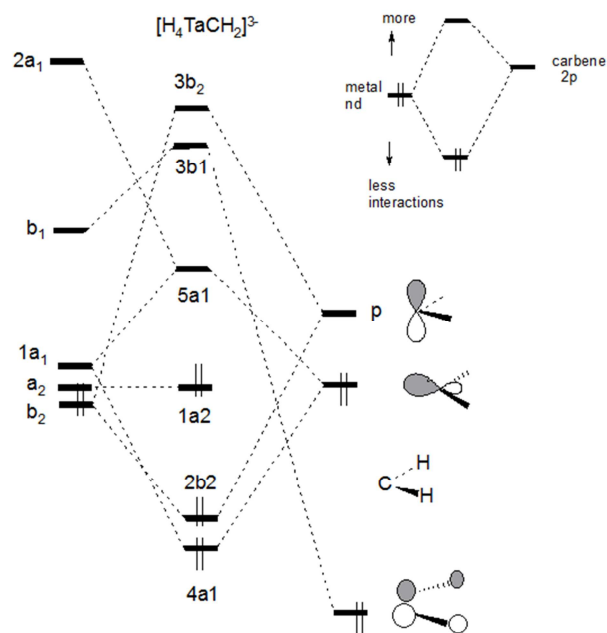


Figure 5. The Interaction of the Frontier Orbitals of H_4M with those of CH_2 in $[H_4TaCH_2]^{3-}$ (1).

According to Fukui the primary feature of electrophilic and nucleophilic reactions is governed by the HOMO and the LUMO and not by charge control; for the Schrock type carbene the HOMO has a maximum coefficient on the carbene carbon and the LOMO has a maximum coefficient on the metal atom, respectively the electrophile attacks the carbene carbon and the nucleophile attacks the metal atom. [43-45] Olefin metathesis assisted by the early transition metals generally have unexpected low energies of activation (6.6 Kcal/mol), that was explained based upon the Pauli principle

[27] rather than orbital symmetry. The participation of a d orbital (from partly filled nd shell of the transition metals with $n = 3, 4, 5$) avoids unfavorable transition-state bonding interactions that are usually the source of a high barrier, and allows orthogonal delocalization to occur leading to a concerted [2 + 2]-cycloaddition. The barrier height can be decreased if the Lewis acidity of the metal center is increased. [26, 28] In the metal d - carbene $p\pi$ interactions, raising or lowering the metal d orbital energies would result in greater or weaker interaction between the metal and the reacting fragment orbitals. [46, 47] As shown in the diagram of the frontier orbitals presented in Figure 5 for the $[H_4TaCH_2]_3$ -complex (1), the primary interaction are the donation of the electron density from σ of the carbene to $1a_1$ of the ML4 fragment and the back-donation from metal b2 to carbene p, leading to the $4a_1$ and $2b_2$ orbitals where most of the

metal-carbene bonding is contained. Other interaction between the b1 of the metal and the πCH_2 orbital of the methylene yields the $3b_1$ orbital. The carbene p orbital, source of electrophilic or nucleophilic reactivity, completely vacant in the free methylene, is occupied by 0.82 electron, from which 0.72 electron is derived from the $2b_2$ orbital, distributed 64% on TaH_4 and 36% on the carbene. A better correlation in size of the Ta d orbital and the carbene p orbital ensure a large overlap, respectively a good b2-p interaction. Any increases in the energy of metal d orbital lead to greater interaction, respectively to more population of carbene 2p orbital. Complexes where the carbene 2p orbital is the lowest unoccupied molecular orbital (LUMO) react with bases such phosphines, whereas in the Ta complex the d-p π interaction push up the d-p π -antibonding combination, as well its ability to interact with bases is diminished. [46]

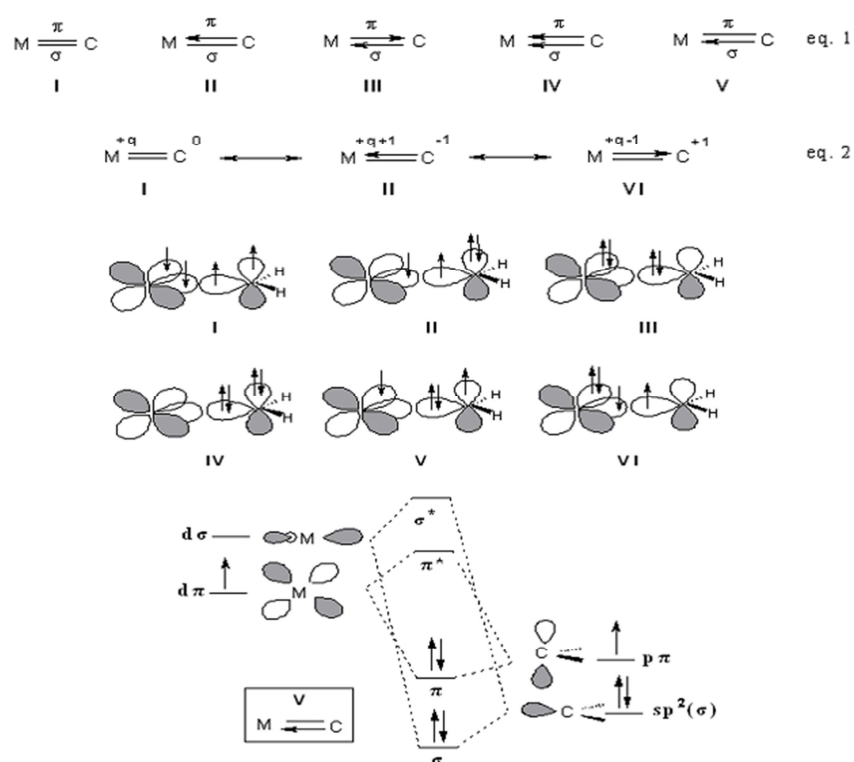


Figure 6. The Resonance Structure in Metal-Carbon Bond and Their Electronic Configuration. Qualitative Orbital Interaction Diagram Between Alkylidene and Transition-Metal Fragments in Resonance Structure V.

Cundari and Gordon classifies the metal-carbon bond of alkylidene complexes in five resonance structures using MC/LMO/CI (multiconfiguration/localized molecular orbital/configuration interaction) procedure (Figure 6, eq. 1): a) ethylene (I), corresponding to the singlet coupling of a neutral species [13], can be described as arising from the low-spin coupling of a triplet (ground state) carbene with a triplet transition-metal which forms a nearly covalent M-C σ and π bonds, b) π ylide (II), [48] corresponding to a covalent M-C σ bond and a dative carbon to metal π -back bond, c) as a dative carbon to metal σ -bond coupled with a dative to carbon π -back bond (III), corresponding to the singlet-carbene model of bonding [13], d) as a four-electron donor corresponding to coordination of the CH_2^{2-} ligand to a $LnMq^{+2}$ fragment in a

ionic fashion (IV), and e) σ ylide (V), corresponding to a dative M-C σ bond coupled with a covalent M-C π bond. [49, 50] Thus, they found that in high-valent alkylidene complexes the M-C σ bond is predominantly ionic or dative in nature, and the M-C π bond is more covalent than considered to date. The resonance structure V can be described as arising from a dative carbon-to-metal σ bond coupled with a covalent M-C π bond, accounting to one-third of the ground-state wave function. In figure 5 the donation of electron pairs from the carbon σ donor orbital into the vacant metal σ acceptor orbital defines the M-C σ bonding, and the interaction between the higher energy carbene $p\pi$ and the lower energy $d\pi$ orbitals the M-C π bonding, therefore for the largest contributor V the energy match between the π pseudosymmetry orbitals will be

better and the bonding more covalent than in the σ counterpart. [49, 50] The stronger π bond character of the nucleophilic complexes, $\text{Cl}_2\text{CpNb}=\text{CH}_2$ (2), 74 Kcal/mol, relative to electrophilic complexes, $(\text{CO})_5\text{Mo}=\text{CH}(\text{OH})$ (3), 60 Kcal/mol, was reported by Taylor and Hall based on the difference in calculated $\text{M}=\text{C}$ dissociation energy. [13]

The reactivity of carbene depends on the predominance of one resonance structure over the other (Figure 6). Therefore, the structure II, IV, and V are responsible for the nucleophilic resonance contribution ($\text{LnM}^{\text{q}+}\text{CH}_2^{\text{q}-}$) which is approximately 50% to the ground-state wave function of the alkylidene complexes, along with 45% neutral resonance structures ($\text{LnM}^0\text{CH}_2^0$) and 5% electrophilic resonance structures ($\text{LnM}^{\text{q}-}\text{CH}_2^{\text{q}+}$). The resonance structure IV was usually applied to the Schrock alkylidene complexes having the metal in its highest oxidation state, and can be used for the singlet-carbene coordination model. While in the resonance structure II the carbon donates two electrons to the new vacant $d\pi$ orbital, in the corresponding electrophilic resonance structure (an inverse ylide structure VI) the $d\pi$ orbital is the donor and the $\text{Cp}\pi$ is the acceptor orbital. [49] In the resonance structure I the unhybridized $2p\pi$ orbital of the carbon shares a pair of electrons with the $d\pi$ orbital of the metal fragment, and the increase metal formal oxidation state by one ($\text{M}^{\text{q}+} \rightarrow \text{M}^{\text{q}+1}$), corresponding to the one-electron reduction, can be viewed as a metal-to-ligand charge transfer from I to II (Figure 6, eq. 2). Since an efficient π -donor M has a preference for the ylide II structure, a negligible π -donor M has a preference for the inverse ylide structure VI ($\text{M}^{\text{q}+1}$). The zwitterionic nature of the $\text{P}=\text{C}$ bond (P^+-C^-) has been used to explain the nucleophilic nature of the carbon in the phosphor ylide. [49, 50] The correlation of the electronegativity of the metal with that of the carbene atom along with the nature of the metal/the ligands on metal/and the carbene substituents are factors which dominated the direction of the bond dipole. The net balance between the π - and σ -components determined the charge distribution in the covalent $\text{M}=\text{C}$ bond. [51]

A high reactivity in olefin metathesis reaction, viewed in terms of the resonance contributors derived from rearranging the electrons in the $\text{M}-\text{C}$ σ and π orbitals, can be achieved increasing the polarization of the metal, *i. e.* a more electron-deficient metal and a more electron-rich α -carbon. [49] That explains the greater stability of an alkylidene complex in comparison with methyldiene complex, while alkyl groups are better electron donors than hydrogen, and are supported by a M^+-C^+ polarization mode. [50] The presence of π -donor substituents (*i. e.* NH_2 , OH , Cl , F) on Ca increases the percentage of electrophilic resonance structures, consequently that transforms the Schrock carbenes in the Fischer carbene. [49, 52, 53] Metal-alkylidene complexes possessing a nucleophilic carbon might be readily trapped by a Michael acceptor, *i. e.* the ethyl-acrylate inhibit complete metathesis. Experimental results show that an electron-deficient double bond is required because neither acetone, ethyl acetate, diethyl ester, nor dimethoxyethane would inhibit metathesis. [54]

Three well definite absorption in the UV/Vis spectra of Fischer metal-carbene complexes were identified: a forbidden

metal-ligand charge transfer (MLCT) absorption around 500 nm, the allowed low-energy ligand-field (LF) absorption in the range of 350-450 nm, and the higher-energy LF absorption in the range of 300-450 nm. Absorption attributed to electronic transition from the higher nonbonding metal-centered b_2 -occupied orbital to the empty carbene-centered $2b_1$ (MLCT), $2a_1$ (low energy LF), and $3a_1$ (high energy LF) orbitals (Figure 7). [55] The bonding $\{a_1(\sigma)\}$ and antibonding $\{2a_1(\sigma^*)\}$ combinations arises from filled sp^2 orbital which overlap with the empty metal $d\pi$ orbital, and the bonding $\{b_1(\pi)\}$ and antibonding $\{2b_1(\pi^*)\}$ molecular orbitals from the overlap between the empty carbene p_x orbital with a filled $d\pi$ orbital. The π^* orbital is the lowest unoccupied orbital in the complex and is localized largely on the carbene atom. [56]

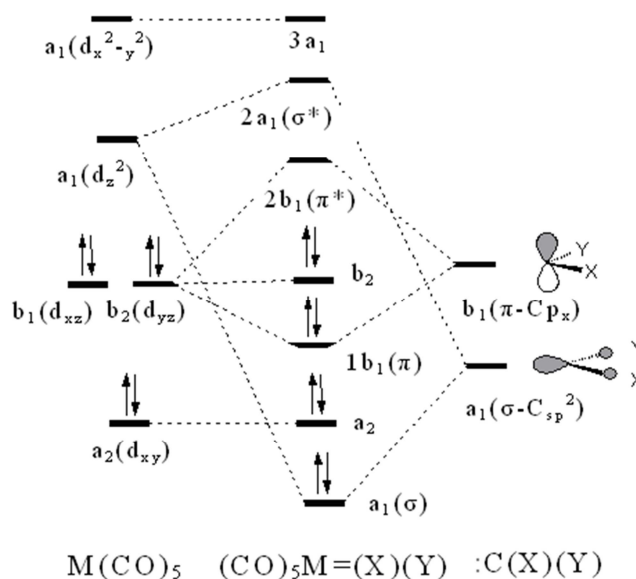


Figure 7. Simplified One-Electron Energy Level Diagram for the Octahedral Structure of Fischer Carbenes in the Ground State.

Frenking et al. studied the characteristic difference in the electronic structure of four Fischer-type and eight Schrock-type tungsten complexes, $\text{LnW}-\text{Ccarb}$ bond, using the Bader analysis - the topography of the total electron density. Significant difference between the Fischer and Schrock complexes are found analyzing Laplacian's in the π plane of the carbene ligand. The Fischer carbene $(\text{CO})_5\text{WCH}_2$ (4a) without a π donor substituent at the carbene ligand display an area of charge depletion in the direction of the $p\pi$ orbitals of the carbene carbon atoms, where the holes in the electron concentration are visible signs for the direction of a possible nucleophilic attacks at the carbene ligand, behavior observed also in the π -donor substituted complex $(\text{CO})_5\text{WCHOH}$ (4b). In contrast, the carbene carbon atoms of the Schrock complexes F_4WCH_2 (5a) and F_5WCH_2 (5b) are shielded by continuous area of charge concentration. The carbene ligand of the Schrock complexes have Laplacians similar to $(3\text{B}1)\text{CH}_2$ as compared with Fischer complex which resembles $(1\text{A})\text{CH}_2$. [14]

The bond critical point $\text{H}(\text{rc})$ of the $\text{W}-\text{Ccarb}$ has larger

negative values for Schrock complexes (-0.530 - -0.931) than Fischer complexes (-0.272 - -0.382). Since, the shared electron (covalent) bonds have strongly negative values of the $H(rc)$, and the close-shell interactions (ionic bonds or van der Waals interactions) have small values of the $H(rc)$, the more negative values of the $W-C_{carb}$ in the Schrock complexes indicated a large degree of covalent character, in accord with the ellipticity at the bond critical point (ϵ_c) calculated using Cioslowski-Mixon bond orders. [14] Because the donation and back-donation are negative for Schrock complexes in

some cases the $W-C_{carb}$ should be discussed in terms of interaction between (3B1) triplet state of the carbene and the triplet ground state of WCl_4 . For the complexes F_5WCH_2 (5b) and F_5WCF_2 (5c) the metal-carbon bonding can be a donor-acceptor interactions between the closed shell fragments WCl_5^- and CX_2 , since WCl_5^- has a singlet ground state and WCl_4 has a triplet. In this light, a Schrock-type high oxidation state may have a donor-acceptor carbene bond like a Fischer-type low oxidation state. [14]

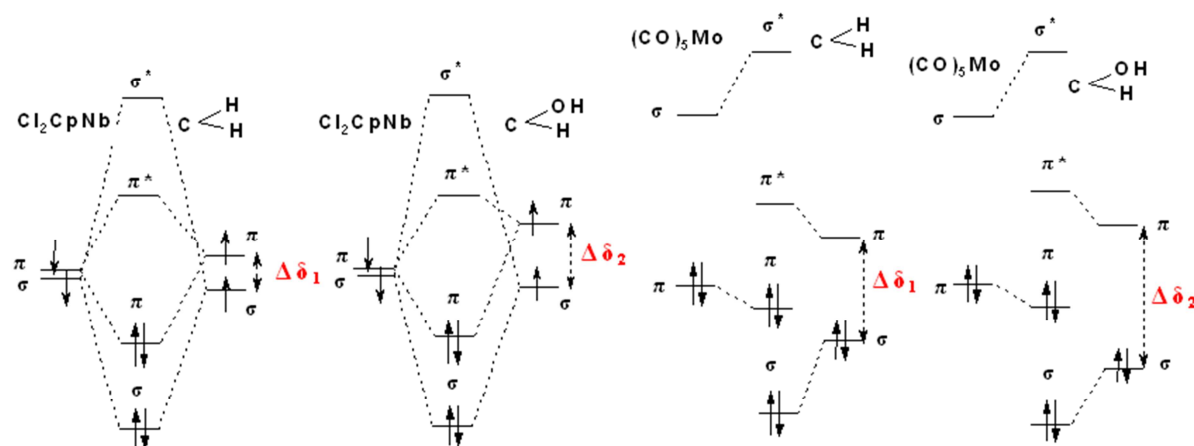


Figure 8. Molecular Orbital Diagrams of $Cl_2CpNb=CH_2$ (2, Triplet Ground-State Fragment) and $(CO)_5Mo=CH(OH)$ (3, Singlet Ground State). The Bonding is Closer to Triplet in $Cl_2CpNb=CH(OH)$ (6), and to Singlet in $(CO)_5Mo=CH_2$ (7).

As reported by Taylor and Hall, the same methylene fragment bonded to a different metal has different deformation density, the Schrock $CpCl_2Nb=CH_2$ (2) complex has the carbene fragment similar to the carbene fragment of ethylene (metal fragment ground state: triplet, carbene fragment ground state: triplet). In the $(CO)_5Mo=CH_2$ (7) complex the molybdenum fragment (singlet \rightarrow triplet energy of 41 kcal mol^{-1}) forces the methylene (triplet \rightarrow singlet 15 Kcal mol^{-1}) into the singlet state, increasing the methylene σ electron density and decreasing the methylene π electron density relative to $CpCl_2Nb=CH_2$ complex. The substitution of a triplet niobium fragment in $CpCl_2Nb=CH(OH)$ [6, triplet on metal/singlet on carbene] with the singlet molybdenum fragment in $(CO)_5Mo=CH(OH)$ [3, singlet on M/singlet on carbene] forces the hydroxymethylene into the triplet state (Figure 8). Heteroatom or phenyl substituent on carbene instead of hydrogen increases the σ - π separation ($\Delta\delta_1 < \Delta\delta_2$), in turn stabilizes the low-spin singlet state relative to the high-spin triplet state. The presence of strong π -acceptor ligands on the Mo complex stabilizes the metal π orbitals, in turn stabilizes the low-spin singlet state. [13] The singlet state is preferentially stabilized by the presence of a lone-pair π donor atom bonded directly to carbene carbon (F, OR, NR_2 , CR_2 -), heteroatom or aryl substituents, and the triplet bonding metal carbenes by strong π -acceptor ligands on the metal, and the hydrogen or alkyl substituents on the carbene. The most π electron acceptor groups (with the exception of CH_2^+) do not alter the T1-So gap sufficiently to alter the nature of the

ground state from triplet to singlet. [52, 53]

The deviation of the double bonds from planarity is related to the singlet-triplet separation ($\Delta E_{S \rightarrow T}$) of the interacting fragments which form the multiple bonds. Unsaturated systems such as: alkenes, olefins, ketenes, cumulenes, allenes, ylides, diazo compounds or metal complexes are built from fragments with a large $\Delta E_{S \rightarrow T}$. The competition between the triplet-triplet and singlet-singlet potential surfaces explains the existence of planar or *trans-bent* equilibrium structures. When the singlet configuration is much more stable than the triplet configuration, the formation of a classical planar $\sigma+\pi$ double bond required for the interaction of triplet state, becomes impossible. As a rule, “the *trans-bent* distortion of the double bond ($R_2X=YR_2$) affords when the carbenoid fragments ($R_2X: YR_2$) have a singlet state and when the sum of the singlet separations in these divalent species is larger than half of the total bond energy of the double bond”; $\Sigma \Delta E_{ST} \geq \frac{1}{2} E_{\sigma+\pi}$. The *trans-bent* double bond structure (I) with pyramidalization of the XR_2 group has been presented in Figure 9. In the local energy minimum with 45° bonding angle (II) the $n\sigma$ pair of one species is partly delocalized into the empty $p\pi$ atomic orbital of the second species. The structure III shows a classical planar $\sigma+\pi$ double bond arising between two triplet carbenes. [57-59, 50] In the MO diagram (Figure 9) the ethylene is distorted from a planar geometry to a typically *trans-bent* geometry. The σ and π MOs of ag symmetry mix when the olefin begins to bent, thus σ is pushed up in energy while π^* is pushed down. The mixing of the bu symmetry

orbitals takes place in a different way, now both are pushed down. The 1bu stabilization is -0.19 eV in ethylene while the 1ag destabilization is +0.38 eV. [57]

The localized molecular orbital (LMO) studies performed by Marynick and Kirkpatrick claim that Fisher-type carbenes have separate σ and π MOs, and Schrock-type carbenes have two localized bent "banana" bonds, respectively more nearly nonpolar double bonds, similar to those found in ethylene. [59] Results which was also confirmed by the Cundari and Gordon LMO analysis, using Hartree-Fock level with Hay-Wadt (HW) or Stevens-Basch-Krauss (SBK) pseudopotentials with a valence basis for the transition metals, *i. e.* the M-C bond distances (HW/SBK, A^0) in the $H_2Ti=CH_2$ complex (8) decrease in the direction planar/singlet minima (1.96/1.87) > twist/singlet second-order saddle point (1.78/1.85) > bent/twisted transition state (1.79/1.84) geometries. The twisted carbene can rotate about the M-C bond leading to the planar structures, or bending of the MH_2 fragment changing from trigonal planar to pyramidal. [49, 50]

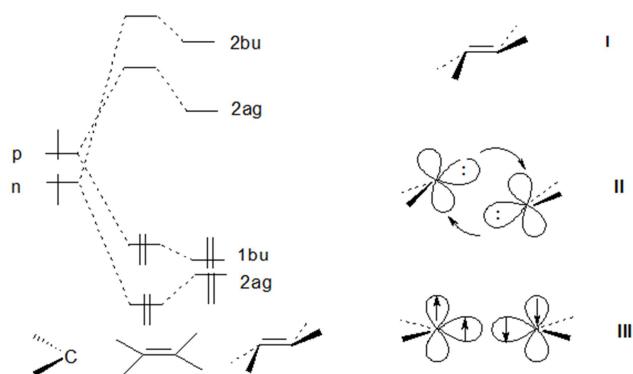


Figure 9. The Trans-Bent (I) and the Planar (III) Double Bond.

The rotational barrier about that double bond was identified with the strength of the π bond, assuming that the σ bond is little changed by the rotation; thus, the ground singlet state has a barrier to rotation, while the singlet and triplet $\pi \rightarrow \pi^*$ vertical excited states have stable minima at the 90° rotated geometries. A diradical character at the heavy atoms displays the rotate-triplet and the ground-singlet states, whereas the excited singlet at its rotated equilibrium geometry displays zwitterionic character. A second zwitterionic state occurs from the rotational stabilization of the doubly π excited molecule positioned above the first. The rotation about a double bond involves the breaking of an electron pair, a process that necessitates a multiconfigurational treatment. [60]

Gordon et. al. estimated the π -bond strengths by the *cis-trans* rotation barriers and by hydrogenation energies. The structures of the lowest triplet state of each double-bonded compound are calculated, along with the singlet-triplet splitting. "The Double Bond Rule" states that elements with a valence principal quantum number of three or greater will not participated in π -bonding. Furthermore, Pitzed claim that heavier elements have longer bond lengths, thus their $p\pi$ - $p\pi$ overlap integrals should be smaller than those for corresponding second period elements, in contrast to the

Hückel theory which considered the bond strengths proportional to overlap integrals. The orbital integrals do not decrease significantly when heavy atoms replaced the second-row elements, thus the differences between the two arising for the missing p orbitals in the case of the latter. [61]

The 90° twisted singlet biradicals of the π -bonded compounds represent the rotational barriers for *cis-trans* isomerization and was calculated at the MCSCF level, which correlated the A=B σ and π bonds with their antibonding counterparts. The MCSCF bond lengths calculated for some of the doubly bonded compounds are all slightly longer than experimental determinations, due to the mixing of some antibonding character into the bond description. The experimental and computational vibrational stretching frequencies also differ for ethylene, *i. e.* exp. 1623, SCF 1853. [61]

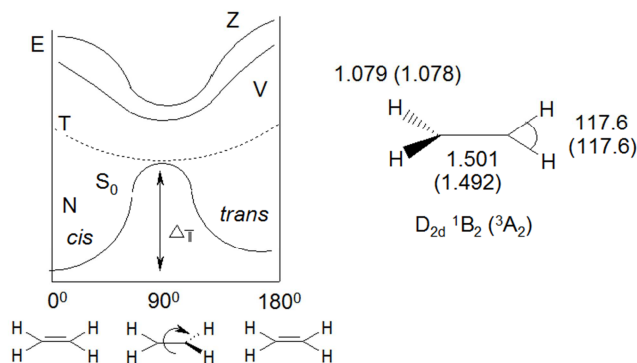


Figure 10. The Representation of the Lowest Singlet and Triplet Rotational Potential Energy Surfaces (A). The A=B bond Lengths of the Singlet Transition State Structures and Equilibrium Triplet Structures (B).

The definition of the π bond strength is obtained from the *cis-trans* isomerization activation energy, when a doubly bonded molecule is rotated by 90° to the biradical transition state for isomerization, the A-B π bond is broken while the A-B, A-H and B-H σ -bonds remain unbroken. The rotation barrier on the S_0 ground-state surface was assimilated with the Gordon definition of $\Delta\pi$. Rotation away from the planarity raises the π and lowers the π^* orbitals in energy, thus the rotation by 90° on the ground (π^2) state singlet (S_0) surface requires an impute of energy as the π bond breaks. Rotation by 90° stabilizes the triplet $\pi \rightarrow \pi^*$ state (T_1), while in a planar geometry the π^* orbital is more antibonding than the π orbital is bonding. [61]

In the Figure 10 was represented the lowest singlet and triplet rotational potential energy surfaces, for the molecules which has lone pairs at either A or B atom ($NH=NH$, $CH_2=NH$) the lowest vertical triplet state may be better described as $n \rightarrow \pi^*$. At their rotational minima the singly occupied orbitals on the atom A or B will consist in a valence p orbital. The relaxed triplet has a biradical electronic structure identical with that of the twisted singlet apart from the spin coupling of the unpaired electrons. Hund's rule would predict that the triplet will lie below the rotated singlet, with the exception of the C=C bond. [61]

The A=B bond lengths of the planar ethene calculated at the MCSCF/3-21G(d) level are presented in figure 10,

respectively the transition states for π bond rotation with triplet equilibrium structures in parentheses. Usually, these two structures are nearly identical as one commonly expected for molecules possessing some electronic configuration. Resulting that while the 90° twisted triplets are at their equilibrium geometries, the very similar rotated singlets are at the transition states for *cis-trans* isomerization on the ground singlet surface. [61]

In the C=C and Si=C molecules the double bond can rotate in two directions leading to equivalent transition states (Figure 10). Because the energies of the “plow” or *s-trans* forms are close to the “tent” or *s-cis* transition states (~ 1 Kcal/mol), both transition states count in *cis-trans* isomerization kinetics. Different energies in the *cis-trans* isomerization leads to a more specific $\Delta\pi$ definition, therefore the activation energy required to rotate from the more stable of the *cis* and *trans* isomers through the lower energy saddle point. In table 1 are

showed the total energies and harmonic zero-point energies of the planar singlets, and twisted singlets and triplets, as well as the rotational barriers and singlet-triplet splitting as a function of both basis set. [61]

Until this paper some proofs for the triplet T state lying below the rotational maximum in the singlet ground state (namely N) in accord with Hund’s rules, or the singlet lies below the triplet, known in the literature as “dynamic spin polarization”, a behavior which represent a violation of the Hund’s rules, have been reported. [61] Yamaguchi et. al. using two-conformational Hartree-Fock wave function predict the triplet lying below the singlet. The planar π and π^* orbitals of planar ground-state C_2H_4 are degenerate at the 90° twisted geometry, thus at this point four low-lying states corresponding to electron configuration e2 appears. The N state is a transition state for the twisting motion, and the T, Z, V are all predicted to be minima at the DZ SCF level of theory. [62]

Table 1. The Harmonic Zero-Point Energy and Total Energies are in Hartrees. Relative Enthalpies are in Kcal/mol.

	Molecule $CH_2=CH_2$	ZPE MCSCF/3-216(d)	Total energies		
			MCSCF 3-216(d)	MCSCF 3-216(d)	MCSCF 3-216(d)
1	Pl.	0.0531	-77.71842	-78.08610	-78.12013
2	Rot.	0.0463	-77.60718	-77.97571	-78.00909
3	Trip.	0.0470	-77.60490	-77.97349	-78.00892
			Relative enthalpies		
4	Pl.		0.0	0.0	0.0
5	Rot.		65.5	65.0	65.4
6	Trip.		67.4	66.8	66.0

Gordon et al. found that the N surface lies entirely below the T surface, furthermore the separation between these states is very small, respectively 0.6 Kcal/mol. The C=C bond is the only case for which the Hund’s rule is violated, and the triplet structures lie 1-3 Kcal/mol below the rotation maxima on the singlet surface. The calculated activation energy for *cis-trans* isomerization in ethene is 65.4 Kcal/mol in agreement with the reported experimental results for ethene and for the isomerization of the 2-butene, 65 kcal/mol. [61]

Recently, Occhipinti and Jensen classified the transition metal carbene bond based on density functional theory (DFT) on a series of W, Mo, Os, Ru carbene: Grubbs olefin metathesis catalysts are “electrophilic covalent” or “electrophilic electron sharing” carbene, relative to “nucleophilic covalent” Schrock carbenes and “ionic” or “donor-acceptor” Fisher carbenes. [63]

2.2. Polarization in Metal-Carbene Complexes

The selectivity of the intermolecular nonpairwise exchange [64-66] between the carbene units and the olefin is determined by the factors that stabilize one carbenium ion more than another through a metallacyclobutane intermediate which is in equilibrium with a metal complex containing both an alkene and a carbene ligand (Figure 11, eq. 1). [1]

The degenerate metathesis of terminal olefins was discussed in terms of steric interaction, or as a result of selective addition of polarized intermediate to a terminal olefin. Gassman explains the selective addition of a polarized intermediate ($LnM^+-CH^+R \leftrightarrow LnM^+-CH^+R \leftrightarrow LnM^+-CH^+R$) to

a terminal olefin in terms of electrophilic *versus* nucleophilic attack. [7]

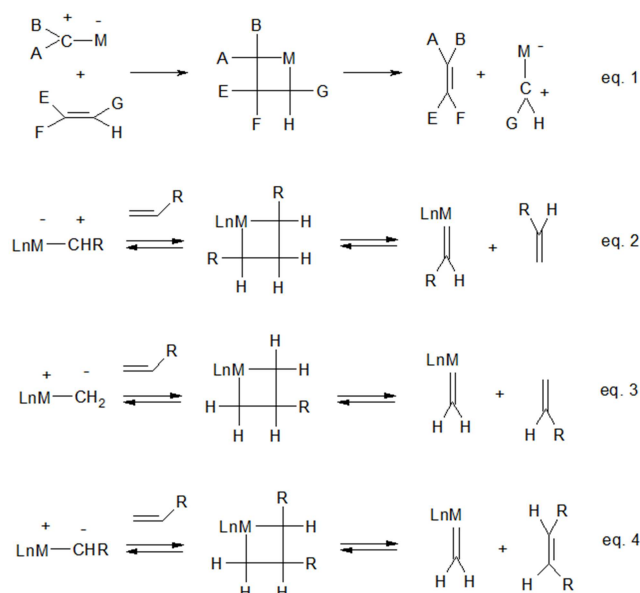


Figure 11. Selective Addition of a Polarized Intermediate to a Terminal Olefin.

Thus, α of a M-alkylidene will be electrophilic (LM^+-CH^+R) relative to α of the corresponding M-methylidene ($LnM^+-CH_2^+$), in consequence the olefin will be oriented with more substituted carbon to the metal in M-alkylidene and with less substituted carbon to the metal in

M-methylidene (Figure 11, eq. 2, 3), in accordance with Katz [67, 64, 68] and Casey [69] reports or with a sterically [70] controlled mechanism. Instead, the formation of the internal alkenes as the major products after cross metathesis reaction of C-alkyl substituted metal-carbenes with terminal olefins could be explained only by the participation of LnM^+-CHR as a major resonance contributor (eq. 4), and would be inconsistent with a sterically controlled mechanism. [7]

The nucleophilic character of the methylene ligand, in the first isolable transition metal methylene complex $\text{Ta}(\eta^5-\text{C}_5\text{H}_6)(\eta^5-\text{C}_5\text{H}_4\text{R})(\text{CH}_3)(\text{CH}_2)$ (9), demonstrated by Schrock experimentally contrasts strongly with the electrophilic character of the Fischer-type carbene ligands,

since the tertiary phosphane ligands attacks the carbene carbon with the formation of the ylide complex only in the latter case. [71]

Unexpected for a Grubbs type complex, an exchange ligand experiment performed by Hansen et al. on the *trans*-10 complex revealed that one of the tBu_2P group of the dtbpm ligand exchange with one of the Ph_3P ligand, but the other one attack the carbene carbon atom, forming the triply chloro-bridged dimeric Ru complex, probably through the ylidic intermediate 13. The reaction of the electron rich phosphane at the carbene unit is in accord with the characteristics of the lowest unoccupied orbital manifold (Figure 12). [72]

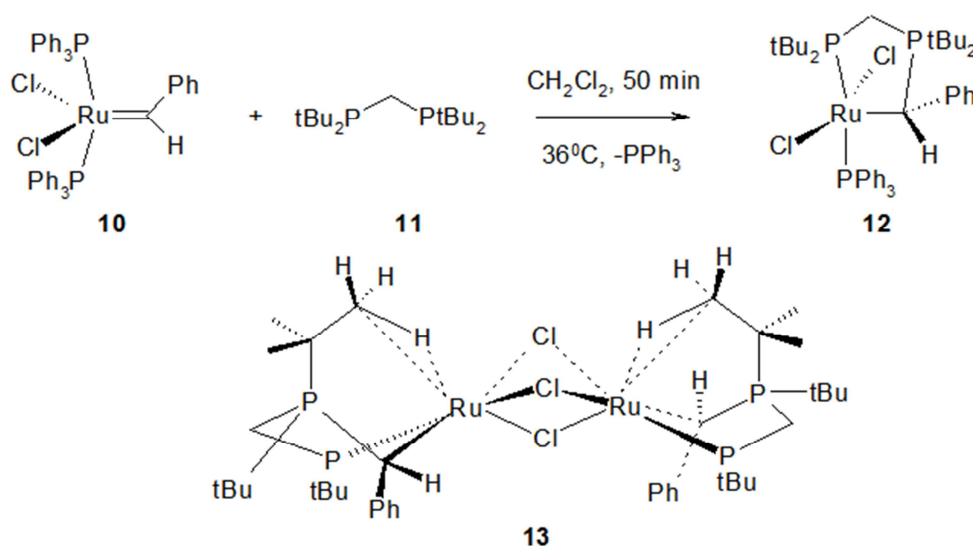


Figure 12. *Trans*-10 Complex Trapped by Dtbpm Ligand.

A polarization in the transition state of the reaction between the Nb and Ta alkylidene complex 14 and olefin, some positive charge on the metal and some negative charge on the olefinic carbon atom, *i. e.* the carbon next to the phenyl group in the case of styrene and the unsubstituted carbon in the case of propylene, forming a single bond between the neopentylidene α -carbon atom and the second olefinic carbon atom dictate the selectivity of the metallacycle (Scheme 13). [73]

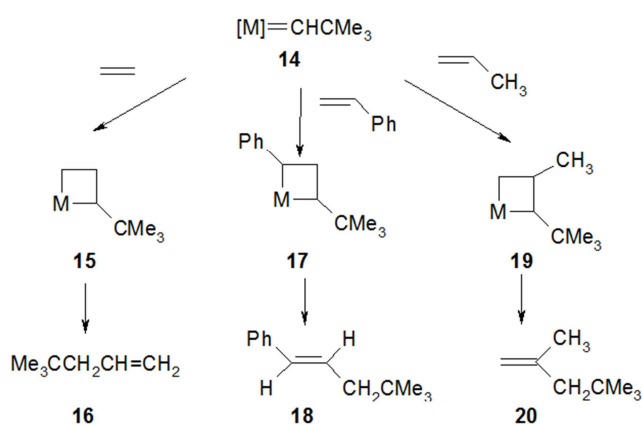


Figure 13. Selective Formation of Metallacyclobutane.

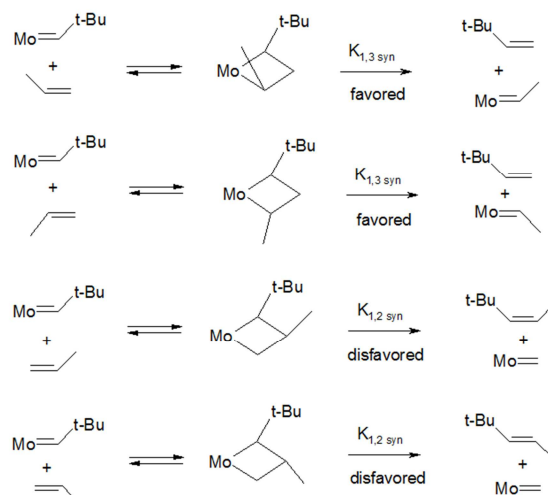


Figure 14. The Selectivity of the Cross-Metathesis Reaction.

The selectivity of the cross-metathesis products between the $[\text{M}]=\text{CHtBu}$ (21) and propene was explained by Schrock et. al. based on the minimization of the interactions between the alkyl substituents, thus 2, 4-additions is favored relative to the 2, 3-additions (Figure 14). [74] Behavior also demonstrated by Wagener et. al. for the metathesis of

3-methyl-1-pentene with Mo- (22) or Ru-carbene catalysts (23a, b) where the productive metathesis implies first 2, 4-addition follow by 2, 3-addition, while two successive 2, 3-additions leads to the unproductive metathesis. The accumulation of the non-productive metallacyclobutane has been observed with Mo-catalyst, whereas with Ru-catalyst the formation of the Ru-methylidene susceptible for decomposition is preferred (Figure 14). [75]

After the first metathesis cycle of functionalized olefins: vinyl esters, vinyl carbonates and vinyl fluorides, in the presence of 23a, b complexes occurs the Fisher carbene intermediates having limited catalytic activity, able to undergo facile deactivation to the corresponding terminal carbide species $L(Cl_2)Ru\equiv$: (24). [76]

The first step in the Ru-carbene metathesis reactions, the

decoordination one ancillary ligand from d_6 -Ru-carbene complexes $L_2RuCl_2(ChPh)$ (23a, b) leads to the formation of the 14-electron Ru-alkylidene complexes $LRuCl_2(ChPh)$ (24a: $L = PCy_3$, 24b: SIMes) bearing a partial negative charge on the carbene carbon, which are considered as having more Schrock than Fischer character (Figure 15). A less electrophilic ruthenium atoms, required for an active metathesis Ru-catalyst, can be obtained performing a good correlation between the σ -donation from the ligand and the dipole moment, thus increasing the electron density on the metal can be decreased the electrophilicity. Theoretical calculations established that the best Lewis structures have a $Ru=CH_2$ double bond, with two natural bonding orbitals between ruthenium and the alkylidene carbon with a partial negative charge in the range -0.1e to -0.5e. [77]

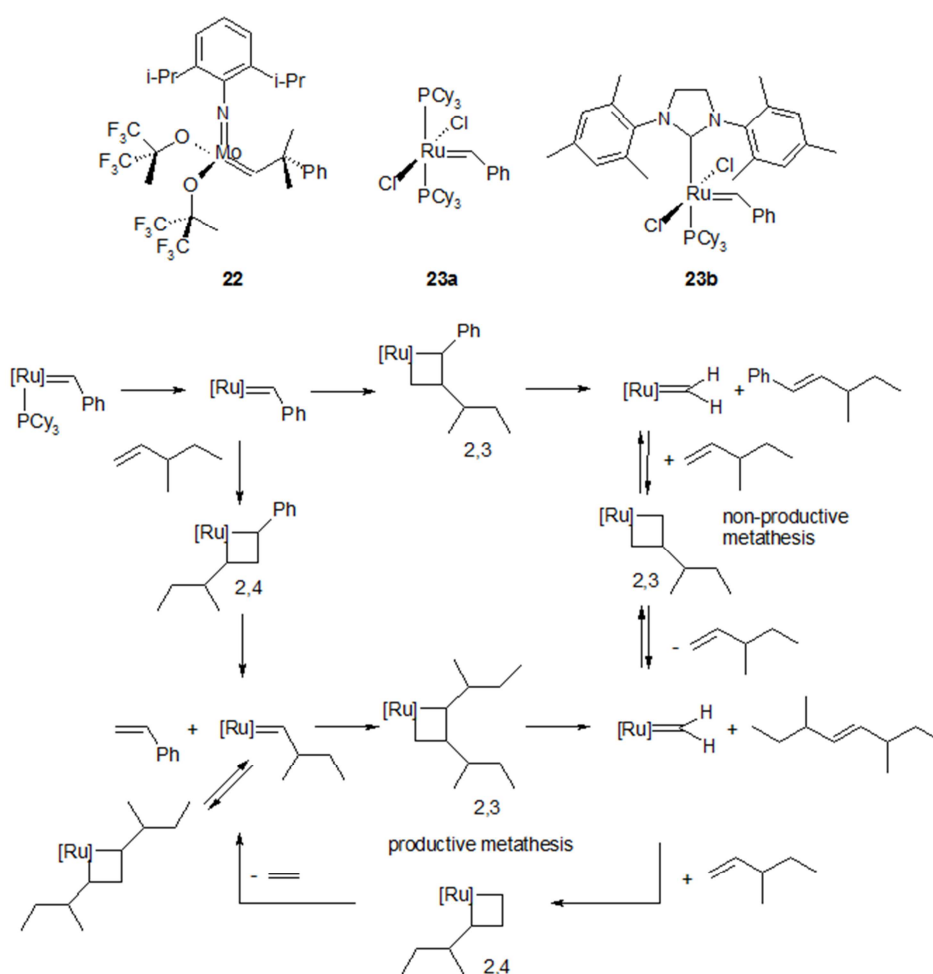


Figure 15. The Catalytic Cycle of 3-Methyl-1-Pentene with Ru-Carbene Catalysts.

The presence of the substituents in the phenyl ring of the Hoveyda-Grubbs chelated complexes have no significant influence on the $Ru=C$ σ -polarization towards the carbon, instead change the $Ru=C$ π -polarization towards the metal (Figure 16), electron withdrawing groups (25a, b) favor the covalent character of the $Ru=C$ ene, and electron donor group (25c-f) favors a more polarized $Ru^{\delta-}-Ccarb^{\delta+}$ bond. Characteristic for π -bond polarization towards the metal, the molecular orbitals of the ligand with the appropriate symmetry

to form the π $Ru=C$ bond lie above those of the metal fragment. Because after the introduction of the electron withdrawing groups in the ruthenafurane ring the energy of the ligand orbitals decreases, the π orbital is less polarized toward the metal, and the $Ru=C$ π bond becomes more covalent, shorter $Ru=C$ distance and higher delocalization index $\delta(Ru, O)$ of the $Ru...O$ bond. Furthermore, electron donor groups increase the energy of the ligand orbitals increasing the polarization toward the metal. [78]

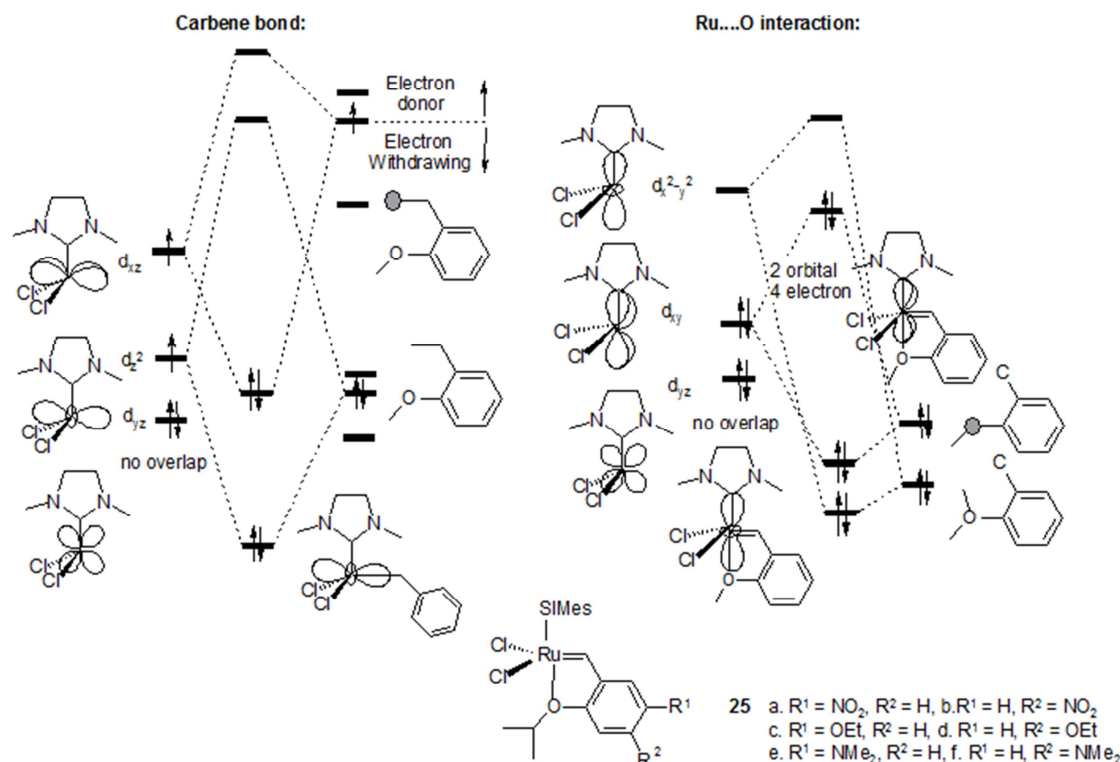


Figure 16. The Molecular Orbital Diagram of the Ru=C and Ru... O Interactions.

The ΔG (Kcal/mol) of the metathesis reactions between the Ru-norbornene carbene (23) with halogenated ethylene (27), calculated at the B3LYP/LACVP* level of theory, changes from 2.5 for ethylene to negative values for halogenated substrates, -2.0 (*trans*-1, 2-dichloro-ethylene), -11.9 (*trans*-1, 2-difluoro-ethylene), -31.6 (tetrafluoroethylene), relative to 0.24 calculated for $\text{CH}_2=\text{CHPh}$, differences explained by Fomine due to the strong +M effect of fluorinated atoms, reflecting the increasing stability of the ruthenium complexes (Figure 17). The lone pairs of the fluorine and chlorine atoms can interact with orbitals of the complex having appropriate symmetry in the 14-electron complexes 28b-d. A contradiction arises between the natural charges calculated for carbene carbon and the ability of sharing p-electron density by substituents, since the most negative charge is observed for Ru-methylidene (-0.25), relative to the -0.15(Cl, H), 0.35(F, H), 0.86(F, F), -0.04(Ph, H), but is in a good shape with the influences of both the mesomeric (+M) and the negative inductive (-I) effects introduced by the halogens. Therefore, while the strong -I effect of the fluorine atoms decrease the total electron density at the carbene atom, the weaker +M and -I effects introduced by the chlorine atom led to more negative value. In fact, fluorine atom is the best p-donor due to effective 2p-2p interaction between pz orbitals of fluorine and carbon atom. [79] Thus, the occupation of pz orbital of carbene atom is highest for 28c and lowest for 28a in accordance with p-donating ability of the substituent. As shown in the figure 10 the 2pz orbital of carbene is overlapped with 4dyz orbital of Ru center, the natural occupation of 4dyz orbital of a Ru atom depending on the nature of substituent at

the carbene center, and following same trend, highest for 28c and lowest for 28a. The Ru atom is positively stabilized by the p-electron density transfer from halogens atoms to metal center through 2px orbital of a carbene. The stability of the fluorinated metallacarbene complexes comes from the stabilization of 4dyz Ru center by 2p electrons of fluorine through 2pz orbital of carbene. In fact, the stabilization is only possible when p-electrons are located at 2p orbital, and strong overlapping with 2p orbital of carbene carbon takes place. In complex 28b the p-orbital located at 3p orbital of chlorine atom decrease the importance of this mechanism. The lowest positive charge at Ru atom (+0.3) in complex 28d offers the highest stability, due to the direct interaction of pz orbital of second fluorine and 4dxz orbital of the metal atom, respectively the occupation of 4dxz orbital increases from 1.16 for 28c to 1.83 for 28d, in accordance with the experimental studies performed by Grubbs [79] on the reaction between 1, 1-difluoroethylene (29) with the complex 23b. Therefore, along the electronic factors, steric factors are of importance for the stabilization of a Ru-carbene. [80]

The reaction of the 23b complex with 1, 1-difluoroethylene (29) gives a mixture of 40% methylidene (28a) and 60% difluorocarbene (28a) at room temperature, whereas at 60°C the amount of difluorocarbene complex increases to > 98%. Thus, at increased temperatures the process follows the eq. 1 instead of eq. 2. As demonstrated by X-ray analysis the $d(\text{Ru}=\text{C})$ of 1.800(2) Å in Ru-methylidene is shorter than that the corresponding ruthenium benzylidene 23b, and the Ru-fluorinated carbene had an even shorter Ru=C bond length of 1.775(3) Å (Figure 18). [79]

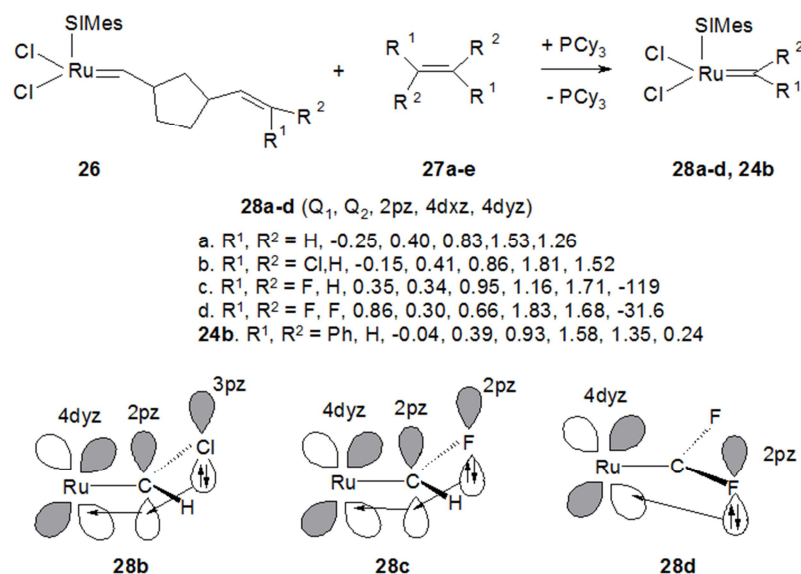


Figure 17. The Interaction of the Atomic Orbitals in Carbene Complexes. The Natural Charge at the Carbene Carbon is Q_1 and at the Ru Center is Q_2 .

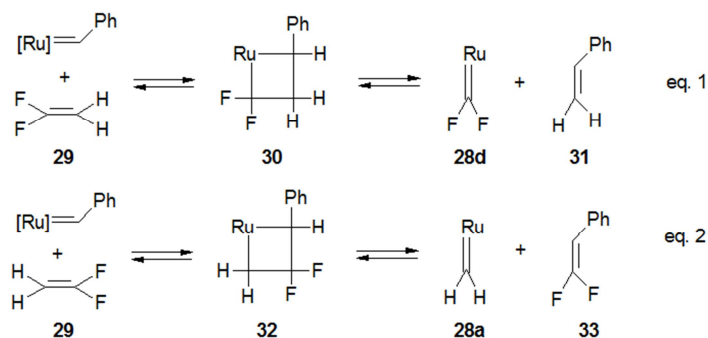


Figure 18. The Metathesis Reactions Between the Ruthenium Benzylidene Complex and 1, 1-Difluoroethylene (29).

In case of phenylcarbene complex ($[\text{Ru}]=\text{CHPh}$, 24b) 2p orbitals of benzene ring are effective donor to stabilize the Ru center, but the charge at the Ru center is similar to that of no stabilized methyldene 28a, because the transfers of p-electron

density from phenyl ring destroy the aromaticity, and the steric hindrances impede the parallel alignment of 2p orbital of carbene and 2p orbitals of a benzene ring (15° between the Ph and CH_2 decrease the efficiency of the orbital overlap). [80]

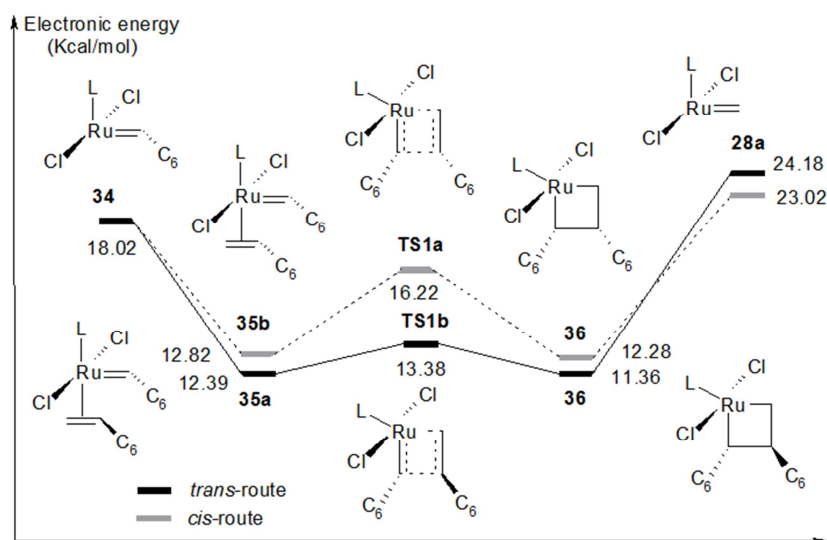


Figure 19. Electronic Energy Profile of the Trans and Cis Routes from the Heptylidene 34 to the Methyldene 28a.

Resulting that, the natural charge at the metal center can be a measure of carbene stability. Thus, the stabilization of a metalcarbene's is due to the stabilization of the metal center and not a carbene carbon itself. The formation of stable ruthenium-halo carbene complexes slow down the metathetic process, an effect which is moderate for chlorine substituent but becomes very strong for fluorine substituents. In conclusions, the metathesis of halogenated olefins is kinetically controlled process where steric factor contributes to the reaction barriers, as shown by the correlation between the molecular volume of the olefin and the free activation

energy of the metathesis. The stability of the halogenated Ru-carbene complexes is a consequence of the stabilization of the Ru center by lone electron pairs of halogen atoms. [80] The 14-electron monofluoro-methylidene intermediate is substantially more thermodynamically stable than the corresponding alkylidene. The decomposition of the ruthenium monohalomethylidene intermediate increases in the direction of the increasing the leaving group character of the halide substituent ($X = \text{Br}, \text{Cl} \gg \text{F}$), the decomposition becomes more rapid than productive cross-metathesis in reactions between vinyl chloride and vinyl bromide. [80]

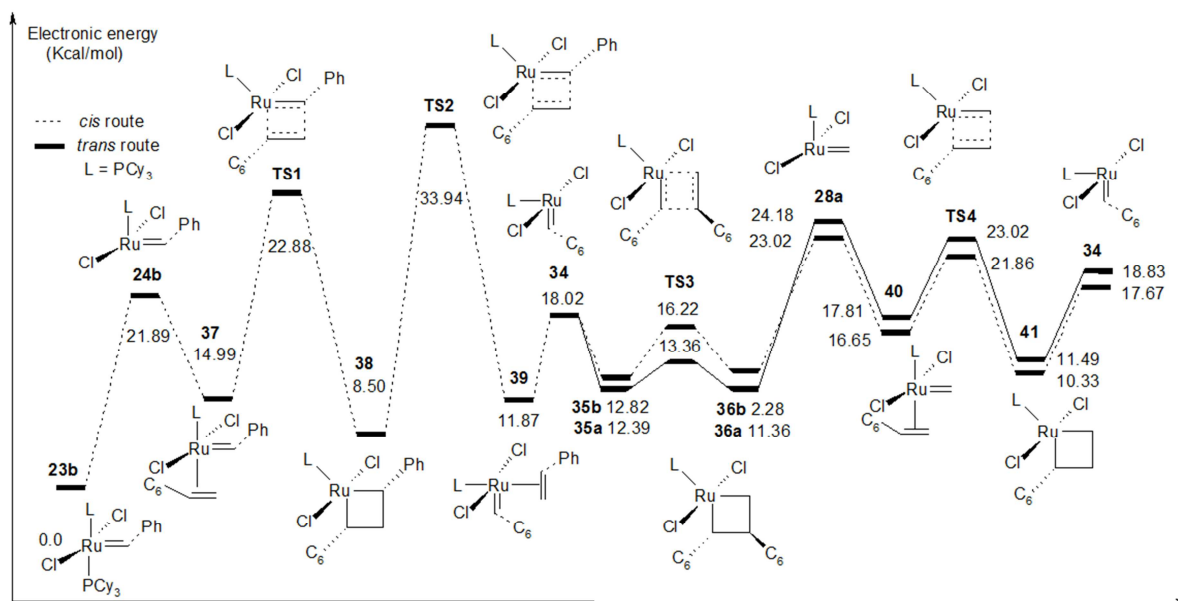


Figure 20. Electronic Energy Profile of the Cross Metathesis of 1-Octene with 23b.

As presented on the Figures 19, 20, 1-octene coordinate in the 2, 4-position relative to the Ru-benzylidene and Ru-methylidene, and in the 2, 3-position relative to the Ru-heptylidene. The coordination of the olefine at the heptylidene 34 metal center take place with the hexyl groups in the *trans* (35a – 0.99Kcal/mol) or *cis* (35b – 3.40 kcal/mol) positions (Figure 19). The *trans/cis* ratio determined experimentally correlates well with the theoretic activation energy ratio. In the most favorable pathway, the *trans* coordination of the alkene relative to the ligand L (PCy_3) is advantaged by the Tolman cone angle of 170° , and the *trans* position relative to the carbene is avoided by a strongly σ -donor effect of the carbene bond. The transformation methylidene to heptylidene (28a – 34) have higher values than the transformation heptylidene to methylidene (34 – 28a) on the electronic energy surface. [81]

Quantum mechanical calculations indicate four modes of substrate olefin coordination to GI alkylidene catalyst (23a) for two consecutive turnovers. [82]

3. Methatesis Versus Cyclopropanation

The formation of cyclopropanes from the presumed

metallacyclobutane intermediate is a side reaction in the presence of Schrock or Grubbs complexes, or a major product in the presence of Fischer complexes. For a stoichiometric reaction, the carbenoid mechanism through a metal-carbene intermediate could be the main process, but for catalytic reactions along the metal-carbene intermediate the formation of unstable carbene that reacts with olefin via a concerted mechanism or a zwitterion intermediate in the earlier days of metathesis was also taken into consideration.

The control of the *cis/trans* diastereoselectivity of olefin cyclopropanation reactions with ethyl diazoacetate in presence of catalysts based on Cu, Ru, Co, Rh, Fe, Os, Co have been reviewed. A higher degree of stereocontrol is achieved in case of styrene or olefins containing aryl groups than for terminal alkenes with no aryl substituents. The major drawback in the cyclopropanation reactions remain synthesis of the catalysts with high chemo-(cyclopropanation *versus* coupling product), diastereo- (dr, *trans/cis*), enantioselectivity (ee value, the ratio of each enantiomer in each diastereoisomer). [83, 84] The electronic effects in the catalytic reactions are better described as combined stereoelectronic effects; the pure electronic effect induces differences in the steric crowding of the two transition states

and the pure steric effect (*i. e.* structures of ligands, interaction between the carbene ester group and the substituents on the olefinic double bonds) leads to the observed differences in the *trans/cis* isomer ratios. [83-87] As reported by Pérez et al. the catalyst structure has little influence on the stereoselectivity of the reaction due to the existence of a transition state where the olefin-Ca interactions remains always at a significant distance

from the metal center, behavior which prevent the influence of the steric bulk of the ligand. [88] Any shortening of the olefin-metal bond length should result in a low ratio of the isomers. The metal-carbene distance for Co and Pd was found to be longer than for Cu or Ru, but only slightly shorter than that estimated for the M-Csp² single bond lengths. [89]

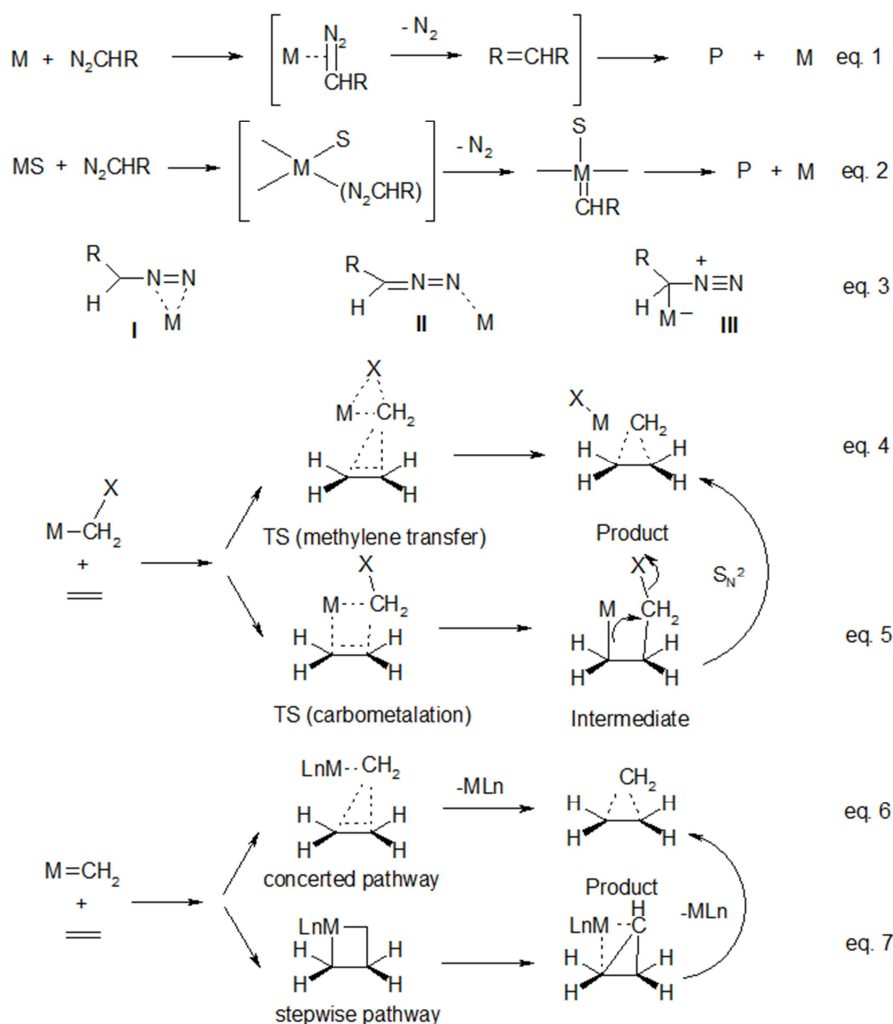


Figure 21. The Mechanism of Cyclopropanation.

Two mechanisms (Figure 21) were proposed for the reactions of diazo compounds with olefins catalyzed by the transition metals, possibly as competitive pathways, a carbenoid mechanism (eq. 1) or a coordination mechanism (eq. 2). In the former case are involves complexes containing only one single coordination site per metal, and in the latter case complexes with several available sites for strong coordination of olefins, *i. e.* rhodium (II) carboxylated complexes promotes a carbenoid mechanism involving an electrophilic attack of uncomplexed olefin, palladium (II) carboxylates a coordination mechanism, and copper derivatives represent a borderline case. [90]

Nitrogen extrusion from the diazo compound is a consequence of nucleophilic attack by the diazo group onto the electrophilic metal complex. The coordination of a diazoalkane molecule to a metal atom can take place in three modes: (I) η^2 (N, N) complex,

(II) η^1 (N) complex, and (III) η^1 (C) complex. Thus, the structure involving η^2 -coordination through two N atoms stabilizes the diazoalkanes against N₂ evolution and thereby hinders carbene complex formation, the η^1 (N) complexation is sterically preferred but will not lead to N₂ evolution, instead the η^1 (C) complexation mode must be kinetically unstable and readily eliminates dinitrogen molecules to give the corresponding carbene complex (Figure 21, eq. 3). [91] Time resolved FT-IR spectroscopy shown two bands for the stretching of the C=O of the methyl diazoacetate, respectively once at 1699 cm⁻¹ assigned to the η^1 (N) complex, and the second one at the 2115 cm⁻¹ assigned to the η^2 (N, N) complex. [89]

The cyclopropanation of ethylene with a metallacarbenoid intermediate (Figure 21), analogue with a lithium or zinc carbenoid-Simmon-Smith reagent, [92-94] involves a concerted

[2+1] process via a methylene transfer (eq. 4), or a stepwise [2+2] cycloaddition via a carbometallation (eq. 5), whereas the cyclopropanation of ethylene with a metal carbene intermediate involves a concerted pathway (eq. 6) [95, 96], or a stepwise pathway (eq. 7) where the carbene complex react with the olefin through an oxidative coupling to form a metallacyclobutane, [97] which decomposes in reductive eliminative mode. The stereochemistry of the cyclopropane products is determined by enantiofacial selection (re face/syn face) upon olefin attack – epimerization during the cyclization steps.

“The spin state of a carbene” rules limits its reaction; [98] a singlet carbene addition process passes through a concerted step and the stereochemistry of alkene is retained in the cyclopropanes, instead a triplet carbene nonstereospecific addition process passes through a stepwise mechanism, in which one bond is first formed between methylene and the olefin giving an intermediate with two unpaired electrons of the same spin. This intermediate must perform a spin flip before the ring can be closed. In the interval between these

steps free rotation around the remaining σ bond of the olefin determines the stereochemistry of the products. [98-101] Geometrical isomerization of the olefin component in the carbenoid cyclopropanation introduces some doubt on the perfect concerted step. [102]

Phenylidonium ylides are good sources of free carbene, recently based on experimental observations a mechanism involving a formal [2+2]-cycloaddition followed by reductive elimination of PhI was proposed by Moriarty et. al., [103] whereas the DFT analysis performed by Kefalidis et al. shown this alternative pathway energetically unfavorable relative to the concerted reaction path. [104]

Sulfonium ylides undergo stepwise methylene insertions across the electrophilic double bond; the nucleophilic attack of the anionic carbon on the electron-poor double bond gives a zwitterionic intermediate, which after cyclization through intermolecular backside displacement gives the cyclopropane adducts. Furthermore, the rotation around the single bond in the zwitterionic structure produces the stereoisomeric adduct. [105]

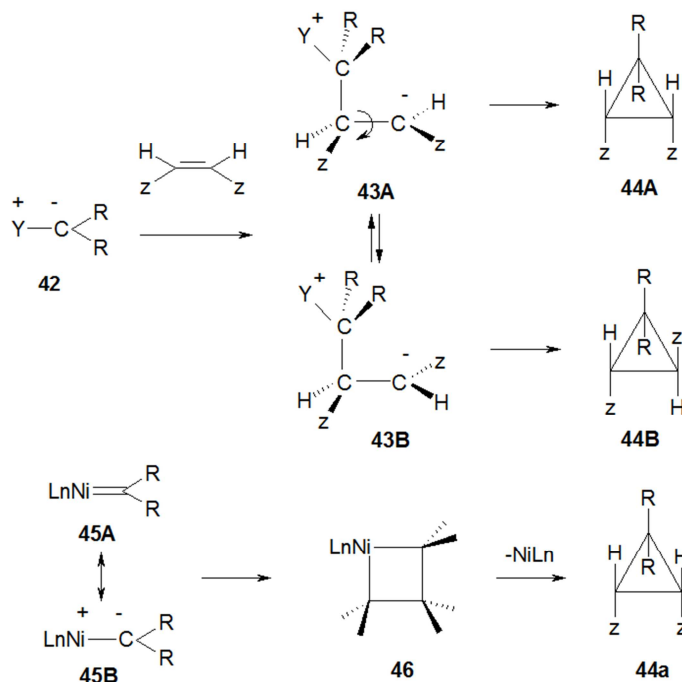


Figure 22. The Noyori Cyclopropanation Mechanism.

Having in mind the ylide character of the carbene complexes Noyori proposed for stereospecific cyclopropanation the formation of the nickelacyclobutane (**46**) which prevents the inversion of stereochemistry, corroborate with a concerted mechanism in the reductive elimination step (Figure 22). [106]

The formation of the cyclopropane **50** from the (butenyloxy)carbene complex **47** take places through the π -complex **48** detected in ¹H NMR. Kinetic studies indicate slow decomposition of **47** on the initial induction period, where CO dissociates with the formation of the π -complex **48**, followed by a rapid autocatalytic decomposition to the cyclopropane and (CO)₄W fragment (**51**). Because the carbene carbon is not stabilized by an electron donating group

the formation of the W-methylidene through the metathesis pathway is expected to be unfavorable. The more stable tungsten-aminocarbene-alkene complex **52** was isolated and characterized by X-ray, its decomposition following a first order kinetics to a cyclopropane without any metathesis product. The *trans*-**55** containing a *trans* vinyl ether side chain undergoes thermal decomposition to both, to cyclopropane **56** and to the olefin metathesis product dihydrofuran **57**. The product distribution and the reaction kinetics depend on the coordination number of the metallacycle, a 7-coordinate metallacycle in coordinating solvents, and a 6-coordinating metallacycle in noncoordinating solvents (Figure 23). [107]

In the former case afforded only the cyclopropanation product with high stereospecificity, and in latter case both, the

metathesis product and the cyclopropanes (Figure 23). [107]

First-order rate law was determined for the conversion of the *trans*-55 to cyclopropane *exo*-56 in CD₃CN. The rate-determining step, the concerted cycloaddition of the alkene to the metal-carbon double bond occurs with the

formation of the metallacycle *trans*-59 with retention of stereochemistry, and then in the reductive elimination step afforded the cyclopropane *exo*-56 also with retention of stereochemistry. [107]

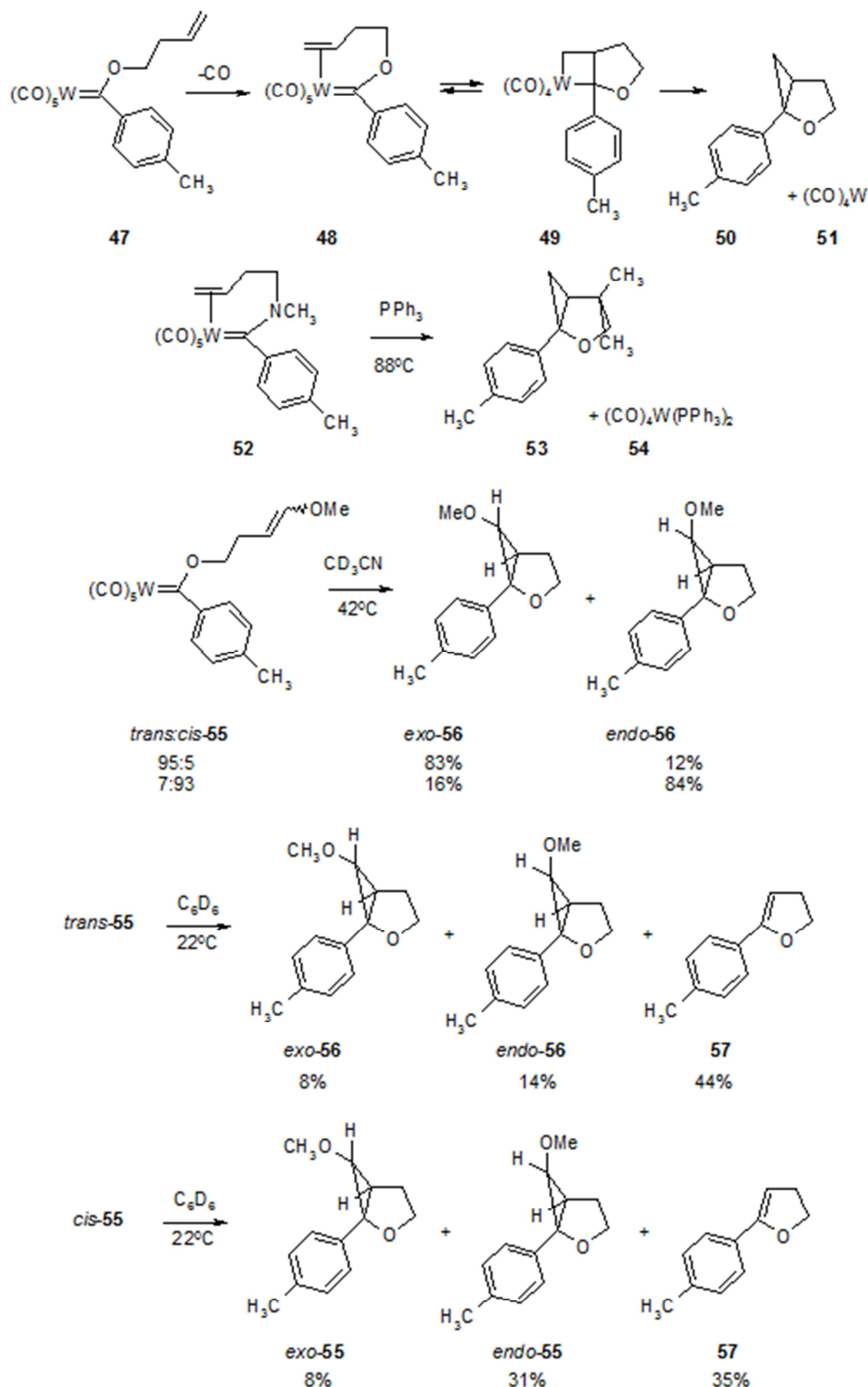


Figure 23. The Cyclopropanation of the W-carbene Complexes.

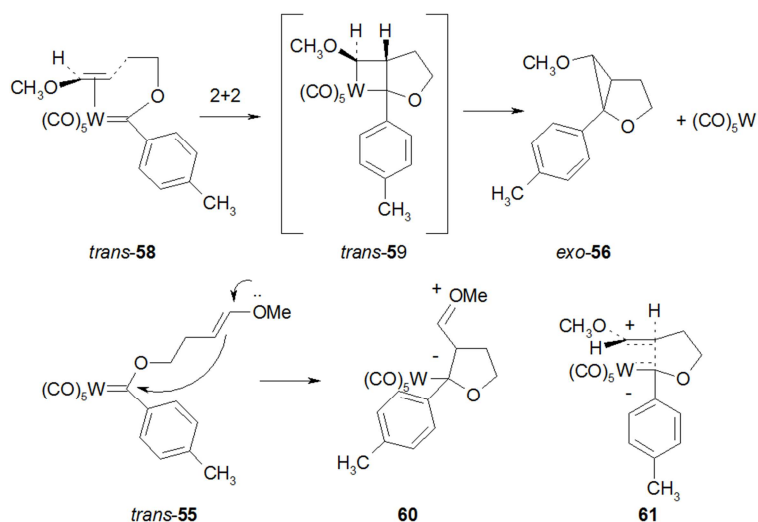


Figure 24. The Mechanism of Cyclopropanation in Coordinating Solvents.

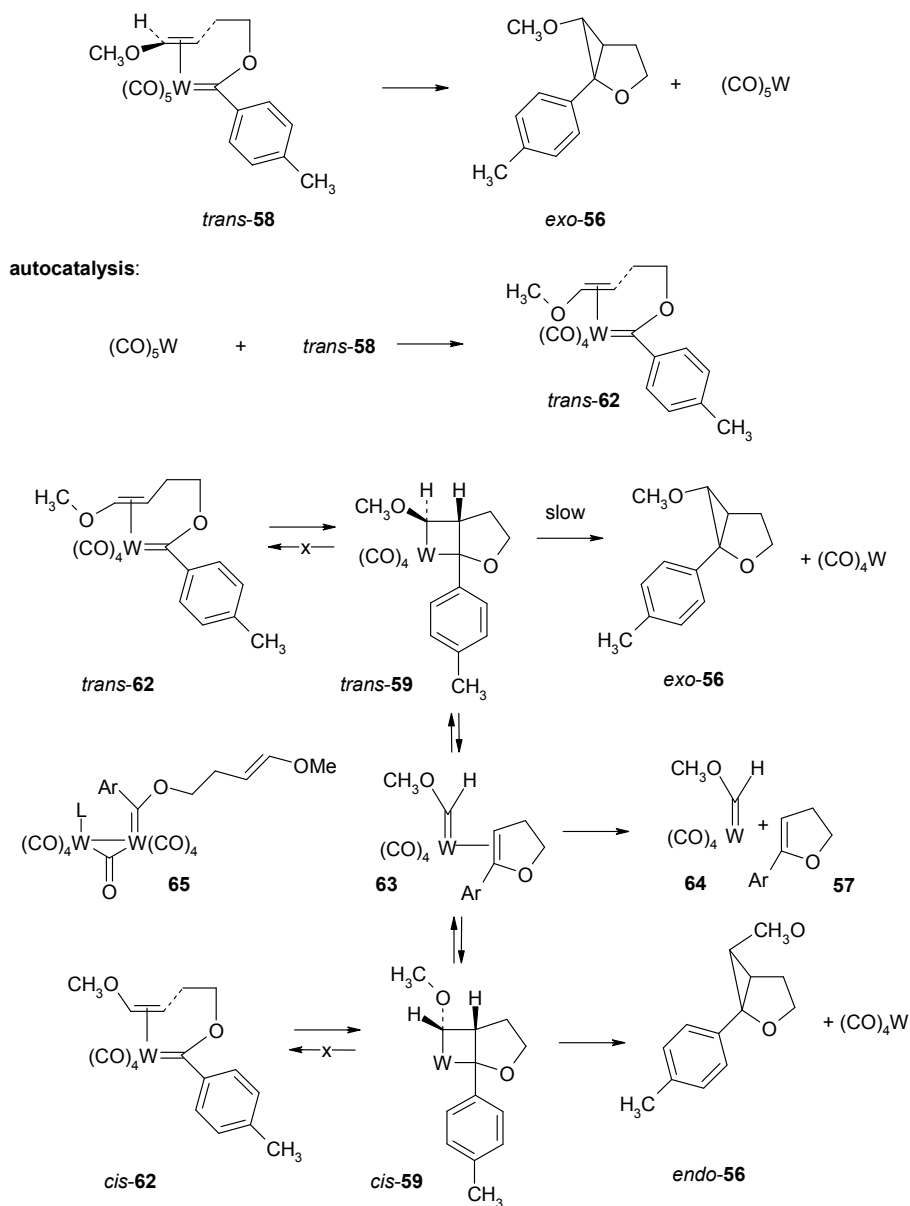


Figure 25. The Mechanism of Cyclopropanation in Noncoordinating Solvents.

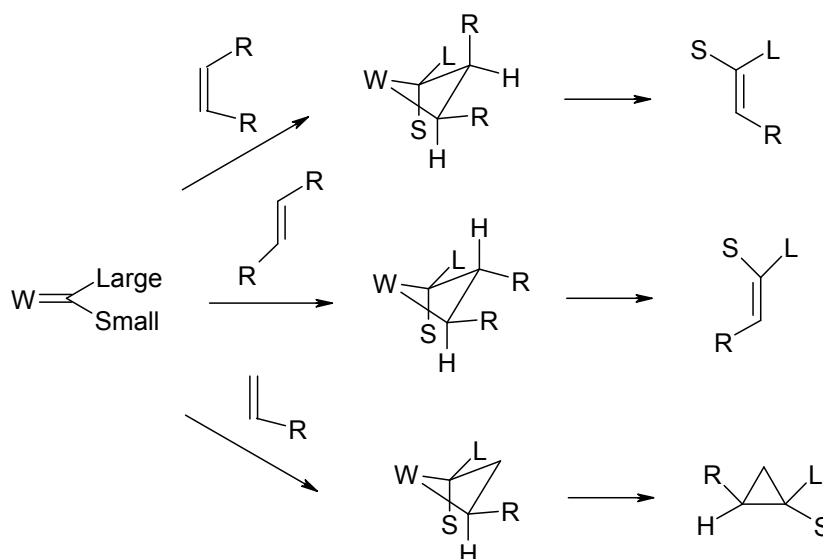


Figure 26. The Stereochemistry of the Metathesis and the Cyclopropanation Reactions.

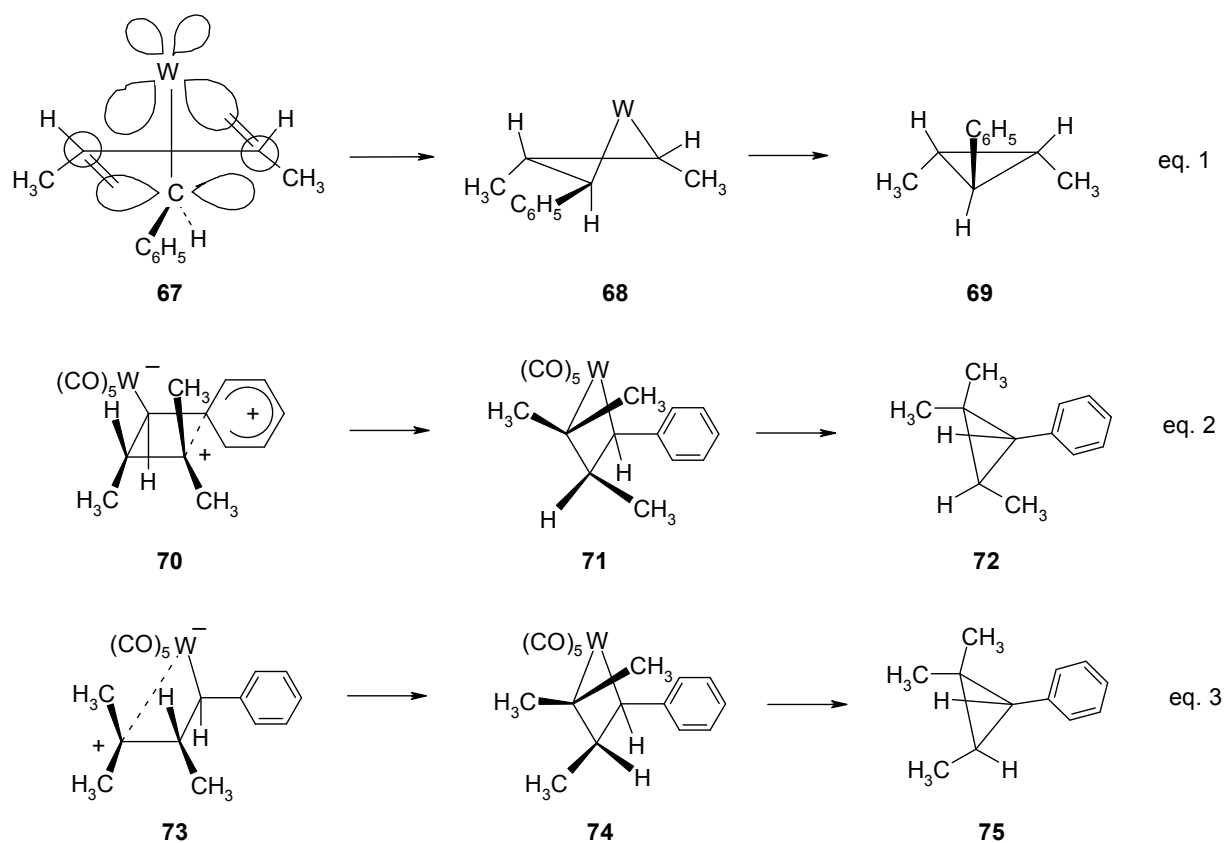


Figure 27. The Casey Cyclopropanation Mechanism.

The resulted $(\text{CO})_5\text{W}$ trapped by solvent or added ligands gives $(\text{CO})_5\text{W-L}$. Olefin metathesis through the metallacycle *trans*-59 apparently is a higher energy process than reductive elimination to give cyclopropane (Scheme 23, 24). In CD_3CN a concerted nonpolar mechanism should exist in competition with a polar mechanism which account for loss of stereochemistry, respectively the isomerization via rotation of the ring-opened dipolar intermediate 60, formed directly from starting material or via reversible ring opening of the

metallacycle (Scheme 24). In noncoordinating solvent the metathesis product is formed as the major products from both, *cis* and *trans*-55, and the mechanism is characterized by an induction period followed by rapid autocatalytic decomposition. [107] Based on the experimental results was proposed the mechanism presented in Scheme 25, where the coordinatively unsaturated intermediate *trans*-62 play an important role in the formation preferentially of the *endo*-56. In the absence of trapping ligand the unsaturated $(\text{CO})_5\text{W}$

ligand abstract CO from the starting material affording *trans*-62, followed by cyclization to 16-electron 6-coordinate metallacycle 59, candidate for slow reductive elimination to *exo*-56, or retroaddition to the π -complex *trans*-62, from which the dihydrofuran 57 is released. The participation of π -complex 63 in a new cycloaddition process leads to the metallacycle *cis*-59, intermediate in the formation of the *endo*-56, after rotation about the tungsten-carbene carbon bond. The unsaturated $W(CO)_4$ species abstract CO from the starting material 58 regenerating the complex 62 through the bridged CO complex 65. [107]

The reaction products obtained with Fischer carbene complexes depends on the coordination number of the metallacycle as well as on the ability of substituents on the alkene to stabilize the new carbene complex. The 18-electron 7-coordinate metallacyclobutanes leads exclusively to the cyclopropanes, as compared with 16-electron 6-coordinate metallacyclobutane. This mechanism explains better the Dotz and Fischer experimental results, where cyclopropanation and olefin metathesis are controlled by external CO pressure, *i. e.* without CO the metathesis reaction dominated, and under 100 atm CO the cyclopropanation dominated. [107]

Casey et. al in a preliminary communication concerning the stereochemistry of the cyclopropanes arises from reaction of $(CO)_5W=CHC_6H_5$ (66) with alkene states as a factor which control the stereochemistry the stability of the puckered metallacyclobutane intermediate. Thus, the “large-small” carbene complex react with *cis*-alkenes to give *cis*-olefins, with *trans*-alkenes to new *trans*-olefins, and *cis*-cyclopropanes from 1-alkene (Figure 26). [108]

Further, detailed studies show that the stereochemistry of cyclopropane formation should be explained by the mode of approach of the alkene toward the phenyl carbene complex. Because the stereochemistry of cyclopropane formation with highly electrophilic complexes could not be explained by the

formation of metallacyclobutane (68) through a $\pi 2s + \pi 2a$ cycloaddition followed by reductive elimination (Scheme 27, eq. 1) an alternative mechanism where the stereochemistry and the rate of the reaction depends on the transition states formed at an earlier stage before the metallacyclobutane formation was proposed. [109]

Upon interaction of the alkene with electrophilic carbene center, the π -electron donation from the phenyl substituent on carbene generates a positive center at the β -carbon which is stabilized in the transition state via interaction with the ipso-carbon of the phenyl ring (70), and subsequent attack of C_β on the M-carbon bond leads to *cis*-cyclopropane. For the formation of *trans*-cyclopropane an “open” transition state (73) was postulated as result of the decreased selectivity with increased size of the alkyl substituent in the monosubstituted olefins. [109]

The highly electrophilic benzylidene iron carbene complex $Cp(CO)_2FeCHC_6H_5^+$ (76a), isolable as a stable crystalline $Pf6^+$ salt, with alkenes forms *cis*-cyclopropanes, probably through a metallacyclobutane, where the substituents lie preferentially *cis* to one another and anti to the Cp ring. Experimental results, such as decreased selectivity in the direction of the increased size of the alkyl substituents in a series of monosubstituted olefins ($R = CH_3, CH_2CH_3, CH(CH_3)_2$), and the increased selectivity 10:1 in presence of *p*-tolyl complex $Cp(CO)_2FeCH(p-CH_3C_6H_4)^+$ (76b) relative to 7.8:1 for the unsubstituted phenyl, are inconsistent with the metallacyclic model and agree the Casey model (79). In the cyclobutane transition state 79a the substituent R is preferentially *trans* to $Cp(CO)_2Fe$ leading to the *cis*-product, after electrophilic attack of C_β on the iron-carbon, and the substituent R ends up *cis* to the phenyl substituent. An open transition state 80 where the substituent R is sterically less crowded than in 79 explain better the decreased selectivity with increased size of the alkyl groups (Scheme 28). [110]

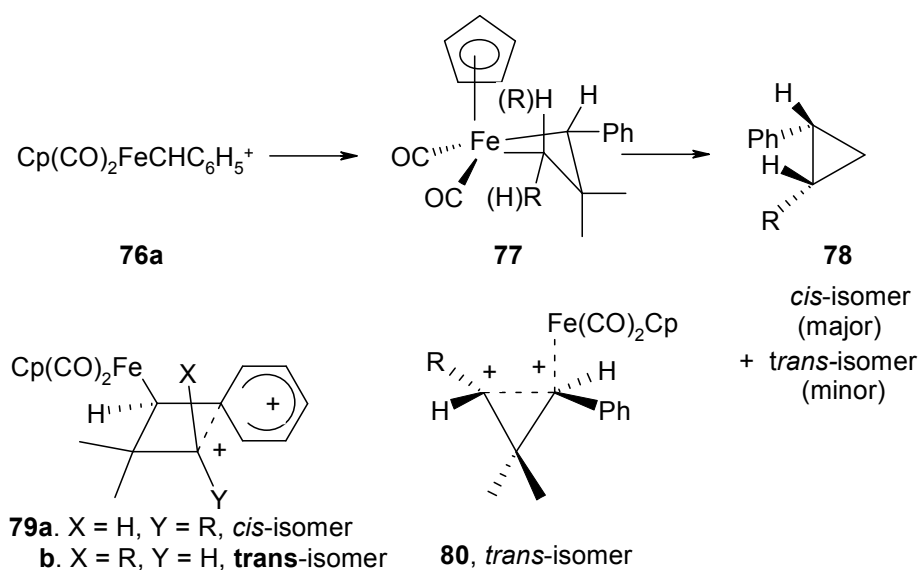


Figure 28. The Brookhart Cyclopropanation Mechanism.

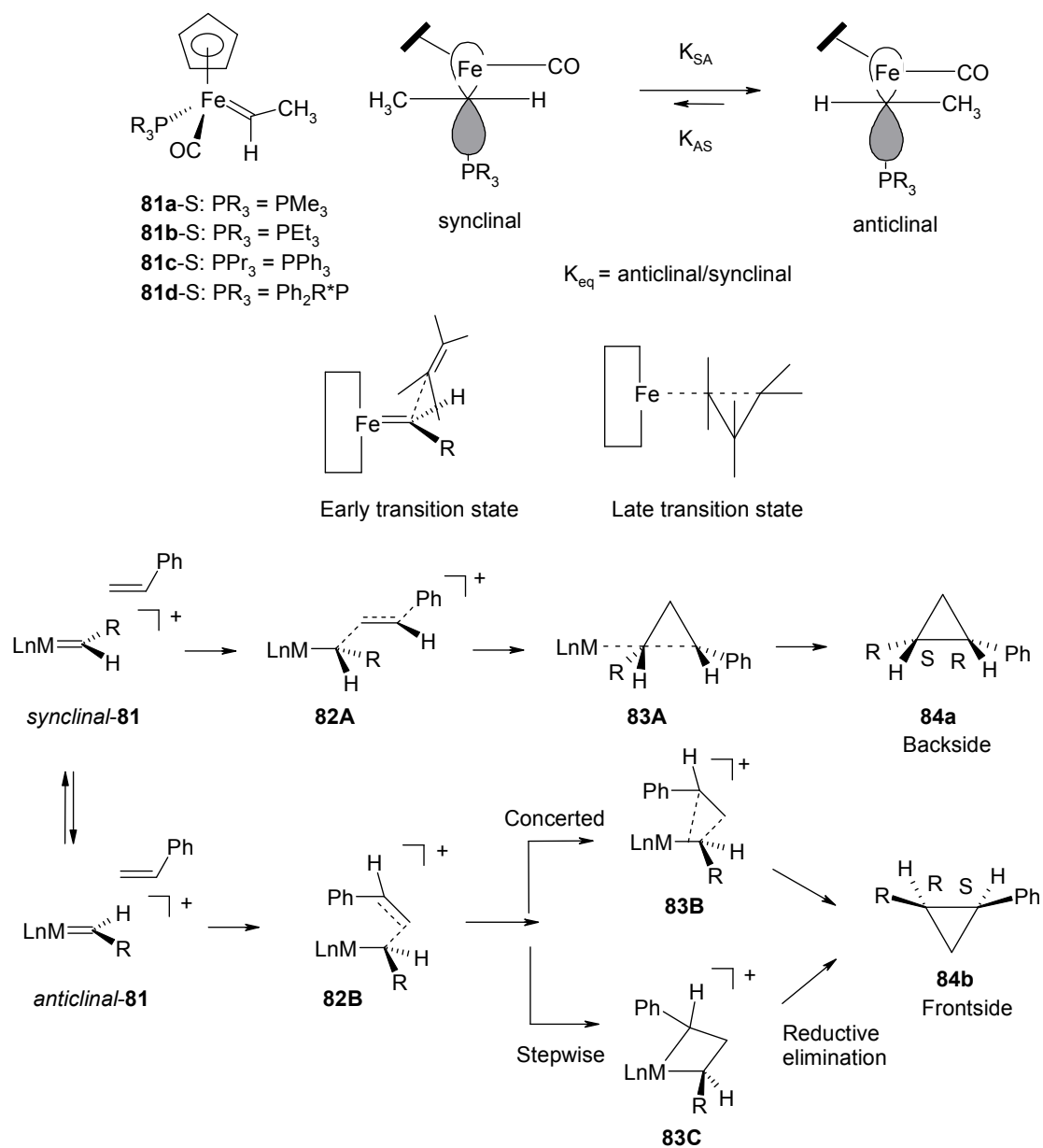


Figure 29. The Brookhart Cyclopropanation Mechanism for "Chiral at iron" Complexes.

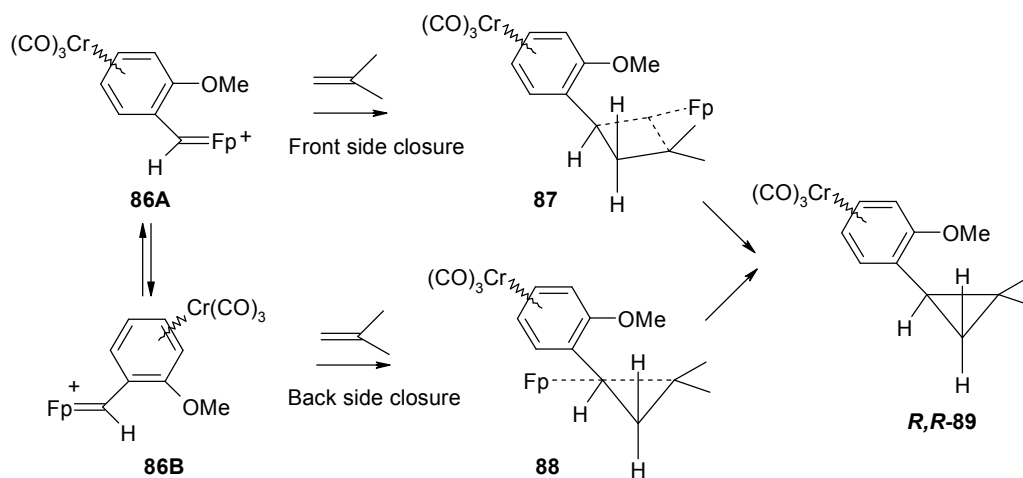


Figure 30. The Hossain Cyclopropanation Mechanism for "Chiral at Carbene" Complexes.

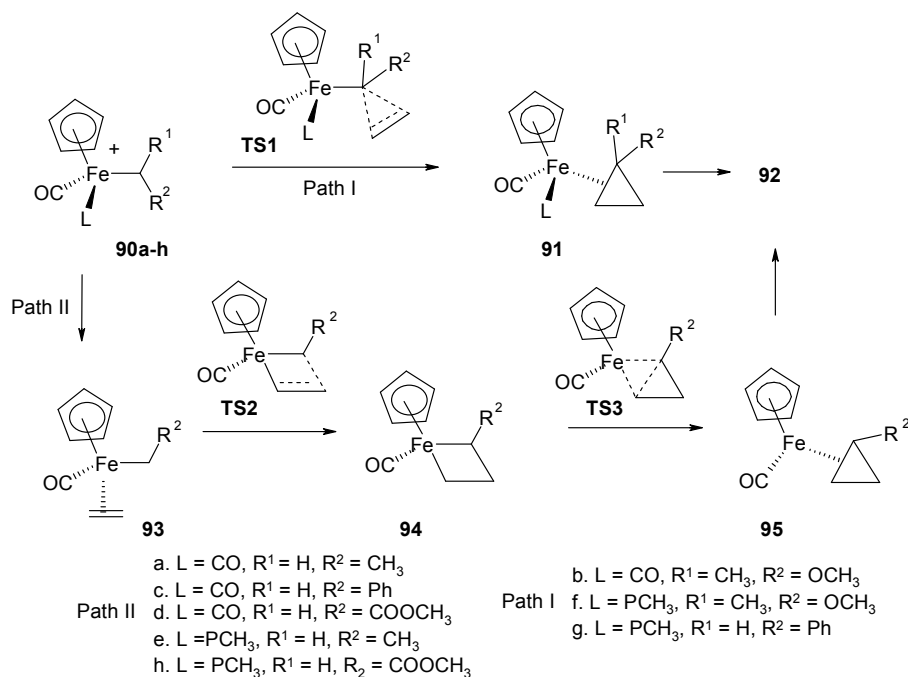


Figure 31. The Proposed Mechanism of Cyclopropanation of Iron Carbene with Ethene Based on DFT Calculation.

Based on the Brookhart's studies on the enantioselectivity of cyclopropane formation performed with "chiral at iron" carbene complex [Cp(CO)PR₃Fe=CHR, 81] the mechanism of cyclopropanation can be rationalized taking in consideration two major factors: (1) the initial attack of the olefin on the synclinal or on the anticlinal-isomer (Figure 29), which are in rapid exchange by rotation around the Fe=C bond, and (2) ring closure occurs through front side closure preserving the configuration at C, or through a back side closure involving inversion at C α . The frontside closure occurs through a concerted process or stepwise process from the major anticlinal isomer, and the backside from the minor synclinal isomer. Experimental results indicate the backside closure from the synclinal isomer as most appropriate pathway. The relative reactivities of the synclinal isomer toward nucleophiles are much higher than the anticlinal isomer, the reactivity difference increasing with decreasing activity of the nucleophile. The attacks of the electrophilic center C α of the carbene complex on the alkene generate partial positive C γ in the transition state, which can be a stabilized carbocation intermediate with sufficient life time to allow C γ -C β bond rotation before product formation leading to change the original alkene stereochemistry, if C γ contain a strongly electron donating group. The stage where the TS is formed "early" or "late", the structure of the transition state and also the diastereoselective, depends on the electrophilicity of ethyldene complex, since dicarbonyl complexes [Cp(CO)₂Fe=CHR, 82] exhibits *cis* selectivity and phosphine substituted complexes [Cp(CO)PR₃Fe=CHR, 85] *trans* selectivity. [111-113]

In contradiction, Hossain et. al. reported that the enantioselectivity of cyclopropanation with "chiral at carbene" complexes [Cp(CO)₂Fe=CH(η 6-(*o*-MeOC₆H₄)Cr(CO)₃)]⁺ (86) is controlled by the higher reactivity of the anti isomer, even it

is the less abundant isomer, and the ring closure occurs through a backside, similar to cyclopropanation with "chiral at iron" complex. Once the chiral center is moved from the metal center to the carbene ligand the rotation around the C α -Cipso play the important role rather than the rotation around the Fe=C α bond. The bulky Cr(CO)₃ group shields the bottom face of the carbene from alkene attack (Figure 30). [114]

The influence of the catalyst structure on the mechanism pathway has been highlighted by the DFT analysis performed by Wang et. al. on the cyclopropanation of ethene catalyzed by Iron (II) carbene complexes [Cp(CO)(L)Fe=CHR, L = CO, PMe₃, R = Me, OMe, Ph, CO₂Me, 90] (Figure 31). The double bond of ethylene attacks directly the carbene carbon of the Fe-carbene complexes through the transition state TS1 (pathway 1), or first the PMe₃ or CO ligand is replaced by ethene, and second the attack of one carbon of ethene on the carbene carbon forms a metallacyclobutane from which the cyclopropane is generated after the elimination reaction (pathway 2). The natural bond orbital energies of the σ and π bonds shown for complexes 90a, d, e, h strong double bonded character of the Fe-Ccarbene bonds, relative to the single bonded character in case of the complexes 90b, c, f, g. The back donation π bonds between iron and π bond of CO in the Fe carbene complexes has been illustrated by the NBO analysis; thus the occupied π orbital of CO with the empty hybrid orbital of the iron forms the σ coordinate bond, and the occupied d orbital of the iron with the empty π^* orbital of CO forms the π -back bonding. The complexes 90a, b, c, d have two back donation π bonds, and the complexes 90e, f, g, h only one back donation π bonds. In complexes 90f, g the occupied π orbital of ethene with empty hybrid orbital of iron forms the σ coordinate bond, and the occupied d orbital of iron with the empty π orbital of ethene forms the π -back bonding orbital. Because for the complex 90b the transition state TS1b

was not found the pathway II remain the preferred one. The natural bond energies of the Fe-P about -1.6000 KJ. mol relative to the -2.000 KJ/mol of the Fe-C(CO) bonds in 90a-d and -1.900 KJ/mol in 90e-h explain well the preference for the pathway II of the complexes 90f, g. [115]

The singlet ironcyclobutene Fe(II) undergo facile [2+2] cycloaddition, activated agnostic CC bonds are present. The spin-crossing to triplet ironcyclobutene favors the cyclopropane formation, analog with Grubbs catalyst. [116, 117]

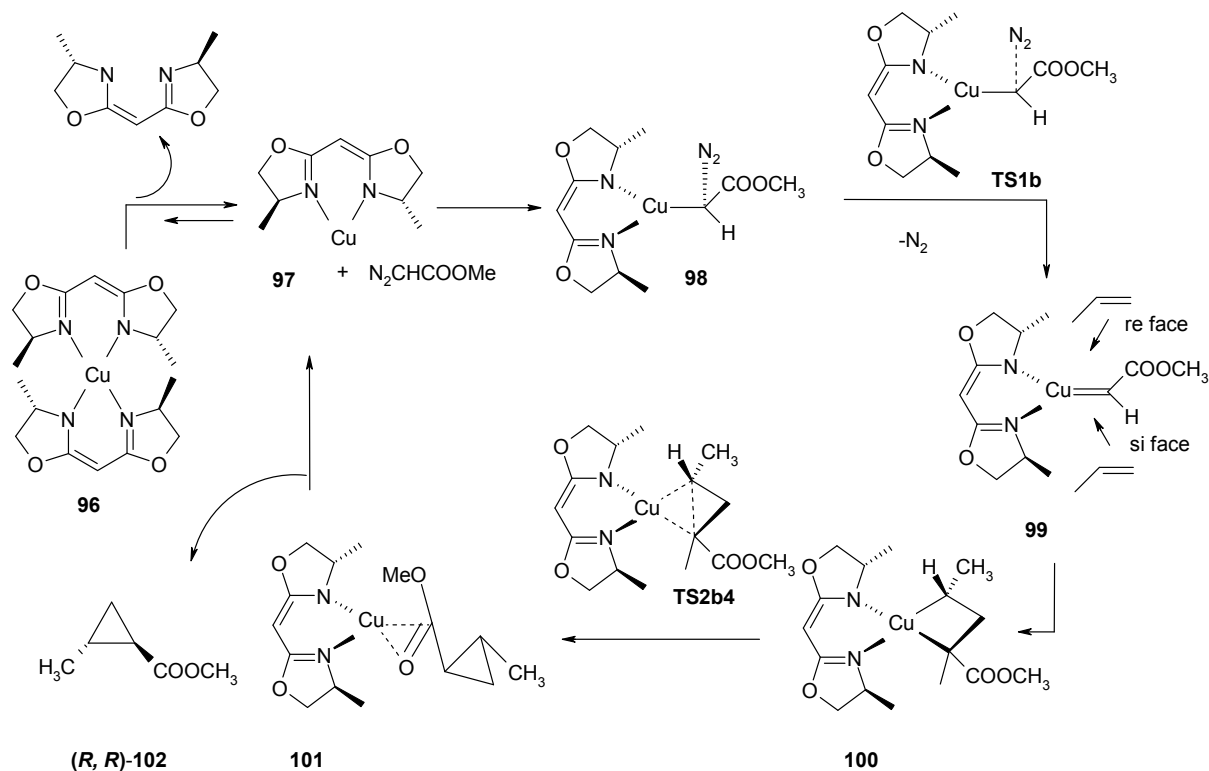


Figure 32. Catalytic Cycle of Cu (I) Catalyzed Asymmetric Cyclopropanation.

Density functional theory (DFT) in accord with experimental results established that the turnover-limiting step for the cyclopropanation with chiral bisoxazoline-Cu(I)-complex 96 is the formation of chiral catalyst-cyclopropyl carboxylate complex 101b4, and from

eight reaction channel, the channel 97-98b-TS1b-99-100b4-TS2b4-101b4-102b4 lead to the formation of the dominant product (R, R)-cyclopropyl carboxylate 102 (Figure 32). [118]

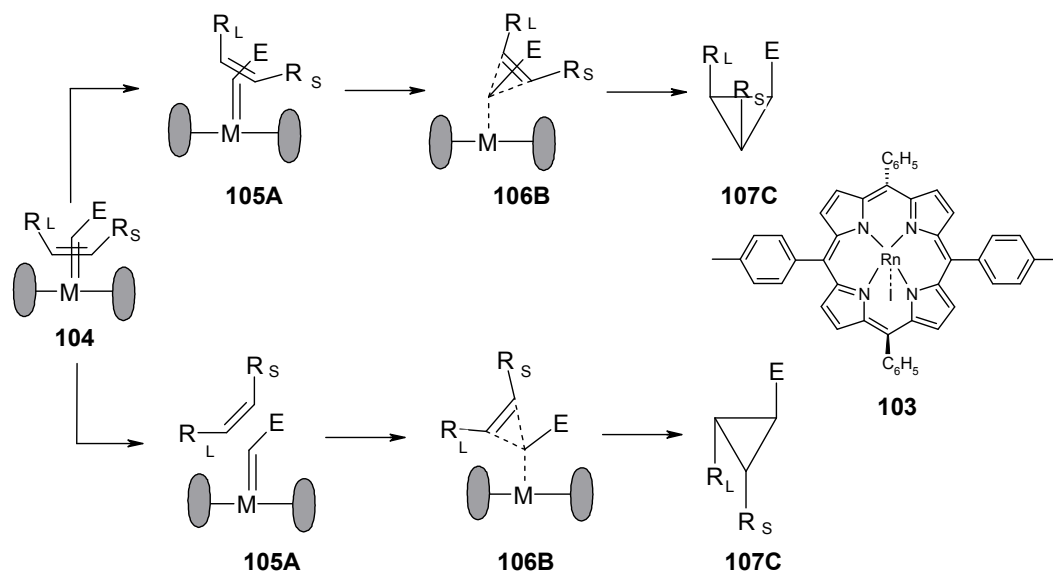


Figure 33. The Kodadek Reaction Coordinate Model for Porphyrin Rhodium Carbene Transfer to an Unsymmetrical Alkene.

Brown and Kodadek based on experimental data established the mechanism presented in Figure 33 where rhodium porphyrin catalysts (103) transfer the carbene fragment to the substrate in a concerted mode through a very early transition state (105), behavior confirmed by secondary isotope effects. The cyclopropanation of styrene and styrene- d_6 with EDA/RhTTPCH₃ take place without detectable secondary isotope effect ($KH/KD = 1.0 \pm 0.07$), results which confirm little rehybridization of the alkene in the transition state of the carbene transfer step. Having as starting point the model proposed previously by Doyle, the olefin approaches perpendicular to the carbene with the large substituent opposite to ester group, realizing a maximum overlap between the HOMO of the alkene and the LUMO of the metallocarbene. Steric factors dictated the rotation of olefin in the Kodadek model, clockwise rotation of the olefin is dominated by the bulky bowl-shaped porphyrins ligand (Path. 1), leading to the syn product, in comparison with the counterclockwise rotation controlled by the ester (Path. 2), leading to the anti product. [119]

The *trans*-cyclopropyl ester occurs as the major product in the presence of the neutral osmium-(II) or iron-(II) catalysts, in opposite to rhodium catalyst bearing bowl-shaped ligand (TMP). The osmium-(II) or iron-(II) is less electrophilic than rhodium-(III), the early transition state found in the case of

Rh-(III) catalyst became relatively late in the Os-(II) or Fe-(II). In the transition state C the alkene carbons probably have some carbocationic (or radicalic) character coming from a full-blown carbonium ion, in agreement with a modest negative Q values in the Hammett plot and the small inverse secondary deuterium isotope effect. [120]

The DFT calculation performed by García et. al. show that the lowest energy transition structure of the cyclopropanation of styrene with a Pybox-RuCl₂ carbene complex (110) at both levels of theory, the full-QM (B3LYP) and QM/MM (B3LYP:UFF), was TStReI, where the relative position of the styrene phenyl and the carbene ester groups was notated with *t*, responsible for *trans* cyclopropane, *Re* represent the stereoface of the carbene carbon atom to which the alkene approaches, and determines the absolute configuration of C₁ in (1*R*)-cyclopropanes, and *I* the conformation of the carbene ester group. The QM/MM method estimated the *trans*/*cis* selectivity of 81:19 relatives to 89:11 obtained experimentally, whereas the full QM calculations predict an almost total *trans*-selectivity (>99:1), because the steric repulsion between the phenyl and the ester groups in the *cis*-TS is overestimated. The absolute configurations of the major (1*R*)-cyclopropanes (112) observed experimentally in the QM/MM calculations occurs when styrene preferential approach to the *Re* face of the carbene atom (Figure 34). [121]

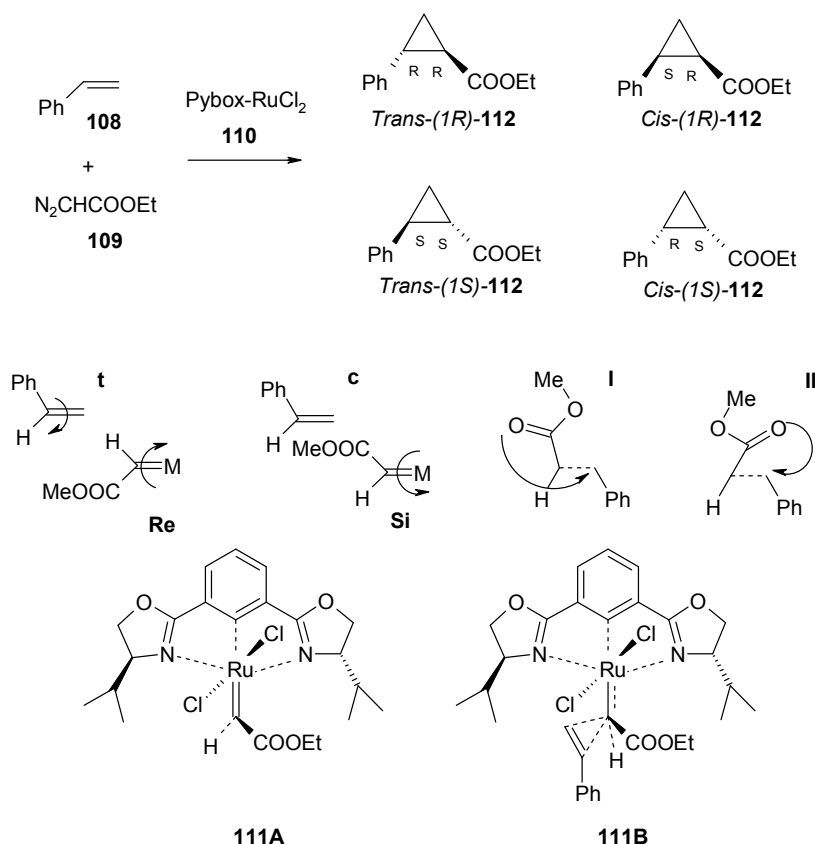


Figure 34. The Reaction Coordinate Model for Ru-Carbene to Unsymmetrical Alkene.

The 18-electron Ru(II) d₆ complex [RuCl(Cod)Cp] (113), able to generate a double coordinative unsaturation in the

intermediate [RuCl(Cp)] (114) after the facile dissociation of the chelated Cod ligand, is a very efficient catalyst in the

decomposition of the diazo derivatives in the presence of olefins to the corresponding cyclopropane or metathesis products through the Ru-carbene/Ru-metallocyclobutane intermediates. The 16-electron metal carbene intermediate A coordinates a molecule of the olefin forming a π -complex, or reacts with a second molecule of diazo compound to form a coupling product. The cyclopropanation can occur without coordination of the olefin to the metal center, but in this case the coordinatively unsaturated metal center seems to favor the formation of the metallocyclobutane by oxidative addition from the corresponding π -complex.

From the metallocyclobutane B occurs the cyclopropanation

product (iii) in the first catalytic cycle, or the metathesis product (iv) and the Ru-carbene intermediate C, involved then in a second cyclopropanation process (vi) or metathesis process (vii), along with the recuperation of the 14-electron $[\text{RuCl}(\text{Cp})]$ complex (114). The selectivity of the process is strongly dependent on olefin substituents, while the formation of the cyclopropanation/homologation products from B is favored by the presence of the cyano substituent at the double bond; the formation of the metathesis product is favored by a phenyl group. A thermodynamic balance should exist between the formation of the 16-electron carbene complex/olefin and the 14-electron complex/cyclopropane pairs (Figure 35). [122]

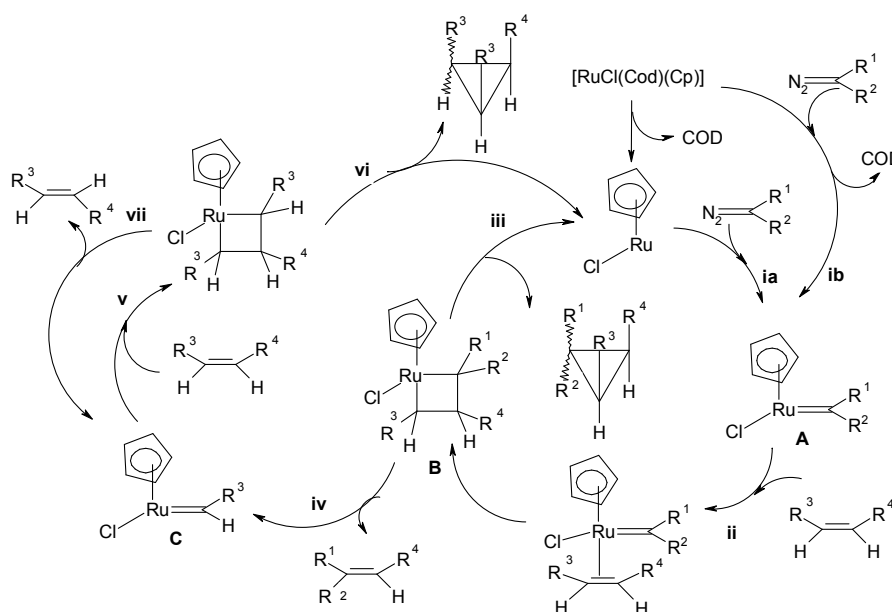


Figure 35. Cyclopropanation Versus Metathesis In Presence of $[\text{RuCl}(\text{Cod})\text{Cp}]$ (113).

The DFT (GGA/PW91/DNP) calculations of the relative equilibrium and transition state free energies (ΔG_{298} , Kcal/mol) performed on the model Ruthenacyclobutane Grubbs bearing simplified PMe_3 ligand $[\text{PMe}_3\text{Ru}(\text{CH}_2)_3\text{Cl}_2]$, [115], [123] in agreement with the experimental results, give less favorable the reductive elimination of cyclopropane [124] than β -hydride transfer.

4. Conclusion

The salient features in olefin metathesis consist in the synthesis of the proper catalysts for a given substrate, as well as the competitive pathways, the metathesis or the cyclopropanation (Scheme 36), to be driven in the right direction.

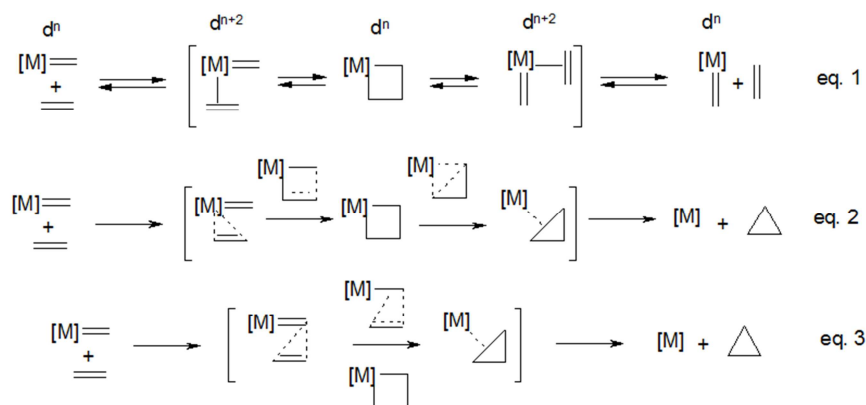


Figure 36. Metathesis Versus Cyclopropanation.

Cyclopropanes occur as side products in the presence of the Schrock or Grubbs metal carbene complexes, or as the major products in the presence of Fischer carbene complexes. Rational control of the catalytic activity and higher stereocontrol can be performed by manipulating the structures of the catalysts in function of the substrates and the reaction conditions. In fact, the structure of the catalyst dictates the mechanism pathway, concerted or stepwise, with the direct attack of the olefin to the carbene carbon or to the metal center.

Acknowledgements

Many thanks to Library of University of Bucharest, „Carol I”, Bucharest, Romania, University of Illinois at Chicago, Chicago, Illinois, US, Institute of Organic Chemistry, Bucharest, Romania.

References

- [1] J. L. Hérisson, Y. Chauvin, Catalyse de transformation des oléfines par les complexes du tungstène. II. Télomérisation des oléfines cycliques en présence d'oléfines acycliques [French], *Makromol. Chem.* 1970, 141, 161.
- [2] D. Astruc, The metathesis reactions: from a historical perspective to recent developments, *New J. Chem.* 2005, 29, 42; doi.org/10.1039/B412198H.
- [3] C. I. Mitan, V. Dragutan, I. Dragutan, New insights into the mechanism of alkene metathesis *Rev. Roum. Chim.* 2011, 56, 299.
- [4] N. Calderon, H. Y. Chen, K. W. Scott, Olefin metathesis – A novel reaction for skeletal transformations of unsaturated hydrocarbons, *Tetrahedron Lett.* 1967, 34, 3327; doi.org/10.1016/S0040-4039(01)89881-6.
- [5] P. G. Gassman, R. Yamaguchi, Electron transfer from highly strained polycyclic molecules, *Tetrahedron* 1982, 38, 1113; doi.org/10.1016/0040-4020(82)80129-4.
- [6] P. G. Gassman, T. Nakai, Chemistry of bent bonds. XXVIII. Transition metal complex specificity and substituent effects in the transition metal complex promoted rearrangement of phenyl substituted bicyclo [1.1.0] butanes, *J. Am. Chem. Soc.* 1972, 94, 2877; doi.org/10.1021/ja00763a066.
- [7] P. Gassman, T. H. Johnson, The chemistry of bent bonds. 51. The relation of polarization in metal-carbene complexes to the degenerate metathesis of terminal olefins, *J. Am. Chem. Soc.* 1977, 99, 622; doi.org/10.1021/ja00444a058.
- [8] R. Z. Hinrichs, J. J. Schroden, F. H. Davis, Competition between C-C and C-H insertion in prototype transition metal-hydrocarbon reactions, *J. Am. Chem. Soc.* 2003, 125, 860; doi.org/10.1021/ja0278842.
- [9] S. Díez-González, S. P. Nolan, Stereochemic parameters associated with N-heterocyclic carbene NHC ligands: A quest for understanding, *Coord. Chem. Rev.* 2007, 251, 874; doi: 10.1016/j.ccr.2006.10.004.
- [10] R. R. Schrock, A. H. Hoveyda, Molybdenum and tungsten imido alkylidene complexes as efficient olefin metathesis catalysts, *Angew. Chem. Int. Ed.* 2003, 42, 4592; doi.org/10.1002/anie.200300576.
- [11] R. R. Schrock, Multiple metal-carbon bonds for catalytic metathesis, *Angew. Chem. Int. Ed.* 2006, 45, 3748; doi.org/10.1002/anie.200600085.
- [12] M. L. Regains, C. F. Bernasconi, Factors that affect the kinetic and thermodynamic acidities of Fischer carbene complexes: New insights from the study of the cationic (methoxymethyl carbene) dicarbonyl pentamethyl cyclopentadienyl iron ([Cp*(CO)₂Fe=C(OMe)Me]⁺), *J. Organomet. Chem.* 2005, 690, 5616; doi: 10.1016/j.jorganchem.2005.07.011.
- [13] T. E. Taylor, M. B. Hall, Theoretical comparison between nucleophilic and electrophilic transition metal carbenes using generalized molecular orbital and configuration interaction methods, *J. Am. Chem. Soc.* 1984, 1576; doi.org/10.1021/ja00318a007.
- [14] G. Frenkling, M. Solá, S. F. Vyboishchikor, Chemical bonding in transition metal carbene complexes, *J. Organomet. Chem.* 2005, 690, 6178; doi: 10.1016/j.jorganchem.2005.08.054.
- [15] Y-D. Wu, Z-H. Peng, Theoretical studies on alkene addition to molybdenum alkylidenes, *J. Am. Chem. Soc.* 1997, 119, 8043; doi.org/10.1021/ja970644f.
- [16] J. H. Oskam, R. R. Schrock, Rate of interconversion of syn and anti rotamers of Mo(CHCMe₂Ph)(NAr)(OR)₂ and relative reactivity toward 2, 3-bis(trifluoromethyl)norbornadiene, *J. Am. Chem. Soc.* 1992, 114, 7588-7590; doi.org/10.1021/ja00045a056.
- [17] R. R. Schrock, A. J. Jiang, S. C. Marinescu, J. H. Simpson, P. Müller, Fundamental studies of molybdenum and tungsten methyldene and metallacyclobutane complexes, *Organometallics* 2010, 29, 5241; doi.org/10.1021/om100363g.
- [18] O. Eisenstein, R. Hoffmann, Activation of a coordinated olefin toward nucleophilic attack, *J. Am. Chem. Soc.* 1980, 102, 6148-6149; doi.org/10.1021/ja00539a032.
- [19] O. Eisenstein, R. Hoffmann, Transition metal complexed olefins: how their reactivity toward a nucleophile relates to their electronic structure, *J. Am. Chem. Soc.* 1981, 103, 4308; doi.org/10.1021/ja00405a005.
- [20] J. S. Yadav, A. Antony, S. T. Rao, B. V. S. Reddy, Recent progress in transition metal catalyzed hydrofunctionalisation of less activated olefins, *J. Organomet. Chem.* 2011, 696, 16; doi.org/10.1016/j.jorganchem.2010.09.052.
- [21] E. V. Anslyn, R. H. Grubbs, Mechanism of titanocene metallacyclobutane cleavage and the nature of the reactive intermediate, *J. Am. Chem. Soc.* 1987, 4880; doi.org/10.1021/ja002500021.
- [22] T. C. T. Chang; B. M. Foxman, M. Rosenblum, C. Stockman, Reactivity of distorted C₅H₅Fe(CO)₂(olefin) cations toward nucleophilic attack, *J. Am. Chem. Soc.* 1981, 103, 7361; doi.org/10.1021/ja00414a066.
- [23] A. K. Keating, S. R. Merrigan, D. A. Singleton, K. N. Houk, Experimental proof of the non-least-motion cycloadditions of dichlorocarbene to alkenes; kinetic isotope effects and quantum mechanical transition states, *J. Am. Chem. Soc.* 1999, 121, 3933; doi.org/10.1021/ja981427x.

- [24] K. Fukui, An M^0 -theoretical illumination for the principle of stereoselection, *Bull. Chem. Soc. Jpn.* 1966, 39, 498; doi.org/10.1246/bcsj.39.498.
- [25] W. A. Goddard III, Selection rules for chemical reactions using the orbital phase continuity principle, *J. Am. Chem. Soc.* 1972, 94, 793; doi.org/10.1021/ja00758a019.
- [26] W. A. Goddard III, Orbital phase continuity principle and selection rules for concerted reactions, *J. Am. Chem. Soc.* 1970, 92, 7520; doi.org/10.1021/ja00728a073.
- [27] T. H. Upton, A. K. Rappé, A theoretical basis for low barriers in transition metal complex $2.\pi + 2.\pi$ reactions: the isomerization of the dicyclopentadienyltitanium complex $Cp_2TiC_3H_6$ to $Cp_2TiCH_2(C_2H_4)$, *J. Am. Chem. Soc.* 1985, 107, 1206; doi.org/10.1021/ja00291a021.
- [28] T. H. Upton, Activation of single-bond cleavage processes on metal surfaces: a comparison of dissociative hydrogen adsorption with simple gas-phase exchange reactions, *J. Am. Chem. Soc.* 1984, 106, 1561; doi.org/10.1021/ja00318a005.
- [29] M. L. Steigerwald, W. A. Goddard III, The $2s+2s$ reactions at transition metals. 1. The reactions of deuterium with dichlorohydrotrititanium ($1+$) ion (Cl_2TiH^+), titanium hydrogen dichloride (Cl_2TiH), and scandium hydrogen dichloride (Cl_2SeH), *J. Am. Chem. Soc.* 1984, 106, 308; doi.org/10.1021/ja00314a009.
- [30] H. K. Hall, P. Ykman, Reactions of the switterions from trisubstituted electron deficient ethylenes and electron-rich olefins, *J. Am. Chem. Soc.* 1975, 97, 800; doi.org/10.1021/ja00837a020.
- [31] J. K. Rasmussen, *o*-Silylated enolates-versatile intermediates for organic synthesis, *Synthesis* 1977, 91; doi: 10.1055/s-1977-24284.
- [32] J. K. Williams, D. W. Wiley, B. C. McKusick, Cyanocarbon Chemistry. XIX. Tetracyanocyclobutanes from tetracyanoethylene and electron-rich alkenes, *J. Am. Chem. Soc.* 1962, 84, 2210; doi.org/10.1021/ja00870a037.
- [33] R. Noyori, I. Umeda, H. Kawauchi, H. Takaya, Nickel-catalyzed reactions involving strained bond. XII. Nickel(0)-catalyzed reaction of quadricyclane with electron-deficient olefins, *J. Am. Chem. Soc.* 1975, 97, 812; doi.org/10.1021/ja00837a022.
- [34] N. Yoshikai, S. C. Ammal, E. Nakamura, L-Shaped three-center two-electron ($C-C-C$)⁺ bonding array, *J. Am. Chem. Soc.* 2004, 126, 12941; doi.org/10.1021/ja6470416.
- [35] F. D. Mango, J. H. Schachtschneider, Molecular orbital symmetry conservation in transition metal catalyzed transformations, *J. Am. Chem. Soc.* 1967, 89, 2484; doi.org/10.1021/ja00986a044.
- [36] F. D. Mango, An orbital symmetry description of transition metal catalyzed butadiene cyclobutanation, *Tetrahedron Lett.* 1969, 54, 4813; doi.org/10.1016/S0040-4039(01)88817-1.
- [37] A. Padwa, H. Lipka, S. H. Watterson, S. S. Hurphree, Phenylsulfonyl ene-allenes as efficient precursors to bicyclic system via intramolecular [2+2] cycloaddition reactions, *J. Org. Chem.* 2003, 68, 6238; doi.org/10.1021/jo6345796.
- [38] K. V. Gothelf, K. A. Jørgensen, Asymmetric 1, 3-dipolar cycloaddition reactions, *Chem. Rev.* 1998, 98, 863; doi.org/10.1021/cr970324e.
- [39] R. Huisgen, G. Steiner, Nonstereospecificity in the [2+2] cycloadditions of tetracyanoethylene to enol ethers, *J. Am. Chem. Soc.* 1973, 95, 5054; doi.org/10.1021/ja00796a051.
- [40] R. Huisgen, G. Steiner, Reversibility of zwitterion formation in the [2+2] cycloaddition of tetracyanoethylene to enol ethers, *J. Am. Chem. Soc.* 1973, 95, 5055; doi.org/10.1021/ja00796a052.
- [41] R. Huisgen, G. Steiner, Tetracyanoethylene and enol ethers. Dependence of cycloaddition rate on solvent polarity, *J. Am. Chem. Soc.* 1973, 95, 5056; doi.org/10.1021/ja00796a053.
- [42] N. D. Epiotis, R. L. Yates, D. Carlberg, F. Bernardi, On the stereochemistry of polar 2+2 cycloadditions, *J. Am. Chem. Soc.* 1976, 98, 453; doi.org/10.1021/ja00418a022.
- [43] K. Fukui, T. Yonezawa, H. Shigu, A molecular orbital theory of reactivity in aromatic hydrocarbons, *J. Chim. Phys.* 1952, 20, 722; doi.org/10.1063/1.1700523.
- [44] J. Ushio, H. Nakatsuji, T. Yonezawa, Electronic structures and reactivities of metal carbon multiple bonds, Schrock-type metal-carbene and metal-carbyne complexes, *J. Am. Chem. Soc.* 1984, 106, 5892; doi.org/10.1021/ja00332a024.
- [45] H. Nakatsuji, J. Ushio, S. Han, T. Yonezawa, Ab initio electronic structures and reactivities of metal carbene complexes, *J. Am. Chem. Soc.* 1983, 105, 426; doi.org/10.1021/ja00341a022.
- [46] R. J. Goddard, R. Hoffmann, E. D. Jemmis, Unusual metal-carbon-hydrogen angles, carbon-hydrogen bond activation, and alpha-hydrogen abstraction in transition-metal carbene complexes, *J. Am. Chem. Soc.* 1980, 102, 7667; doi.org/10.1021/ja00546a008.
- [47] A. K. Rappé, T. H. J. Upton, SIGMA. Metathesis reactions involving group 3 and 13 metals Cl_2MH+H_2 and $Cl_2MCH_3+CH_4$, $M = Al$ and Se , *J. Am. Chem. Soc.* 1992, 114, 7507; doi.org/10.1021/ja00045a026.
- [48] R. R. Schrock, Multiple metal-carbon bonds. 5. The reaction of niobium and tantalum neopentylidene complexes with the carbonyl function, *J. Am. Chem. Soc.* 1976, 98, 5399; doi.org/10.1021/ja00433a062.
- [49] T. R. Cundari, M. S. Gordon, High-valent transition-metal alkylidene complexes: effect of ligand and substituent modification, *J. Am. Chem. Soc.* 1992, 114, 539; doi.org/10.1021/ja00028a022.
- [50] T. R. Cundari, M. S. Gordon, Principal resonance contributors to high-valent, transition metal alkylidene complexes, *J. Am. Chem. Soc.* 1991, 113, 5231; doi.org/10.1021/ja00014a015.
- [51] R. Noyori, On the nature of carbenoids generated from bicyclo [1.1.0]butanes and transition metal complexes, *Tetrahedron Lett.* 1973, 1691; doi.org/10.1016/S0040-4039(01)96030-7.
- [52] C. N. Baird, K. F. Taylor, Multiplicity of the ground state and magnitude of the T_1-S_0 gap in substituted carbenes, *J. Am. Chem. Soc.* 1978, 100, 1333; doi.org/10.1021/ja00473a001.
- [53] J. F. Harrison, R. C. Liedtke, J. F. Liebman, The multiplicity of substituted acyclic carbenes and related molecules, *J. Am. Chem. Soc.* 1979, 101, 7162; doi.org/10.1021/ja00518a006.
- [54] P. G. Gassman, T. H. Johnson, Quenching of olefin metathesis. Evidence for the generation of metal-carbene intermediates from noncarbenoid precursors, *J. Am. Chem. Soc.* 1976, 98, 6055; doi.org/10.1021/ja00435a056.

- [55] I. Fernández, M. A. Sierra, M. Gómez-Gallego, M. J. Mancheño, F. P. Cossío, Computational and experimental studies on the mechanism of the photochemical carbonylation of group 6 Fischer carbene complexes, *Chem. Eur. J.* 2005, 11, 5988; doi.org/10.1002/chem.200400944.
- [56] H. C. Foley, L. M. Strubinger, T. S. Targos, G. L. Geoffroy, Photochemistry of $[W(CO)_5\{C(OMe)Ph\}]$. Formation of alkyne-carbene complexes and studies of their decomposition reactions, *J. Am. Chem. Soc.* 1983, 105, 3064; doi.org/10.1021/ja00348a020.
- [57] G. Trinquier, J.-P. Malrieu, Nonclassical distortions at multiple bonds, *J. Am. Chem. Soc.* 1987, 109, 5303; doi.org/10.1021/ja00252a002.
- [58] J.-P. Malrieu, G. Trinquier, Trans-bending at double bonds. Occurrence and extent, *J. Am. Chem. Soc.* 1989, 109, 5916; doi.org/10.1021/ja00197a061.
- [59] D. S. Marynick, C. M. Kirkpatrick, Localized molecular orbital studies on transition-metal complexes. III. Localized valence structures of transition-metal carbenes complexes, *J. Am. Chem. Soc.* 1985, 107, 1993; doi.org/10.1021/ja00293a032.
- [60] M. W. Schmidt, M. S. Gordon, M. Dupuis, The intrinsic reactions coordinate and the rotational barrier in silaethylene, *J. Am. Chem. Soc.* 1985, 107, 2585; doi.org/10.1021/ja00295a002.
- [61] M. W. Schmidt, P. N. Truong, M. S. Gordon, pi-Bond strengths in the second and third periods, *J. Am. Chem. Soc.* 1987, 109, 5217; doi.org/10.1021/ja00251a029.
- [62] Y. Yamaguchi, Y. Osamura, H. F. Schaefer III, Analytic energy second derivatives for two configuration self-consistent-field wave functions. Application to twisted ethylene and to the trimethylene diradical, *J. Am. Chem. Soc.* 1983, 105, 7506; doi.org/10.1021/ja00364a004.
- [63] G. Occhipinti, V. R. Jensen, Nature of the transition Metal-Carbene bond on Grubbs olefin metathesis catalysis, *Organometallics* 2011, 30, 3522; dx.doi.org/10.1021/om20018y.
- [64] T. J. Katz, J. McGinnis, Mechanism of the olefin metathesis reaction, *J. Am. Chem. Soc.* 1977, 99, 1903; doi.org/10.1021/ja00839a063.
- [65] R. H. Grubbs, P. L. Burk, D. D. Carr, Mechanism of the olefin metathesis reaction, *J. Am. Chem. Soc.* 1975, 97, 3265; doi.org/10.1021/ja00844a082.
- [66] R. H. Grubbs, D. D. Carr, C. Hoppin, P. L. Burk, Consideration of the mechanism of the metal catalyzed olefin metathesis reaction, *J. Am. Chem. Soc.* 1976, 98, 3478; doi.org/10.1021/ja00428015.
- [67] T. J. Katz, J. McGinnis, Metathesis of cyclic and acyclic olefins, *J. Am. Chem. Soc.* 1977, 99, 1903; doi.org/10.1021/ja00448a036.
- [68] T. J. Katz, R. Rothchild, Mechanism of the olefin metathesis of 2, 2' divinylbiphenyl, *J. Am. Chem. Soc.* 1976, 98, 2519; doi.org/10.1021/ja00426a021.
- [69] C. P. Casey, H. E. Tuinstra, Stereochemistry of the degenerate metathesis of terminal alkenes-the nature of the chain-carrying metal-carbene complex, *J. Am. Chem. Soc.* 1978, 100, 2270; doi.org/10.1021/ja00475a070.
- [70] M. T. Mocella, M. A. Busch, E. L. Muetterties, Olefin metathesis reaction. III. Mechanistic considerations, *J. Am. Chem. Soc.* 1976, 98, 1283; doi.org/10.1021/ja00421a051.
- [71] R. R. Schrock, First isolable transition metal methylene complex, and some simple reactions, *J. Am. Chem. Soc.* 1975, 97, 6577; doi.org/10.1021/ja00855a048.
- [72] Hansen, F. Rominger, M. Metz, P. Hofmann, The first Grubbs-type metathesis catalyst with cis stereochemistry: synthesis of $[(\eta^2\text{-dtbpm}) Cl_2Ru=CH-CH=CMe_2]$ from a novel, coordinatively unsaturated dinuclear ruthenium dihydride, *Chem. Eur. J.* 1999, 5, 557; doi.org/10.1002(SICI)1521-3765(19990201)5:2<557::AID-CHEM557>3.0.CO;2-A.
- [73] S. J. McLain, C. D. Wood, R. R. Schrock, Multiple metal-carbon bonds. 6. The reaction of niobium and tantalum neopentylidene complexes with simple olefins: a route to metallocyclopentanes, *J. Am. Chem. Soc.* 1977, 99, 3519; doi.org/10.1021/ja0045a064.
- [74] F. Blanc, C. Copéret, J. Thivolle-Cazat, J. M. Basset, A. Lesage, L. Emsley, A. Sinha, R. R. Schrock, *Angew. Chem. Int. Ed.* 2006, 45, 1216-1220.
- [75] F. C. Courchay, T. W. Baughman, K. B. Wagener, Understanding the effect of allylic methyls in olefin cross-metathesis, *J. Organomet. Chem.* 2006, 691, 585; doi.org/10.1016/j.jorganchem.2005.09.030.
- [76] M. L. Macnaughtan, J. Gary, D. L. Gerlach, M. J. A. Johnson, J. W. Kampf, Cross-metathesis of vinyl halides. Scope and limitation of ruthenium based catalysts, *Organometallics* 2009, 28, 2880; doi.org/10.1021/om800463n.
- [77] G. Occhipinti, H.-R. Bjorsvik, V. R. Jensen, Quantitative structure activity relationships of ruthenium catalyzed for olefin metathesis, *J. Am. Chem. Soc.* 2006, 128, 6952; doi.org/10.1021/ja060832i.
- [78] F. Nuñez, J. Poater, L. Rodríguez-Santiago, X. Solans-Monfort, M. Solà, M. Sodupe, On the electronic structure of second generation Hoveyda-Grubbs alkene metathesis precursors, *Comp. Theor. Chem.* 2012, 996, 57; doi.org/10.1016/j.comptc.2012.07.015.
- [79] T. M. Trnka, M. W. Day, R. H. Grubbs, Olefin metathesis with 1, 1-difluoroethylene, *Angew. Chem. Int. Ed.* 2001, 40, 3441; doi.org/10.1002/1521-3773(20010917)40:18<3491.
- [80] S. Fomine, M. A. Tlenkopatcher, Metathesis of fluorinated olefins by ruthenium alkylidene catalysts. Fluorine substituent effects on a Ru-carbene(alkylidene) complex stability, *Appl. Catal. A*, 2009, 355, 148; doi.org/10.1016/j.apcata.2008.12.011.
- [81] M. Jordaán, P. van Helden, C. G. C. E. van Sittert, H. C. M. Vosloo, Experimental and DFT investigation of the 1-actene metathesis reaction mechanism with the Grubbs 1 precatalyst, *J. Mol. Cat. A: Chem.* 2006, 245, 145; DOI: 10.1016/J.MOLCATA.2006.03.022.
- [82] P. Tobón, S. Gómez, A. Restrepo, F. Núñez-Zarur, Role of substrate substituent in alkene metathesis mediated by a Ru alkylidene catalyst, *Organomet* 2021, 40, 119; doi.org/10.1021/acs.organomet.0c00482.
- [83] A. Caballero, A. Prieto, M. M. Díaz-Requejo, P. J. Pérez, Metal-catalyzed olefin cyclopropanation with ethyl diazoacetate: control of the diastereoselectivity, *Eur. J. Inorg. Chem.* 2009, 1137; doi.org/10.1002/ejic.200800944.

- [84] M. P. Doyle, M. N. Protopopova, New aspects of catalytic asymmetric cyclopropanation, *Tetrahedron* 1998, 54, 7918; doi.org/10.1016/S0040-4020(98)00222-1.
- [85] A. Berkessel, P. Kaiser, J. Lex, Electronically tuned chiral ruthenium porphyrins: extremely stable and selective catalysts for asymmetric epoxidation and cyclopropanation, *Chem. Eur. J.* 2003, 9, 4746; doi.org/10.1002/chem.200305045.
- [86] A. Tudose, A. Demonceau, L. Delaude, Imidazol(in)ium-2-carboxylates as N-heterocyclic carbene precursors in ruthenium-arene catalysts for olefin metathesis and cyclopropanation, *J. Organomet. Chem.* 2006, 691, 5356; doi.org/10.1016/j.jorganchem.2006.07.035.
- [87] A.-M. Abu-Elfotouh, K. Phomkeona, K. Shibatani, S. Iwasa, Asymmetric inter and intramolecular cyclopropanation reactions catalyzed by a reusable macroporous-polymer-supported chiral ruthenium (II) phenyl-oxazolium complex, *Angew. Chem. Int. Ed.* 2010, 49, 8439; doi.org/10.1002/anie.201002240.
- [88] M. M. Díaz-Requejo, T. R. Belderrain, S. Trofimenko, P. J. Pérez, Unprecedented highly cis-diastereoselective olefin cyclopropanation using copper homoscorpionate catalysts, *J. Am. Chem. Soc.* 2001, 123, 3167; doi.org/10.1021/ja0155736.
- [89] T. Ikeno, I. Iwakura, T. Yamada, Cobalt-carbene complex with single-bond character intermediate for the cobalt complex-catalyzed cyclopropanation, *J. Am. Chem. Soc.* 2002, 124, 15152; doi.org/10.1021/ja027713x.
- [90] A. J. Anciaux, A. J. Hubert, A. F. Noels, N. Petiniot, P. Feyssie, Transition metal catalyzed reactions of diazo compounds. 1. Cyclopropanation of double bonds, *J. Org. Chem.* 1980, 45, 695; doi.org/10.1021/jo0192a029.
- [91] A. Nakamura, A. Konishi, R. Tsujitani, M. Kudo, S. Otsuka, Enantioselective carbenoid cyclopropanation catalyzed by chiral vicdioximatocobalt(II) complexes prepared from natural camphor and beta-pinene. Mechanism and stereochemistry, *J. Am. Chem. Soc.* 1978, 100, 3449; doi.org/10.1021/ja00479a029.
- [92] M. Nakamura, A. Hirai, E. Nakamura, Reaction pathways of the Simmons-Smith reaction, *J. Am. Chem. Soc.* 2003, 125, 2341; doi.org/10.1021/ja026709j.
- [93] N. Yoshikai, S. C. Ammal, E. Nakamura, L-Shaped three-center two-electron, *J. Am. Chem. Soc.* 2004, 126, 12941; doi.org/10.1021/ja0470416.
- [94] Y.-B. Zho, F.-L. Cao, Mechanistic competition variations due to the substituents in the lithium carbenoid promoted cyclopropanation reactions, *J. Organomet. Chem.* 2007, 692, 3723; doi.org/10.1016/j.jorganchem.2007.05.014.
- [95] J. R. Wolf, C. G. Hamaker, J.-P. Djukic, T. Kodadek, K. L. Woo, Shape and stereoselectivity cyclopropanation of alkenes catalyzed by iron porphyrins, *J. Am. Chem. Soc.* 1995, 117, 9194; doi.org/10.1021/ja00141a011.
- [96] C.-M. Che, J.-S. Huang, F.-W. Lee, Y. Li, T.-S. Lai, H.-L. Kwong, P.-F. Teng, W.-S. Lee, W.-C. Lo, S.-M. Peng, Z.-Y. Zhou, Asymmetric inter and intramolecular cyclopropanation of alkenes catalyzed by chiral ruthenium porphyrins. Synthesis and crystal structure of a chiral metalloporphyrin carbene complex, *J. Am. Chem. Soc.* 2001, 123, 4119; doi.org/10.1021/ja001416f.
- [97] H. Nishiyama, Y. Itoh, H. Matsumoto, S.-B. Park, K. Itoh, New chiral ruthenium bis (oxazoliny) pyridine catalyst. Efficient asymmetric cyclopropanation of olefin with diazoacetates, *J. Am. Chem. Soc.* 1994, 116, 2223; doi.org/10.1021/ja00084a104.
- [98] D. Griller, A. S. Nazran, J. C. Scaiano, Flash photolysis studies of carbenes and their impact on the skill-woodworth rules, *Tetrahedron* 1985, 41, 1525; doi.org/10.1016/S0040-4020(01)96392-6.
- [99] A. P. Marchand, N. M. Brockway, Carbalkoxy carbenes, *Chem. Rev.* 1974, 74, 431; doi.org/10.1021/cr60290a002.
- [100] R. Noyori, M. Yamakawa, A molecular orbital study of carbomethoxycarbene and dicarboxycarbene, *Tetrahedron Lett.* 1980, 21, 2851; doi.org/10.1016/S0040-4039(00)78625-4.
- [101] R. J. Miller, H. Shechter, Electronic effects in the unimolecular decomposition of substituted diphenyldiazomethanes, *J. Am. Chem. Soc.* 1978, 100, 7920; doi.org/10.1021/ja00493a022.
- [102] D. E. James, L. F. Hines, J. K. Stille, The palladium(II) catalyzed olefin carbonylation reaction. The stereochemistry of methoxypalladation, *J. Am. Chem. Soc.* 1976, 98, 1806; doi.org/10.1021/ja00423a027.
- [103] R. M. Moriarty, S. Tyagi, M. Kinck, Metal free intramolecular cyclopropanation of alkenes through iodonium ylide methodology, *Tetrahedron* 2010, 66, 5801; doi.org/10.1016/j.tet.2010.05.005.
- [104] C. E. Kefalidis, A. A. Kanakis, J. K. Gallos, C. A. Tsipis, DFT study of the mechanism of Cu(I)-catalyzed and uncatalyzed intramolecular cyclopropanation of iodonium ylides, *J. Organomet. Chem.* 2010, 695, 2030; doi.org/10.1016/j.jorganchem.2010.05.013.
- [105] C. R. Johnson, M. Haake, C. W. Schrock, Chemistry of sulfoxides and related compounds. XXVI. Preparation and synthetic applications of (dimethylamino) phenyloxosulfonium methylide, *J. Am. Chem. Soc.* 1970, 92, 6594; doi.org/10.1021/ja00725a035.
- [106] R. Noyori, H. Kawauchi, H. Takaya, Stereochemistry of the nickel(0) catalyzed reaction of bicyclo [1.1.0]butane and electron-deficient olefins, *Tetrahedron Lett.* 1974, 19, 1749; doi.org/10.1016/S0040-4039 (01)82570-3.
- [107] C. P. Casey, N. L. Hornung, W. P. Kosar, Intramolecular cyclopropanation and olefin metathesis reactions of (CO)₅W: C(OCH₂CH₂CH: CHOCH₃)C₆H₄CH₃-p, *J. Am. Chem. Soc.* 1987, 109, 4908; doi.org/10.1021/ja00250a025.
- [108] C. P. Casey, S. W. Polichnowski, Generation and reaction of (phenylmethylcarbene) pentacarbonyl tungsten(0), *J. Am. Chem. Soc.* 1977, 99, 2533; doi.org/10.1021/ja00450a021.
- [109] C. P. Casey, S. W. Polichnowski, A. J. Shusterman, C. R. Jones, Reactions of benzylidene penta carbonyl-tungsten with alkenes, *J. Am. Chem. Soc.* 1979, 101, 7282; doi.org/10.1021/ja00518a025.
- [110] M. Brookhart, M. B. Humphrey, H. J. Kratzor, G. O. Nelson, Reactions of .eta.5-C₅H₅(CO)₂FeCHC₆H₅+ with alkenes alkynes. Observation of efficient benzylidene-transfer reactions, *J. Am. Chem. Soc.* 1980, 102, 7802; doi.org/10.1021/ja00546a039.
- [111] M. Brookhart, Y. Liu, E. W. Goldman, D. A. Timmers, G. D. Williams, Enantioselective cyclopropane synthesis using the chiral carbene complexes (SFe)-and(RFe)-C₅H₅(CO)(PR₃)Fe: CHCH₃⁺. A mechanistic analysis of carbene transfer reaction, *J. Am. Chem. Soc.* 1991, 113, 927; doi.org/10.1021/ja00003a028.

- [112] M. Brookhart, Y. Liu, Investigation of the stereochemistry of iron-carbon.alpha.bond cleavage when phenylcyclopropane is generalized by gamma.-ionization of stereospecifically deuterate $C_5H_5(CO)_2FeCHDCHDCH(OCH_3)C_6H_5$ complexes. A transition-state model for transfer of the carbene ligand from $C_5H_5(O)_2Fe:CHR+$ to alkenes, *J. Am. Chem. Soc.* 1991, 113, 939; doi.org/10.1021/ja00003a029.
- [113] M. Brookhart, Y. Liu, R. C. Buck, Diastereoselective reactions of chiral at iron carbene complexes $C_5H_5(CO)(PR_3)Fe:CHR+$, synclinal isomers are more reactive than anti-clinal isomers, *J. Am. Chem. Soc.* 1988, 110, 2337; doi.org/10.1021/ja00215a074.
- [114] Q. Wang, F. H. Försterling, M. M. Hossain, Study of the origin of enantioselectivity in cyclopropanation reactions using the chiral iron carbene complex $[(\eta^5-C_5H_5)(CO)_2Fe=CH[(\eta^6-O-MeOC_6H_4)Cr(CO)_3]]^+$, *J. Organomet. Chem.* 2005, 690, 6238; doi.org/10.1016/j.jorganchem.2005.09.025.
- [115] F. Wang, Q. Meng, M. Li, Density functional computations of the cyclopropanation of ethene catalyzed by iron(II)carben complexes $Cp(CO)(L)Fe=CHR$, $L = CO, PMe_3$, $R = Me, OMe, Ph, CH_2Me$, *Int. J. Quantum Chem.* 2008, 108, 945; doi.org/10.1002/qua.21559.
- [116] G. S. Remya, C. H. Suresh, On the ineffectiveness of Grubbs type iron olefin methathesis catalysts: Role of spin state isomerism and cyclopropanation, *Inorganica Chimica Acta*, 2022, 538, 120971; doi.org/10.1016/j.ica.2022.120971.
- [117] M. Mauksch, S. B. Tsogoeva, Iron-Catalyzed olefin metathesis: Recent theoretical and experimental advances, *Chem. Eur. J.* 2022, 28, e202201414; doi.org/10.1002/chem.202201414.
- [118] Meng, Q.; Li, M.; Tang, D.; Shen, W.; Zhang, Density functional studies on copper-catalyzed asymmetric cyclopropanation of diazoacetate with alkene, *J. J. Mol. Str.* (THEOCHEM) 2004, 711, 193; doi.org/10.1016/j.theochem.2004.06.050.
- [119] K. C. Brown, T. Kodadek, A transition-state model for the rhodium porphyrin catalyzed cyclopropanation of alkenes by diazoesters, *J. Am. Chem. Soc.* 1992, 114, 8336; doi.org/10.1021/ja00047a081.
- [120] J. R. Wolf, C. G. Hamaker, J. P. Djukic, T. Kodadek, L. K. Woo, Sape and stereoselective cyclopropanation of alkenes catalyzed iron porphyrins, *J. Am. Chem. Soc.* 1995, 117, 9194; doi.org/10.1021/ja00141a011.
- [121] J. I. García, G. Jiménez-Osés, V. Martínez-Merino, J. A. Mayoral, E. Pires, I. Villalba, QM/MM Modeling of enantioselective Pybox ruthenium and box-copper-catalyzed cyclopropanation reactions: scope, performance, and applications to ligand design, *Chem. Eur. J.* 2007, 13, 4064; doi.org/10.1002/chem.2006.01358.
- [122] M. Basato, C. Tubaro, A. Biffis, M. Bonato, G. Buscemi, F. Lighezzolo, P. Lunardi, C. Vianini, F. Benetollo, A. Del Zotto, Reactions of diazo compounds with alkenes catalyzed by $[RuCl(cod)(Cp)]$: Effect of the substituents in the formation of cyclopropanation or metathesis products, *Chem. Eur. J.* 2009, 15, 1516; doi.org/10.1002/chem.200801211.
- [123] DFT Prediction and experimental observation of substrate induced catalyst decomposition in ruthenium catalyzed olefin metathesis, *J. Am. Chem. Soc.* 2004, 126, 14332; doi.org/10.1021/ja0453174 (Supporting information).
- [124] M. Jawiczak, A. Marczyk, B. Trzaskowski, Decomposition of ruthenium olefin metathesis catalyst, *Catalysts* 2020, 10, 887; doi.10.3390/catal10080887.