1 Theoretical Survey

1.1 Carbenes

Carbenes are characterized by their divalent nature, an unshared electron pair, and a resulting total number of six valence electrons. One can distinguish between two different kinds of carbenes based on the electronic situation of the lone pair. In singlet carbenes, the two electrons with antiparallel spins are located in the σ-orbital while the p_π-orbital is vacant. In a triplet carbene, only one electron is located in the σ-orbital while the other electron is located in the p_π orbital and the spins are parallel (Figure 3).[15]

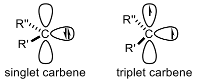
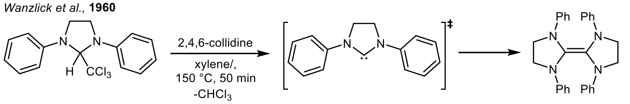


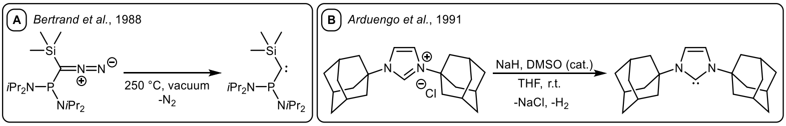
Figure 3. Frontier orbitals of a singlet and a triplet carbene.

Due to their very reactive nature carbenes have long been elusive. The first evidence for the formation of free carbenes was reported by *Wanzlick et al.* in 1960.[16] Upon heating 1,3-diphenyl-2-trichloromethylimidazolidine, the dimer of 1,3-diphenylimidazolin-2-ylidene was obtained, indicating the initial formation of the free carbene (Scheme 5A).



Scheme 5. Transient formation of 1,3-diphenylimidazolin-2-ylidene from its chloroform adduct and subsequent dimerization.[16]

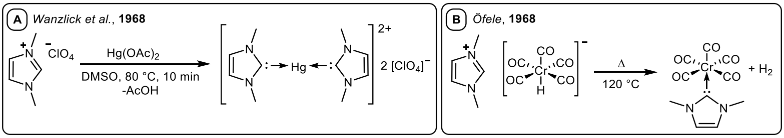
However, only in 1988, *Bertrand et al.* were able to isolate the first free carbene (Scheme 6A).[17] Three years later, *Arduengo et al.* prepared 1,3-diadamantylimidazol-2-ylidene (IAd), the first free carbene that could be stored indefinitely, albeit only in the absence of moisture and oxygen (Scheme 6B).[18] The latter was also the first example of an isolable free *N*-heterocyclic carbene (NHC), a class of ligands that grew vastly important as ligands in transition metal chemistry and catalysis in the following 30 years.



Scheme 6. A) Synthesis of the first isolable carbene by flash pyrolysis of a phosphino-substituted diazomethane.[17] B) Synthesis of the first stable *N*-heterocyclic carbene by deprotonation of 1,3-diadamantylimidazolium chloride.[18]

1.1.1 *N*-Heterocyclic Carbenes

In NHCs, the carbene is part of a heterocycle containing at least one nitrogen atom.[19] The first complexes bearing NHC-ligands were already reported in 1968 by *Wanzlick et al.* and *Öfele* (Scheme 7A and B); however, no free carbenes were employed in their synthesis.[20]



Scheme 7. A) Synthesis of a carbene complex by deprotonation of 1,3-dimethylimidazolium perchlorate with mercury(II) acetate.[20a] B) Synthesis of a carbene complex by heating 1,3-dimethylimidazolium hydrogenpentacarbonylchromate(II).[20b]

The earliest and to this day most prominent family of NHCs are undoubtedly imidazol(in)-2-ylidenes such as IAd (*vide supra*, Scheme 6B). NHCs are a particularly stable class of carbenes since the -I-effect of the adjacent nitrogen atoms stabilizes the singlet carbene by lowering the energy of its HOMO (highest occupied molecular orbital). Further stabilization stems from the +M-effect of the nitrogen's lone pair, i.e. the lone pair donates electron density to the empty p_π-orbital of the carbene, thus increasing the LUMO (lowest unoccupied molecular orbital) energy.[21] Initially, steric encumbrance of the carbene by bulky substituents at the nitrogen atoms was considered to be another important factor for stabilizing NHCs.[18] However, in 1992 *Arduengo et al.* reported the synthesis of 1,3-dimethylimidazol-2-ylidene (IMe) and 1,3,4,5,-tetramethylimidazol-2-ylidene (IMeMe$_2$).[22] While the former can be isolated, it decomposes rather quickly. The latter, however, was found to be stable indefinitely. Since the steric demand of the *N*-methyl substituents is comparably small, the additional electronic stabilization by the methyl groups in 4- and 5-position must be decisive, which illustrates that electronic stabilization far outweighs steric factors. Besides imidazole- and imidazoline-based NHCs, carbenes based on a multitude of other heterocycles have been reported. Examples include thiazol-2-ylidenes,[23] benzimidazol-2-ylidenes,[24] triazolylidenes,[25] ring-expanded NHCs such as 3,4,5,6-

tetrahydropyrimidin-2-ylidenes,[26] diamidocarbenes (DAC)[27], and pyrrolidin-2-ylidenes, often referred to as cyclic alkyl amino carbenes (CAACs)[28]. An overview can be found in Figure 4.

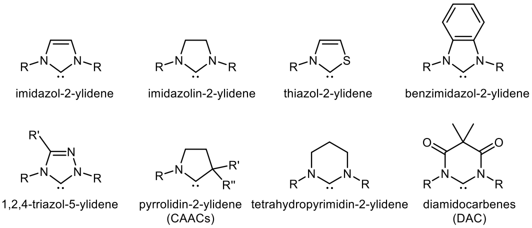
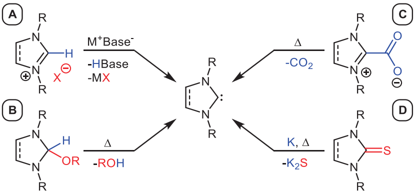


Figure 4. Examples of common classes of NHCs.

In most cases, the free carbenes can be generated by deprotonation of the corresponding salt (Scheme 8A), however, other methods for the preparation of free NHCs exist. In some cases, heating of an NHC adduct can lead to the formation of the free NHC and a volatile side product such as methanol,[25] pentafluorobenzene[29], or chloroform[29] (Scheme 8B). A similar concept is the use of NHC carboxylates, which can release carbon dioxide and a free NHC upon heating (Scheme 8C).[30] Finally, the desulfurization of cyclic thioureas using elemental potassium also yields free NHCs and potassium sulfide as a side product (Scheme 8D).[31]



Scheme 8. Important methods for the preparation of free NHCs.

1.1.1.1 Quantifying the Steric and Electronic Properties of NHCs

One of the reasons why NHCs, in particular imidazole and imidazoline-derived NHCs, have become very popular, e.g. as ligands in transition metal catalysis[32] and as organocatalysts[33], is their structural versatility. Both the sterics and the electronics of NHCs can vary widely, and various efforts have been made to quantify those differences.

1.1.1.1.1 Tolman Electronic Parameter (TEP)

NHCs can act as strongly σ-donating ligands in transition metal complexes. A common system to quantify the donor properties of ligands is the Tolman electronic parameter

(TEP). Originally designed by *C. Tolman* to compare the donor strength of various tertiary phosphines, the system utilizes the C-O stretching vibration of a nickel complex of the general formula $Ni(CO)_3L$ (L = phosphines).[34] The complexes form readily by combining equimolar amounts of ligand L and $Ni(CO)_4$ (Figure 5A). The increased electron density at the metal center leads to backdonation to the π^*_{CO}-orbital, thus weakening the C-O-triple bond (Figure 5B).[35] Consequently, the frequency ν of the A_1 C-O vibrational mode is shifted towards lower wavenumbers.[34]

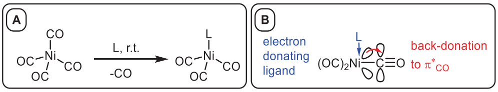


Figure 5. A) Synthesis of nickel complexes of the type $Ni(CO)_3L$ (L = phosphines, NHCs) from $Ni(CO)_4$. B) Influence of the donor ligand on the C-O-stretching vibration.

This system was later extended to NHCs, however, very bulky NHCs such as IAd led to the loss of two carbonyl ligands, yielding complexes of the formula $Ni(CO)_2L$.[36] Therefore, and due to the health hazards associated with $Ni(CO)_4$, subsequent studies employed $[IrCl(CO)_2(NHC)]$[37] or $[RhCl(CO)_2(NHC)]$.[38] The TEP can be calculated from the frequencies obtained from Ir and Rh complexes by linear regression. Interestingly, the TEP of almost all NHCs exceeds that of even the most strongly donating phosphines, such as tri-*tert*-butylphosphine (ν = 2056.1 cm^{-1}).[34, 36] The TEP of NHCs is highly dependent on the parent heterocycle but also on the nitrogen substituents as well as the backbone of the NHC. Quantum chemical calculations by *Gusev* showed that oxazol-2-ylidenes, thiazol-2-ylidenes, and 1,2,4-triazol-5-ylidenes are among the least electron-donating NHCs, while imidazol-2-ylidenes are the strongest donors among the examined five-membered NHCs. Ring expansion to the six-membered 3,4,5,6-tetrahydropyrimidin-2-ylidenes results in decreased TEPs, while the saturated imidazolin-2-ylidenes and benzimidazol-2-ylidenes are slightly weaker donors than the corresponding imidazol-2-ylidene (Figure 6A).[39] *Plenio et al.* showed that the introduction of electron-withdrawing and electron-donating groups at the substituents of the nitrogen leads to increased and decreased TEPs, respectively (Figure 6B).[40] Finally, modification of the NHC's backbone strongly influences its donor capabilities. Electron withdrawing groups, such as halide groups, reduce the donor strength of the NHC, while electron-donating groups, such as alkyl substituents, increase the donor strength of the NHC (Figure 6C). [12] Due to this structural variability, the donor strength of NHCs can be tuned depending on the requirements, oftentimes even while maintaining the steric demand.

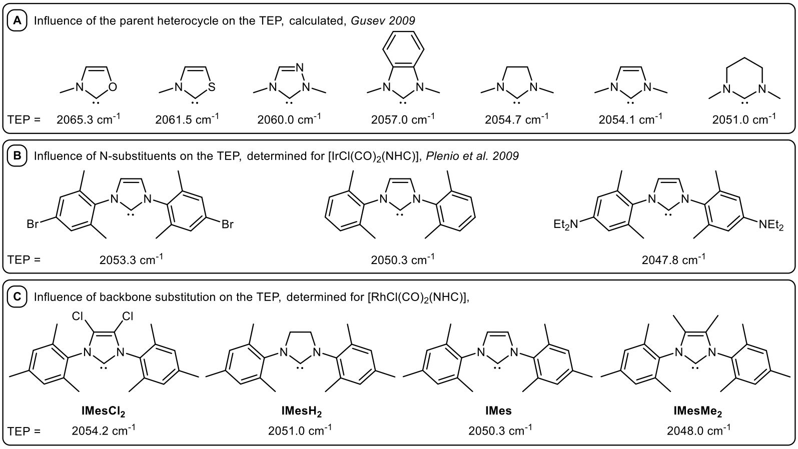
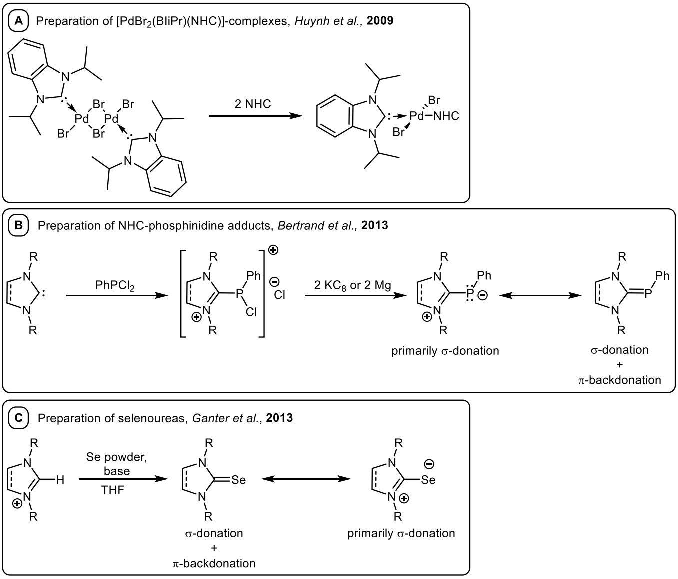


Figure 6. A) Influence of the parent heterocycle on the TEP of NHCs. Quantum chemically calculated values.[39] B) Influence of the *N*-substituents on the TEP of NHCs. Values determined using [IrCl(CO)$_2$(NHC)].[35, 40] C) Influence of backbone substitution on the TEP of NHCs. Values determined using [RhCl(CO)$_2$(NHC)].[12, 35]

1.1.1.1.2 Quantification of the Electronic Properties of NHCs by Other Means

A number of other methods have been explored for quantifying the electronic properties of NHCs; however, they have not gained the same widespread use as the TEP. *Huynh et al.* proposed the use of palladium complexes of the formula [PdBr$_2$(BIiPr)(L)] (BIiPr = 1,3-diisopropylbenzimidazol-2-ylidene, L = NHC, PR$_3$, imidazoles) as a probe to quantify the electronic properties of NHCs, phosphines, and imidazoles. The complexes, which can be prepared in a straightforward manner by reacting two equivalents of the ligand of interest with the dimeric palladium complex [Pd(BIiPr)Br$_2$]$_2$, (Scheme 9A) are subjected to ^{13}C NMR spectroscopy in CDCl$_3$.[41] In some cases, the palladium compounds were inaccessible and therefore, gold complexes of the formula [Au(BIiPr)(L)]$^+$[BF$_4$]$^-$ may be employed as a probe. Linear regression allows for interconversion between the gold and palladium-based scale.[42] Due to the *trans* configuration of the two donor ligands, the chemical shift of the carbene in ^{13}C NMR of the diisopropylbenzimidazol-2-ylidene ligand is influenced by the donor ligand of interest. A stronger donor ligand leads to a weaker bond between the BIiPr-ligand and the metal center, thereby leading to a downfield shift of the carbene carbon. So far, 45 NHCs have been analyzed by this method and the chemical shift of the carbene ranges from $\delta = 175.2$ ppm for the weakest to $\delta = 185.0$ ppm for the strongest donor.[43] One advantage of this technique is the lower error margin of NMR spectra compared to IR spectra.[41]



Scheme 9. A) Preparation of complexes of the general formula [PdBr$_2$(BIiPr)(L)] for ^{13}C NMR experiments.[41] B) Preparation of NHC phosphinidine adducts for ^{31}P-NMR experiments and their mesomeric structures.[44] C) Preparation of selenoureas for ^{77}Se-NMR experiments and their mesomeric structures.[45]

In order to quantify the π-acceptor capabilities of NHC-ligands, *Bertrand et al.* proposed the use of ^{31}P-NMR spectroscopy of NHC-phosphinidine adducts.[44] The most widely applicable way to prepare these adducts is to react an NHC with one equivalent of dichlorophenylphosphine, followed by reduction with potassium graphite or magnesium. These compounds can be described by two structures, either as a phosphinidine NHC adduct with a dative bond or as a phosphaalkene (Scheme 9B).[44] If an NHC can act as a π-acceptor, the structure will be more close to that of a phosphaalkene, while a poorly π-accepting NHC forms a true adduct. This is also reflected by the ^{31}P-NMR shifts: the better the π-accepting properties of the NHC, the further the signal is shifted downfield. Several NHCs have been examined with this technique, and values ranging between δ = 83 ppm for diamidocarbenes[46], which are relatively good π-acceptors due to the carbonyl groups in the backbone, to δ = -61 ppm for 1,3-diisopropylimidazol-2-ylidene (IiPr) at the other end of the scale.[44] This approach inspired a similar study by *Ganter et al.,* who prepared selenoureas from the corresponding azolium salts by the addition of a base and elemental selenium.[45] Again, these compounds can be described by two mesomeric structures (Scheme 9C). Analogously to the phosphinidine-adducts, NHCs with strong π-accepting properties cause a downfield shift of the signal in ^{77}Se-NMR. However, the chemical shift range is much broader with a cyclic (alkyl)(amido)carbene on the one end (δ = 1180 ppm)[47] to 1,3-dicyclohexylimidazol-2-ylidene on the other (δ = -4 ppm) end. Due to the simpler preparation compared to the phosphinidine adducts, selenoureas have been employed significantly more often.[48]

1.1.1.1.3 Buried Volume

The buried volume %V_{bur} was first introduced by *Cavallo* and *Nolan et al.* as a means of quantifying the steric demand of various NHC and phosphine ligands.[49] The buried volume calculates which volume fraction of a sphere around a metal center is occupied by the ligand in question (Figure 7).

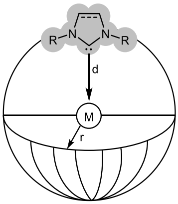


Figure 7. Graphical representation of the concept of the buried volume %V_{bur}.

To obtain comparable data, the radius of the sphere r and the distance d between the coordinating carbon or phosphorous atom and the center of the sphere has to be set to the same values for every calculation. Typically, r = 3.5 Å and d = 2.00 Å or d = 2.28 Å are chosen.[50] A single-crystal X-ray structure of a complex containing the ligand or a structure obtained by DFT calculations is required as input for the calculation. Interestingly, the nature of the metal complex influences the obtained values, e.g. 1,3-dimesitylimidazol-2-ylidene (IMes) has a buried volume of %V_{bur} = 33.8 % in case the single-crystal X-ray structure of [(IMes)IrCl(CO)$_2$] was employed, while the structure of [(IMes)AuCl] led to a value of %V_{bur} = 36.5 %.[21] This is due to a change in the conformation of the NHC in the presence of a sterically more crowded environment. For this reason, divalent metal complexes are often used as a base for the calculation, most often Au-based. The buried volume of an NHC is highly influenced by the substituents at the nitrogen (Figure 8A+B). NHCs bearing methyl groups at the nitrogen (IMe) are naturally at the lowest end of the scale with a buried volume of around %V_{bur} = 26 %.[51] Due to their flexibility, secondary alkyl substituents do not lead to a significant increase in steric demand. Tertiary alkyl groups, however, lead to a strong increase in buried volume, e.g. 1,3-di-*tert*-butylimidazol-2-ylidene (ItBu) with a buried volume of $\%V_{bur} = 39.6\,\%$.[51] NHCs with aromatic substituents at nitrogen generally display a relatively large buried volume, which can be increased further by increasing the steric demand at the *ortho* position of the aromatic group (Figure 8B). In most cases, backbone substitution only results in minor changes in the buried volume (Figure 8C). Finally, expansion of the heterocycle towards six-and seven-membered rings leads to an increase in steric demand (Figure 8D). This is due to the increased N-C-N-angle, which forces the substituents towards the metal center. For this reason, 7-Dipp (Figure 8D) is among the most sterically demanding NHCs that have been reported to date.[51-52]

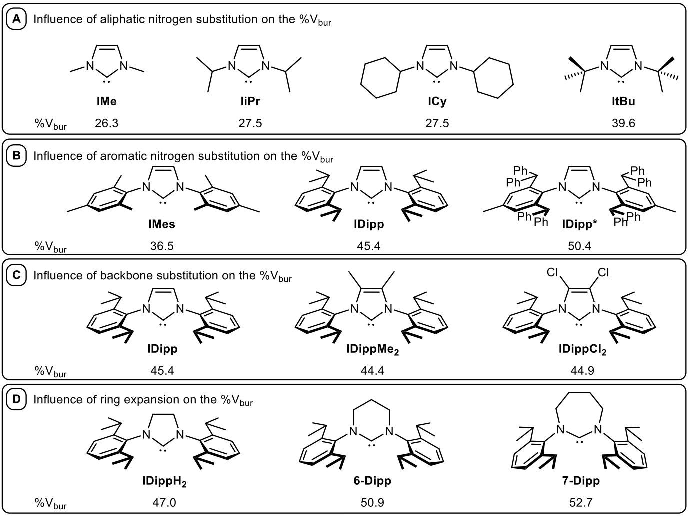
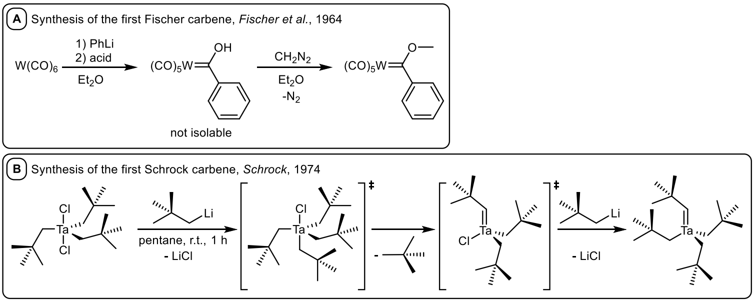


Figure 8. Buried volumes of selected NHCs to illustrate: A) The influence of aliphatic nitrogen substitution on $\%V_{bur}$; B) The influence of aromatic nitrogen substitution on the $\%V_{bur}$; C) The influence of backbone substitution on the $\%V_{bur}$; D) The influence of ring expansion on the $\%V_{bur}$.[51-52]

1.1.2 Fischer and Schrock Carbene Complexes

The first complex containing a metal-carbon double bond was prepared by *Fischer* and *Masbööl* in 1964 by reacting tungsten hexachloride with phenyllithium, followed by protonation and finally alkylation with diazomethane (Scheme 10A).[53] The resulting compound was the first example of a class of complexes that was later dubbed Fischer carbenes. They typically contain a late transition metal in a low oxidation state and an electrophilic carbene ligand, which is stabilized by a π-donating heteroatom substituent. In 1974, *Schrock* reported that the reaction between tris(neopentyl)tantalum(V) dichloride and neopentyl lithium yielded a tantalum carbene complex that did not contain any stabilizing heteroatoms at the carbene ligand (Scheme 10B).[54] Opposite to what had been described for Fischer carbenes, the metal was in its highest oxidation state and the carbene displayed nucleophilic behavior. The reaction likely proceeds via the tetrakis(neopentyl)tantalum(V) chloride intermediate, which undergoes α-hydrogen elimination and loss of one equivalent of neopentane to form a carbene complex. A subsequent second alkylation step then yields the observed product.[55] Since their properties and structures are fundamentally different from the previously reported Fischer carbenes, this class of compounds was named Schrock carbenes.



Scheme 10. A) Synthesis of the first Fischer carbene.[53] B) Synthesis of the first Schrock carbene.[54]

Electronically, Fischer and Schrock carbenes are also vastly different from each other. Fischer carbenes can formally be described as a singlet carbene acting as a σ-donor and π-acceptor, while the metal acts as a σ-acceptor and π-donor. A Schrock carbene, on the other hand, consists of a triplet carbene and an open shell metal fragment, i.e. the fragments are bound by covalent σ and a π-bonds (Figure 9).[56] Due to their classical double bond character, Schrock carbenes are often also referred to as alkylidenes.

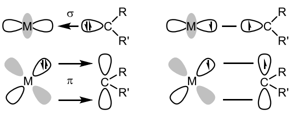
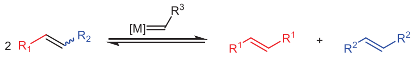


Figure 9. Binding situation in A) Fischer carbenes and B) Schrock carbenes.

1.2 Olefin Metathesis

Olefin metathesis describes the exchange of the alkylidene fragments of two olefins in the presence of catalytic amounts of a metal alkylidene complex.



Scheme 11. The exchange of alkylidene fragments of olefins, catalyzed by a metal alkylidene complex.

Ziegler's seminal reports on the polymerization of olefins in the 1950s[57] sparked great interest in olefin polymerization reactions and quickly led to the first discoveries of olefin metathesis reactions. In 1957, *Eleuterio*[58] reported the polymerization of cyclic olefins such as norbornene or dicyclopentadiene by immobilized, ill-defined molybdenum compounds. In 1964, *Banks* and *Bailey* reported the disproportionation of propylene to 2-butene and ethylene, again catalyzed by molybdenum and tungsten compounds immobilized on alumina.[59] Eventually, the term olefin metathesis was coined by *Calderon et al.* in 1967.[60] Several mechanistic proposals followed these initial publications.[61] However, it was not until 1971 that *Chauvin* and *Hérisson* proposed the mechanism that was later confirmed experimentally (Figure 10).[62] The mechanism entails [2+2]-cycloaddition of a metal alkylidene and an olefin to form a metallacyclobutane. The metallacyclobutane then undergoes [2+2]-cycloreversion to form an alkylidene and an olefin. All steps of the mechanism are reversible, i.e. a metallacyclobutane can open up to form a new alkylidene and olefin or it can reform the starting alkylidene and olefin.

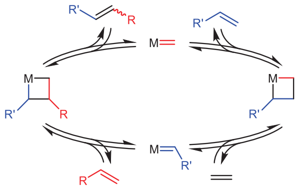


Figure 10. The mechanism of olefin metathesis as proposed by *Chauvin* and *Hérisson*.[62]

Experimental proof of the mechanism was obtained by *Katz* and *Grubbs* by analyzing olefin metathesis reactions with deuterium-labeled substrates.[63] Furthermore, *Grubbs* was able to isolate titanacyclobutanes from the reaction of Tebbe's reagent with olefins. Moreover, *Grubbs et al.* showed that these titanacycles can open to form alkylidene complexes and catalyze olefin metathesis.[64] Soon thereafter, the development of the first well-defined olefin metathesis catalysts followed (this topic will be discussed in detail in section 1.3). In