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METATHESIS REACTIONS IN POLYMER SYNTHESIS

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Abstract. Despite the fact that the Ring-Opening Metathesis Polymerization has relatively recently appeared in the chemistry of polymers, it has already established itself as a widely used method for producing polymeric materials. Particularly attractive are the processes that result in the formation of linear and cyclic polymers. These polymers have unique performance characteristics. Currently, several processes have been developed and introduced into the petrochemical industry utilizing homogeneous catalysts using the Ring-Opening Metathesis Polymerization principle.

For systems subject to metathesis polymerization with ring opening, there are three main factors that determine the microstructure of the polymer: cis / trans, tact and head-to-head configuration, head to tail, or tail to tail.

The repeating units in the main polymer chain are in the cis and trans configuration. The distribution of the configuration depends on the type of solvent, monomer, catalyst, and concentration of the reactants.

1.   Introduction

The discovery of the metathesis reaction paved the way for not only the possibility of obtaining new organic compounds but also made it possible to significantly simplify the production of those substances for the synthesis of which, previously, it was necessary to use complex multistage processes (Singh, 2006).

At the early stage of development, the metathesis process was carried out using homogeneous catalytic systems based on transition metal salts such as Mo, W, and Os. The organoaluminum compounds most often acted as cocatalysts (Calderon *et al*., 1967; Calderon *et al.,* 1968). Heterogeneous catalysts, which were also manufactured on the basis of tungsten and molybdenum compounds deposited on oxide substrates (Trnka & Grubbs, 2001), were used to a greater extent in industry. The presence of strong Lewis acids in catalysts and often-harsh reaction conditions caused the incompatibility of the first-generation catalysts with the majority of polar functional groups of monomers, in essence, limiting the metathesis process only to the hydrocarbon region.

The discovery of "well-defined" catalysts had significantly increased the ability of ROMP to obtain polymers that have unique properties. The large practical potential of the metathesis reaction application, which lies behind the solution of the problem of compatibility of catalysts with various substrates, motivated extensive work aimed at a deeper understanding of the metathesis process and the underlying mechanism.

The initial ruthenium complexes do not have catalytic activity and require activation. One of the main goals of studying the mechanism of metathesis is the possibility of designing new ruthenium complexes with better catalytic properties. An important parameter for Ring-Opening Metathesis Polymerization (ROMP) is a ratio of the chain growth and initiation constants (k_g/k_i) because these two constants determine the molecular weight characteristics of the polymers. Once activated, ruthenium catalysts have similar growth constants (catalysts of the same type are implied), it is possible to affect k_g/k_i ratio by changing the initiation constant k_i.

There are two main factors that can affect the activity of the catalyst. The first factor refers to the internal one and is determined by the structure of the substrate and the catalytic complex itself. The second one is external, which depends on the experimental conditions: temperature, solvent, various chemical additions. Both of these factors are closely related to each other. For example, a ligand environment determines activation energy and, thus, will determine the choice of the experiment temperature.

Ring-opening metathesis polymerization is one of the types of polymerization where strained cyclic compounds are often used as monomers. At present, various metathesis catalysts have been developed that are effective in ROMP and rather quickly initiate living polymerization of selected monomers. In some cases, norbornenes are converted to polymers with a polydispersity index of approximately 1 (Choi & Grubbs, 2003).

Obviously, the polydispersity index depends on polymerization conditions, monomer structure, and the type of catalyst. With the development of ruthenium-based catalysts, ROMP has become widely used in organic and polymeric chemistry. Ring-opening metathesis polymerization is used to synthesize polymers that have microstructures with a specific double bond (cis/trans), monomer configuration (head to head, head to tail, etc.) and tact (isotactic, syndiotactic and atactic) (Peeck *et al.*, 2010; Liu *et al.,* 2012; Morgan *et al.,* 2002), where each parameter can determine the property, and therefore the purpose of the polymer.

2.   Types and mechanism of metathesis reactions

A large number of different types of metathesis reaction are distinguished. The main and most applicable are (Scheme 1): Cross-Metathesis (CM), Ring-Closing Metathesis (RCM), Ring-Opening Metathesis (ROM), Acyclic Dienes Metathesis (ADMET), Ring-Opening Metathesis Polymerization (ROMP) (Grubbs, 2004).

Ring-Closing Metathesis is the cyclization of dienes to produce various cycloalkenes from 5-membered to macrocycles. The stereochemistry of the resulting cycloalkenes depends on the substrates, for example, the small and medium size rings formed by RCM are in a less intense cis-conformation, while the stereochemistry of non-rigid macrocyclic derivatives is difficult to predict and they may include a mixture of cis- and trans-stereoisomers (Armstrong, 1998). RCM is used for the synthesis of natural substances (Pat. 5936100 US; Ivin, 1998), drugs (Rivkin *et al*., 2004) and new materials (Xu *et al.,* 1996).

Reverse RCM reaction is Ring-Opening Metathesis, where the cycloalkyl ring is torn to form an active intermediate diene, which can undergo cross-metathesis with other acyclic alkenes, with the formation of a new product.Also, under certain conditions, the product obtained by the ROM method can undergo polymerization and this process is called the ring-opening metathesis polymerization. ROMP has a greater practical value compared with the ROM process.
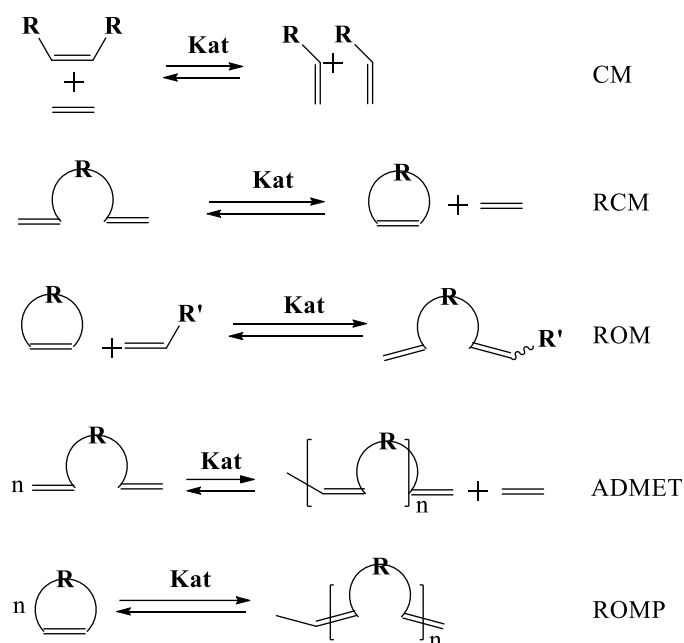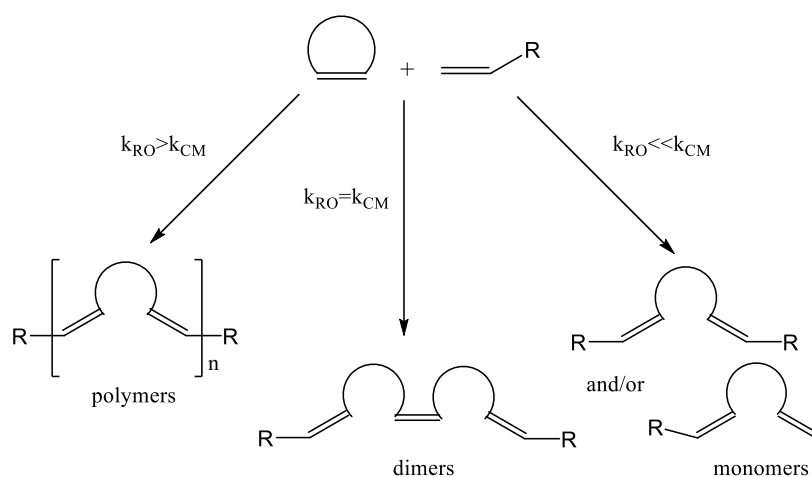

Scheme 1.

Cycloalkenes having a strained cycle, such as norbornene, cyclopentene, cyclooctene, easily enter into ring-opening metathesis polymerization (Bazan *et al.,* 1991). The use of second-generation Grubbs catalysts with high resistance to various functional groups in ROMP allows synthesizing various new materials that find practical applications starting with the development of nonlinear optics to biological polymers (Rivkin *et al*., 2004).

The acyclic diene metathesis refers to a stepwise type of polycondensation (Wagener *et al.,* 1991), which makes it possible to obtain linear chains from non-conjugated dienes (Baughman & Wagener, 2005; Lehman & Wagener, 2005; Lehman & Wagener, 2001; Buchmeiser, 2010). To obtain high molecular weight polymer chains by an ADMET reaction, a very high monomer conversion rate is required. Thus, the most active second-generation catalysts are better suited for use in ADMET than bisphosphines ruthenium-based catalysts (Lehman & Wagener, 2008), and effective removal of a low molecular weight product from the reaction mixture is very important for the formation of a high molecular weight polymer (Connon & Blechert, 2003). Although olefin metathesis using ruthenium catalysts usually takes place under very mild conditions and does not require air removal, ADMET is best performed with process parameters that promote diffusion and removal of the light coproduct, most often ethylene (i.e., higher reaction temperature, application of vacuum and intensive mixing).In addition, the use of a concentrated or even pure monomer solution,

commonly used in polycondensation reactions, is not applicable to ADMET, since the high viscosity of the solution adversely affects the mixing and removal of ethylene. As a result, poor molecular weight control at the growth stage of the reaction usually leads to a rather large polydispersity index (PDI) of the polymers obtained by these methods. However, an important advantage of ADMET is that a large number of monomers are polymerized by this method since terminal olefins are quite available in the industry. Also, many monomers with polar functional groups can be involved in this polymerization process due to their high tolerance to ruthenium catalysts.

One of the alternative ways of producing polymers by the metathesis reaction is the ROM-CM process (Pat. 2013025284 WO). This process is a type of metathesis process, including metathesis polymerization with ring-opening and cross metathesis, which can lead to the production of new monomers, dimers or polymers (Scheme 2).
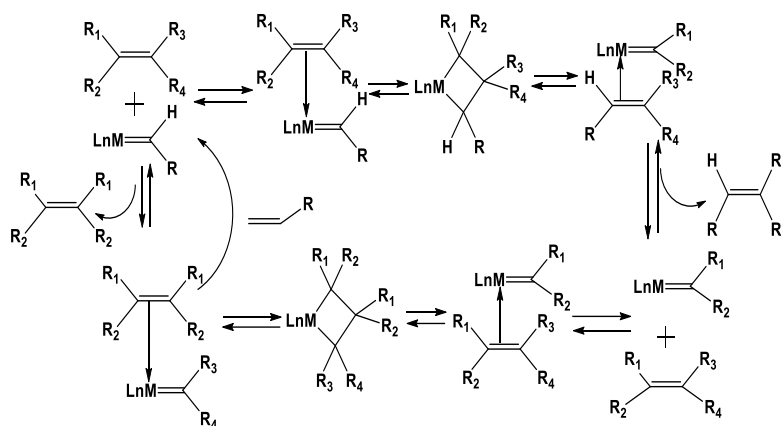

Scheme 2.

Depending on the ratio of the rate constants of the reactions, the direction of the process shifts towards the formation of certain products. If the cross-metathesis reaction rate constant is larger than the metathesis reaction with the opening of the cycle, monomers are predominantly formed. In case of exceeding the reaction rate constant with a ring opening above the cross-metathesis reaction rate constant, products with a higher molecular weight are obtained.

ROM-CM monomers can be cyclic (dicyclopentadiene, norbornene and norbornadiene) and linear (pentene-1, decene-1, octene-1) olefins. Typically, the polymerization is carried out in the presence of Ru- or Os-containing metathesis catalysts.

As proposed by Exxon-Mobil (Pat. 2013025284), the ROM-CM process isa method to makepolymers used in the production of components of lubricating oils, additives, compatibilizers, tie layers, adhesives, and surface modifiers.

After the discovery of the metathesis reaction, it became clear that the mechanism of this reaction was unusual (Grubbs, 2004). One of the first proposed mechanisms was the two-step exchange of alkylidene via a "quasi-cyclobutane" mechanism (Jacobsen, 2006). The authors assumed that the two olefin molecules are coordinated to the metal center and then exchange substituents through the formation of a symmetric intermediate (Grubbs, 2004). These hypotheses had some flaws and, in contrast to these mechanisms, Herisson and Chauvin proposed a mechanism in the early 1970s (Chauvin,

2006). The mechanism for the metathesis of the Herisson-Chauvin olefins involves the formation of a metal-cyclobutane intermediate due to the coordination of the olefin molecule on the metal-carbene complex of the transition metal (Scheme 3) (Mitan *et al.*, 2016).
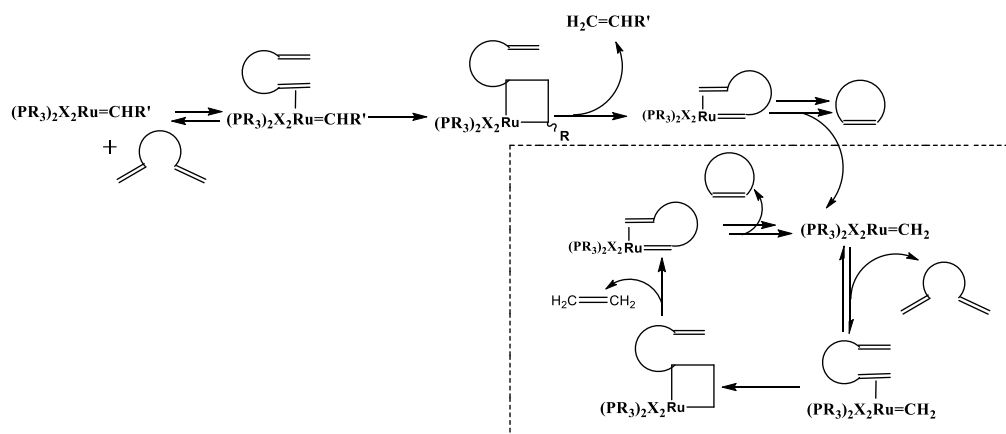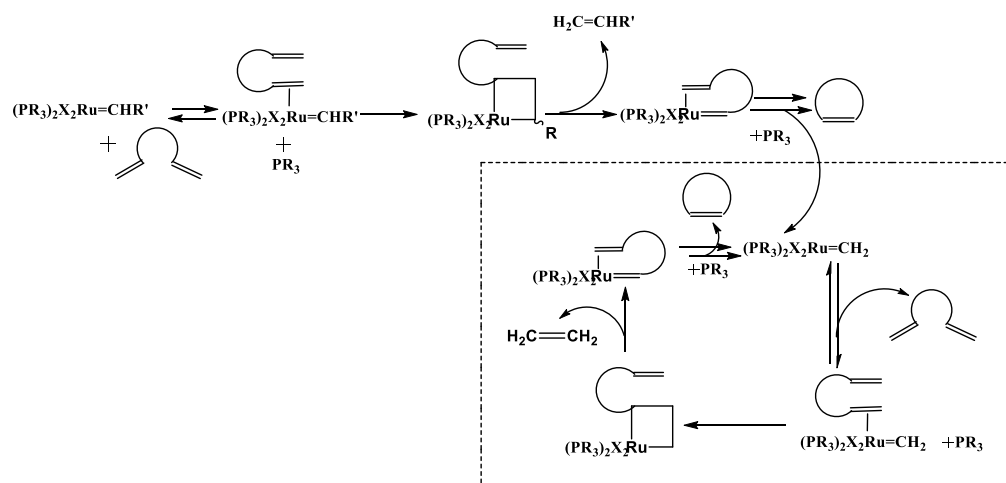

Scheme 3.

In the conventional catalytic cycle, where the role of the active intermediate is played by a transition metal carbenein its structure, the formation of a new double bond consists in successive reversible [2+2]-cycloaddition of the alkene to the metal-carbene complex, cycloaddition, breaking of two bonds and formation of a new alkene. After coordinating with a new alkene molecule, the newly formed metal-carbene complex forms a metal-cyclobutane, the double bond is redistributed, and a metathesis product and a ruthenium initiator are formed, which again initiates the catalytic cycle. Since the product no longer participates in the catalytic cycle, the equilibrium shifts towards the formation of the product (Scheme 3). According to the principle of equilibrium, the rates of the forward and reverse reactions are the same, and the reverse reaction proceeds through the same series of elementary stages as the forward reaction (Dias *et al.*, 1997).

The mechanism of olefin metathesis occurring under the action of ruthenium catalysts exhibitssome differences from the classical mechanism. In 1997, the Grubbs research group presented evidence of the existence of two competing mechanisms: dissociative and associative (Sanford *et al.*, 2001a). The proposed mechanisms have a fundamental difference, consisting of the presence or absence of the dissociation of phosphine, which occurs before the formation of the metal-cyclobutane intermediate. The dissociative mechanism is the loss of the phosphine ligand after coordinating the alkene to the metal. On the contrary, it was proposed that the associative mechanism involves the coordination of olefins with a catalyst to form an18-electron intermediate complex. The associative path was initially more attractive since all the intermediate complexes have either 16 or 18 electrons (Scheme 4). However, contrary to the expectations, according to the kinetic data, the dissociative mechanism was dominant.
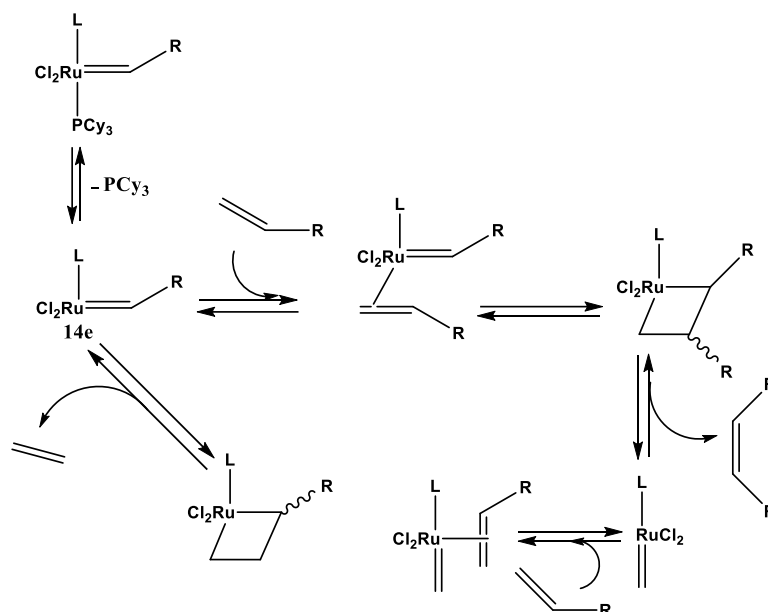
Associative mechanism

Dissociative mechanism

Scheme 4.

Since a huge amount of obtained data confirmed that the actual reaction proceeds through the dissociative metathesis mechanism comprising a [2+2]-cycloaddition (Jacobsen, 2006; Dias *et al.,* 1997; Sanford *et al.*, 2001a; Ulman & Grubbs, 1998; Adlhart *et al.,* 2000; Sanford *et al.,* 2001b; Adlhart & Chen, 2000). The first stage involves the dissociation of a labile phosphine ligand to produce a 14-electron intermediate complex of the general form $LX_2Ru=CHPh$. Presumably, the intermediate is not captured by free phosphine, this electrophilic intermediate complex is free to coordinate to the olefin (Colacino *et al.,* 2007). The resulting π-complex is then rearranged by the migration of olefins into the metal-carbene bond, after which the intermediate complex is cleaved to form the isomeric π-complex and the final product (Jacobsen, 2006) the mechanism is shown in Scheme 5
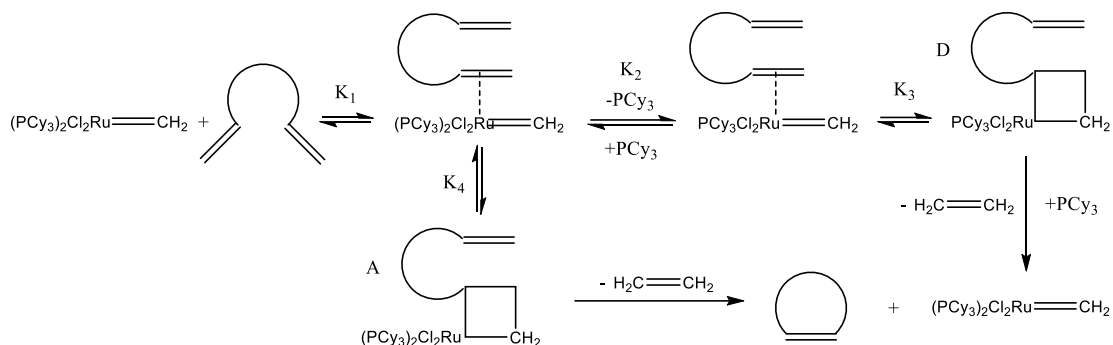
Scheme 5.

Thus, all the metathesis reactions of linear and cyclic olefins obey the single generally accepted mechanism of Herisson-Chauvin. Reactions under the influence of Grubbs catalysts occur along the dissociative pathway, which has been established and confirmed by numerous studies.

3.   Mechanism of metathesis reaction catalyzed by ruthenium complexes

Detailed study of the coordination environment of the metal, built on the knowledge of the metathesis mechanism, is one of the reasons for the high persistence and activity of ruthenium complexes. The structure of a catalytic complex determines several closely interrelated features of the mechanism of the catalytic process such as the activity of the catalyst, its selectivity, and stability. The features of the mechanism of olefins metathesis proceeding with the ruthenium catalysts are considered below.

One of the first papers in which the mechanism of metathesis is considered in more detail by Grubbs et al. (Dias *et al.,* 1997) is devoted to the catalytic activity study of Grubbs I ruthenium complexes in the metathesis with the cyclisation of the acyclic diene-diethylallylmalonate as an example. The presence of the catalyst influenced the kinetics of the diene consumption in a complicated way. The addition of tricyclohexylphosphine not only reduced the catalytic activity of the complex but led to the first-order reaction. The authors proposed two mechanisms called dissociative and associative. These mechanisms fundamentally differ from each other by the phosphine dissociation step occurring immediately before the formation of the metal-cyclobutane intermediate (Scheme 6):

Scheme 6.

Thus, two active ruthenium forms generate the metal-cyclobutane, with 14(D)-and-16(A)-electron configurations, take part in the reaction at once. The rate of consumption of the diene is described by equation 1:

$$-\frac{d[\text{diene}]}{dt} = \left(k_3 \cdot \frac{K_1 \cdot K_2}{[\text{PCy}_3]} + k_4 \cdot K_1 \right) \cdot [\text{cat}] \cdot [\text{diene}] \tag{1}$$

The equation shows that the rate of the dissociative path, unlike the associative one, is in inverse proportion to the phosphine concentration (Scheme 6). The addition of phosphine to the reaction mixture suppresses the dissociative pathway, reducing the catalytic activity and leading to afirst-order kinetic reaction.

Later, Grubbs et al.(Sanford *et al.,* 2001a; Sanford *et al.,* 2001b) investigated the mechanism of activation of bis-phosphine and imidazole monophosphine ruthenium catalysts in a reaction with ethyl vinyl ether. It was demonstratedthat these ruthenium complexes are characterized by the dissociative activation mechanism. The authors made their conclusions based on the fact that the dissociation of phosphine limited the reaction even under conditions of high saturation of the reaction mixture with an olefin (Scheme 7). Moreover, it was confirmed by a good correlation of the initiation constants with the values of the dissociation constants of phosphine measured with the DANTE NMR method.

Scheme 5 shows that the dissociation of phosphine precedes the addition of an olefin. Thus, the olefin is built into a four-coordinated form of ruthenium with a formation of a 14-electron metal-cyclobutane. According to k_{-1}/k_2 constants ratio, it was found that substitution of one phosphine ligand for the N-heterocyclic carbene ligand gets the addition of an olefin to a four-coordinated ruthenium compound easier.

The reveling of the phosphine ligand dissociation as a limiting step of the metathesis catalyzed by ruthenium complexes of Grubbs I and II generations helped to develop rapidly-activated catalysts. Using these catalysts allows acquiringpolymers with a narrow MMD (Louie & Grubbs, 2001).

Several years ago, Plenio et al. (Thiel *et al.,* 2012) showed that the most suitable mechanisms to explain the kinetics of the process are dissociative and exchanging ones. He used three different stericallyinequivalent olefins and a number of Hoveyda-Grubbs II catalytic complexes in the cross-metathesis (CM) reaction to distinguish between three possible activation mechanisms of these catalysts (Scheme 8).
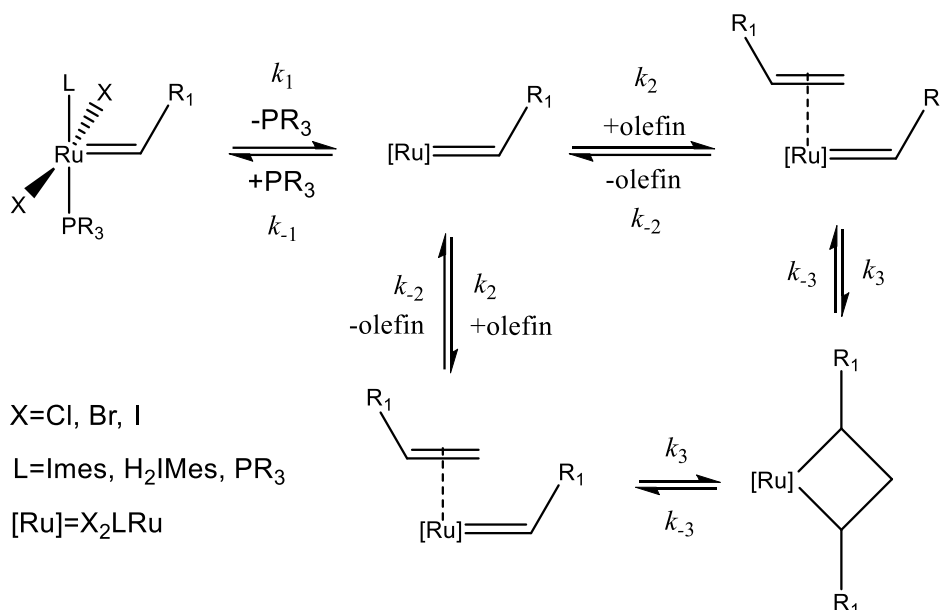
Scheme 7.

The stages sequence of each proposed mechanisms is identical after the olefin coordination step. The dissociative mechanism has one additional stage. The formation of the catalyst 14-electron form through the dissociation of the bond with the chelating ligand takes place before the addition of the olefin. The exchange mechanism involves the interaction of the 16-electron catalyst form with the olefin in one step. Since the addition of the olefin and the detachment of the chelating ligand occurs simultaneously, ruthenium does not change its coordination number. The associative mechanism implies the formation of an 18-electron complex. The authors conclude that the associative mechanism has a low probability referring to the low probability of the existence of a six-coordinated ruthenium.

The dissociative mechanism is realized in the case of bulky olefins and sterically inaccessible complexes when the addition of an olefin to the catalyst is difficult. The observed rate constant of this process is described by Equation 2.
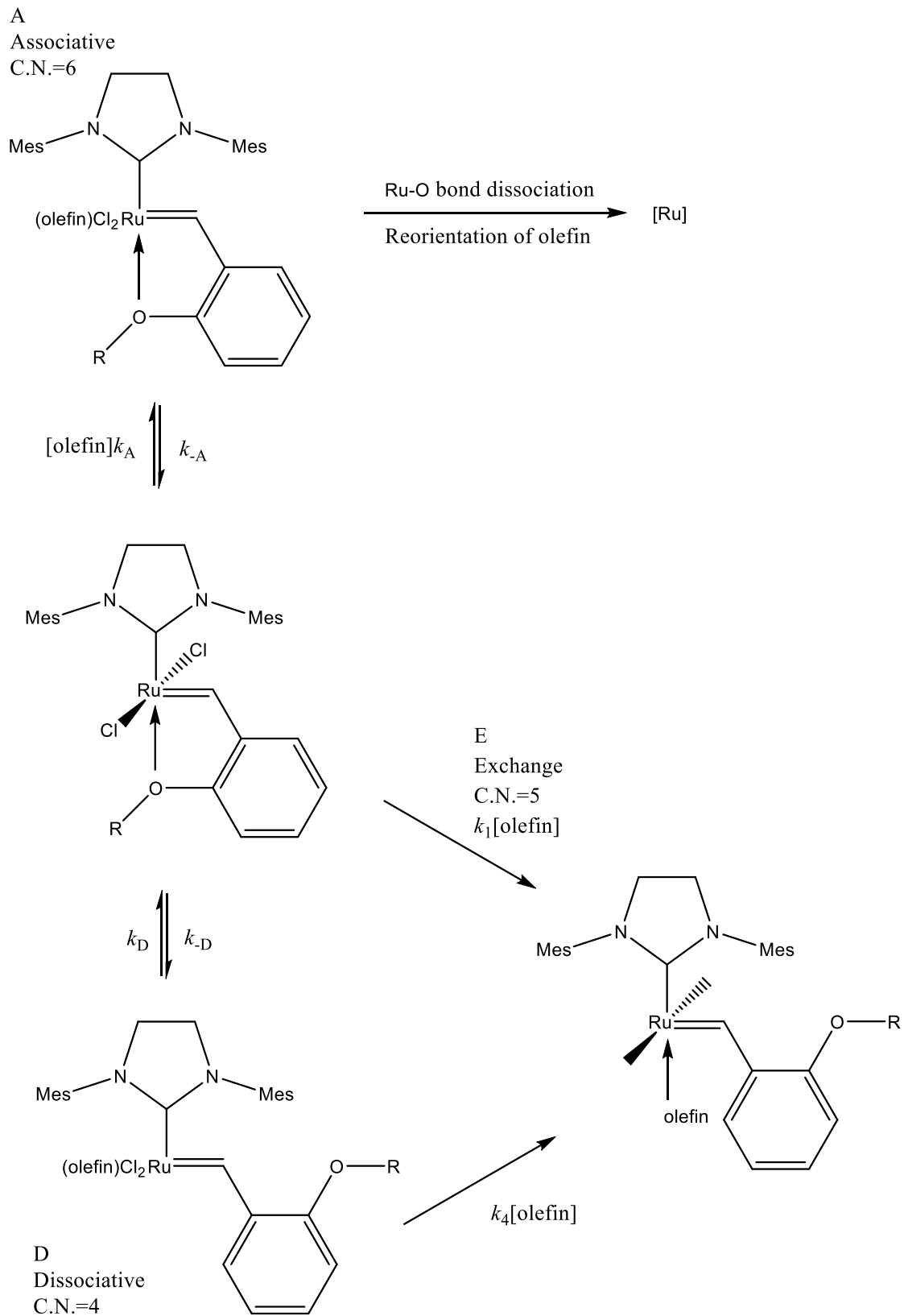
$$k_o = \frac{k_D k_4 / k_{-D} [\text{olefin}]}{1 + k_4 / k_{-D} [\text{olefin}]} \qquad (2)$$

When the catalyst and the olefin do not have steric hindrances, the probability of the reaction proceeding through the exchange mechanism is high, and the observed rate constant is described by Equation 3:

$$k_o = k_1 [\text{olefin}] \qquad (3)$$

Therefore, the dissociative mechanism has the step of attaching an olefin to four-coordinated ruthenium (Scheme 8), which is described by the constant $k_4[\text{olefin}]$, analogous to the exchange mechanism constant $k_1[\text{olefin}]$, then the dissociative mechanism has a kinetic law identical to exchange mechanism when the solution is depleted with olefin. That happens because the limiting step of the process is the addition of an olefin, but not the dissociation of the complex. To distinguish between these two mechanisms, the authors show their differences in activation parameters. An exchange path has a negative value of activation energy due to the interfusion of two molecules, and a small value of enthalpy. By contrast, the dissociative mechanism has a

positive activation energy due to the appearance of additional degrees of freedom after Ru-O bond breaking, and a high enthalpy.

A
Associative
C.N.=6

Ru-O bond dissociation
_____
Reorientation of olefin

[Ru]

$[olefin]k_A$ k_{-A}

E
Exchange
C.N.=5
$k_1[olefin]$

k_D k_{-D}

$k_4[olefin]$

olefin

D
Dissociative
C.N.=4

Scheme 8.

Later, Hillier, Percy et al. (Ashworth *et al.,* 2011) investigated the activation of Hoveyda-Grubbs II catalysts in a reaction with ethylene using DFT calculations. Their calculations not only confirmed the experimental values of the activation parameters but also showed that the exchange mechanism had the lowest free energy and best correlated with activation parameters obtained from experiments with ethylene. They also showed that increasing the coordination number of ruthenium to six is a less likely pathway for the activation of ruthenium catalysts than the chelating ligand dissociation and its replacement with an olefin.

DFT calculations made by Solans-Monfort et al. (Nuñez-Zarur *et al.,* 2012) revealed that an associative mechanism has the highest energy barrier. The dissociation becomes a limiting step only for phosphine-containing catalysts. For catalysts with a Hoveyda ligand, decoordination is a part of cross-metathesis, which is the limiting step (and has the highest energy barrier).

To summarize, it may be noticed that the Grubbs catalysts I and II provide a dissociative mechanism of the reaction. The limiting step is the dissociation of the phosphine ligand. It leads to a high value of activation energy (80...100 kJ·mole^{-1}) and positive entropy (10...20 J·mole^{-1}·K^{-1}) (Thiel *et al.,* 2012; Ashworth *et al.,* 2011; Nuñez-Zarur *et al.,* 2012; Ashworth *et al.,*2013; Benitez *et al.,*2009). To activate a catalyst (to overcome the energy barrier of 14-electron form formation) the activation energy from 75 to 110 kJ·mole^{-1}is required (Sanford *et al.,*2001a; Ulman & Grubbs, 1998; Benitez *et al.,* 2009). The appearance of a Hoveyda-ligand in the catalyst structure has a significant effect on the activation mechanism. The limiting stage of some catalysts includes olefin participates, causing the appearance of an exchange mechanism. Both exchange and dissociative mechanisms are applicable for Hoveyda-Grubbs catalysts. These mechanisms can occur simultaneously, and their competition (Thiel *et al.,* 2012) depends on the structure of the substrate and the catalyst itself. Since the olefin addition through the exchange path comes with simultaneous decoordination of the chelating ligand, the activation parameters change. The entropy of that pathway has a high negative value (–50...–80 J·mole^{-1}·K^{-1}) when a value of activation energy (60...70 kJ·mole^{-1}) becomes less than for the dissociative path (Thiel *et al.,* 2012; Ashworth *et al.,*2011; Nuñez-Zarur *et al.,* 2012; Ashworth *et al.,* 2013; Benitez *et al.,* 2009).

It should be noted that most studies of the metathesis mechanism were carried out using the CM and RCM reactions and they are more concerned with the activation of catalytic complexes (Sanford *et al.,* 2001a; Ulman & Grubbs, 1998; Adlhart *et al.,* 2000; Sanford *et al.,* 2001b; Adlhart & Chen, 2000,Colacino*et al.,* 2007; Louie & Grubbs, 2001; Thiel *et al.,* 2012; Ashworth *et al.,* 2011; Nuñez-Zarur *et al.,* 2012; Ashworth *et al.,* 2013; Benitez *et al.,* 2009). Studies of ROMP reactions catalyzed by ruthenium complexes are not as popular as molybdenum Schrock catalysts. Perhaps the cause is the complexity of ROMP reactions for the study of metathesis mechanisms. It is obvious that the active ruthenium intermediate formed after the initiation step will behave in ROMP just like in other metathesis reactions. Therefore, the factors known for CM and RCM are valid for ROMP.

4. Activity and structure of ruthenium catalytic complex

The activity of catalytic complexes, depending on their structure, is already studied quite widely (Ashirov *et al.,* 2013; Ashirov *et al.,* 2014; Dias *et al.,* 1997; Sanford *et al.,* 2001; Louie *et al.,* 2001; Thiel *et al.,* 2012; Ashworth *et al.,* 2011;

Nunes-Zarur *et al.,* 2012; Ashwort *et al.,* 2001; Benitez *et al.*, 2009; Schwab *et al.,* 1996; Demel *et al.,* 2003; Michrowska *et al.*, 2004; Zaja *et al.*, 2003). Grubbs (Schwab *et al.,* 1996) found that the para-substituent relative to the double bond of the benzylidene ligand in complexes of the $RuCl_2(=CH-p-C_6H_4X)(PPh_3)_2$ structure affects the constants (k_g/k_i) in ROMP norbornene. The highest initiation constant is provided by H- and F-substituted catalysts while the Cl-substituted ones show the lowest initiation constant. An electron-acceptor substituent in the para position stabilizes the catalytic complex, the polymers obtained viasuch catalysts have a narrow MMD.

In the above-mentioned study of Grubbs et al. (Sanford *et al.*, 2001) on the base of the constants k_{-1}/k_2 ratio (Scheme 7), the authors investigated the influence of the ligand environment of ruthenium on its catalytic activity. The N-heterocyclic ligand (NHC) showed a significant effect, increasing the selectivity of olefin addition to the 14-electron form of the catalyst. The carbene complex increases the affinity to the olefin compared with the complex including phosphine ligand, for example, PPh_3. In ROMP of cyclooctadiene, the catalyst with H_2IMes ligand is more active than the ligand complex bearing IMes.

The replacement of the PPh_3 ligand by PCy_3 increases the value of k1 by two orders of magnitude, which is easily explained by the greater basicity of PCy_3 compared to PPh_3. However, the replacement of PPh_3 by PBn_3 does not result in such an effect, despite the great basicity of PBn_3. The replacement of chlorine by iodine in phosphine and NHC catalysts leads to an increase in the rate of initiation by almost 350 times. The replacement of chlorine by bromine in both cases is not significant and gives a threefold increase in the initiation constant.

In the work (Demel *et al.,* 2003), the activity of six Grubbs catalytic complexes in ROMP with diethyl ester of exo,endo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid was determined by NMR in situ. The catalysts **4-7** (R=PCy_3, Fig. 1) form a sequence **4>7>6>5** by the magnitude of the initiation constant (Chloroform-d, Table 1).
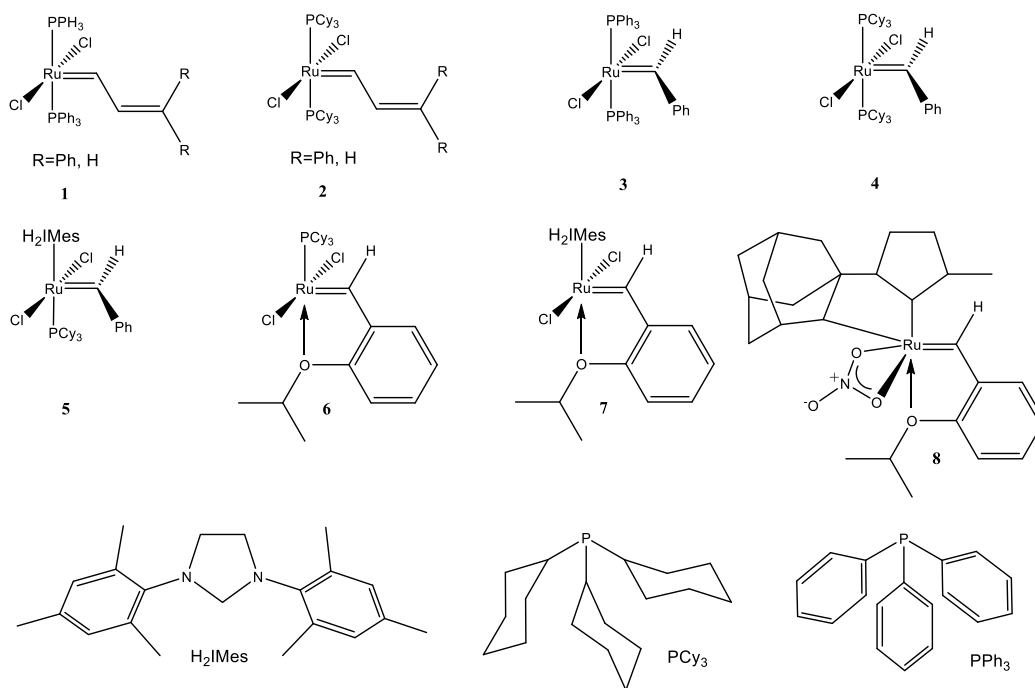

Figure 1. Main types of ruthenium catalysts

All of these catalysts have a unique set of ligands, so they show different growth constants, which form such sequence by their activity **7**>**5**>**4**>**6** (in chloroform-d). An interesting fact is that when the solvent is changed, the sequence of activity changes to **7**>**5**>**6**>**4** (in benzene-d6).

Table 1. Constants k_i and k_g in ROMP diethyl ester exo,endo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid for catalysts **4–7** at 20 °C in various solvents (Demel et al., 2003)

Catalyst	Solvent	$10^3 \cdot k_i$, l·mole^{-1}·s^{-1}	$10^3 \cdot k_g$, l·mole^{-1}·s^{-1}	k_i / k_g
4	Chloroform-d	3,90	0,34	11,5
	Benzene-d6	0,57	0,23	2,4
6	Chloroform-d	0,06	0,12	0,5
	Benzene-d6	0,04	0,33	0,1
5	Chloroform-d	0,17	4,7	0,04
	Benzene-d6	0,52	10,5	0,05
7	Chloroform-d	2,6	11,2	0,23
	Benzene-d6	>10	>67	0,15

The highest ratio of k_g/k_i is demonstrated bycatalyst **4** in both polar and low polarity solvents. Replacement of one of the two phosphine ligands by NHC leads to a significant decrease in the lability of the phosphine ligand, which influences the initiation constant (k_i **4** and **5** are compared). The reason is that NHC has better electron-donor properties in comparison with phosphine. It also determines easy dissociation of ester group on the NHC-ligand catalysts. Substituent effects in positions **4** and **5** of the benzylidene ether ring on the rate of catalytic complex initiation have been extensively studied in a number of papers (Michrowska *et al.,* 2004; Zaja *et al.,* 2003). Various combinations of substituents showed that an activation of a catalyst is largely determined by the electron density of the oxygen in benzylidene ether. Substituents reducing the electron density of the aromatic ring promote the dissociation of the Ru-O bond, thereby increasing the rate of initiation.

The mutual influence of electronic and steric properties of substituents in positions **4** and **5** of benzylidene ether (Fig.2) on the initiation rate of the catalyst is shown in (Thiel *et al.,* 2012).
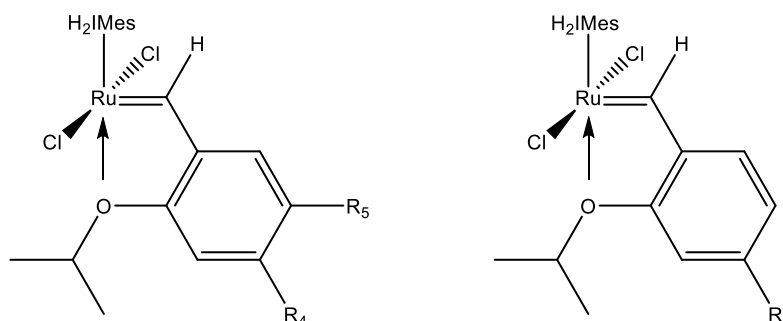
1(R_4), 2(R_5), 3(R_4): 1(NEt$_2$). 1(OiPr), 1(H), 1(F), 1(NO$_2$),
2(NEt$_2$), 2(OiPr), 2(Me), 2(F), 2(NO$_2$), 3(H), 3(NO$_2$)

Figure 2. Catalysts of the Hoveyda-Grubbs II type with various substituents (Thiel *et al.,* 2012)

The usage of three stericallyinequivalent olefins (diallylmalonate, butylvinylether, and styrene) showed that the rate of initiation in the metathesis reaction increased with decreasing electron density of the aromatic ring in the catalyst structure (in the presence of electron-acceptor substituents) and with the growth of the steric availability of the ruthenium atom. The structure of the olefin also affects the initiation rate of the reaction. Thus, the rate increases by the electron density growth of the olefin double bond and decrease in its steric hindrances. The electron-withdrawing substituent in the 4-position of the benzylidene ether accelerates the initiation more than the same substituent in the 5-position. The substitution of a bulky isopropoxy substituent with a small methoxy group results in an increase in the catalyst activation rate.

Aromatically controlled metathesis was studied by Grela's group using catalysts with a naphthylgroup which showed different activation rates depending on the structure (Fig. 3). Complexes with a delocalized ruthenfuranic structure exposed low activation rates (Fig.3, a and c), however, complexes without delocalization displayed high activation rates (Fig.3, b), (Tzur *et al.,* 2010; Grela *et al.,* 2002; Bujok *et al.*, 2004; Bieniek *et al.,* 2006; Barbasiewicz *et al.,* 2007 ; Barbasiewicz *et al.,* 2008).
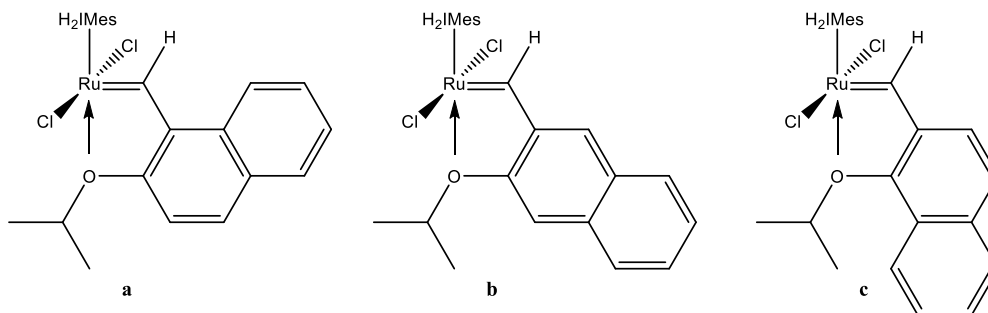

Figure 3. Grela complexes bearing naphthyl group

A few years later Solans-Monfort et al. confirmed the relationship between catalyst activity and the degree of delocalization in DFT studies of RCEYM (Nuñez-Zarur *et al.,* 2011).

The structure of the NHC ligand also affects the activity of ruthenium catalytic complexes. Furthermore, Cavallo et al. showed the importance of steric studies based on the principle of "a buried volume" of a number of catalysts with different NHC ligands (Ragone *et al.,* 2010; Clavier & Nolan, 2010). Grubbs et al. used the computer studies to explain the selectivity of the ruthenium complex containing the NHC chelating ligand (Liu *et al.*, 2012). The influence of the N-heterocyclic ligand structure on the metathesis reaction rate of initiation has not been fully studied. In the work of French authors (Nelson *et al.*, 2013), it was disclosed that the replacement of the ligand H_2IMes with H_2IPr reduces the rate of initiation of the metathesis in the RCM reaction by 5...9 times, and increases the stability of the catalytic complex in the dichloromethane-d2 solution.

5.   Effect of additives and solvent

The catalyst activity and the constants ratio k_i/k_g can be altered using various additives and solvents. In order to increase the activity of phosphine-containing catalysts, substances that promote the dissociation of phosphine (Scheme 9) should be

added to the reaction. These substances include some copper halides and phosphine-binding acids (Dunbar *et al.,* 2009; Huang *et al.,* 1999, Voigtritter *et al.,* 2011). They inhibit the association of active ruthenium with free phosphine, thereby increasing the amount of active 14-electron ruthenium, which causes a simultaneous increase of both initiation and growth constants (Scheme 9):
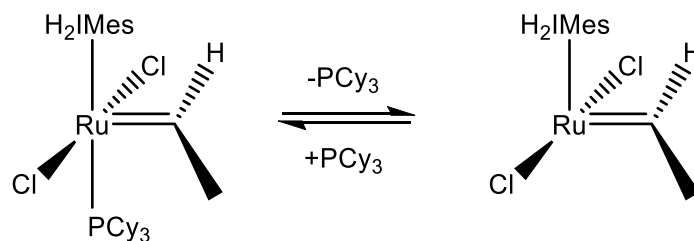
Scheme 9.

To reduce the catalyst performance, it is necessary to shift the equilibrium towards the associated complex. To this purpose, an excess amount of phosphine is added to the reaction mixture. It significantly reduces the rate of chain growth and reflects the ratio of the constants k_i/k_g. This approach was implemented by Myers et al.in order to control the polymerization of cyclopentene and they obtained a polymer with a narrow MMD (Myers & Register, 2008). Either addition or change of the solvent has a significant effect on the activity of the catalyst. Grubbs et al. showed that the reaction initiation constant is directly proportional to the dielectric permittivity of the solvent ε (Table 2) (Sanford *et al.,* 2001).

Polar solvents stabilize better the 14-electron form of the rutheniumspecies, thereby they increase the activity of the catalyst. The use of electron-donor solvents, such as acetone or isopropanol, increases the activity of the catalyst by stabilizing its active form. Solvents such as acetonitrile, dimethylsulphoxide, and pyridine decrease the activity since they act as ligands and thus compete with olefins for joining the active ruthenium complex (Slugovc, 2004).

Table 2. The constants of initiation of the cyclooctadiene polymerization reaction under the action of the metathesis catalyst **5** (Sanford *et al.,* 2001)

Solvent	ε, F·m⁻¹	$10^4 \cdot k_i$, s⁻¹
Toluene-d8	2,38	4,6
Chloroform-d	8,9	6,1
Tetrahydrofuran-d8	7,32	10,0

The addition of perfluorinated solvents increases the activity of second-generation Grubbs catalysts in CM reactions interacting with the mesityl NHC group (Samojłowicz *et al.,* 2011). In the context of activity of the catalyst dependence on the temperature,a variable character can be observed. For example, in the work of Verpoort (Allaert *et al*., 2006) in which catalytic Schiff base containing ruthenium complexes were investigated for olefin metathesis, it was found that the new catalysts were more active, and also more stable than the second-generation Grubbs catalysts. However, the latter demonstrates still greater catalytic activity at high temperatures than brand-new catalysts.

In the study (P'Pool & Schanz, 2007), 1-methylimidazole, N,N-dimethylaminopyridine and pyridine were used to reduce the activity of the Grubbs 1 catalytic complex. The present compounds substituted the phosphine ligand thus inhibited the catalyst in ROMP and RCM reactions with cyclooctadiene and diethyldialylmalonate. Addition of an excess of phosphoric acid caused the reactivation of the catalytic complex and gave an increase in the reaction rate.

6.   Influence of monomer structure on ROMP

In addition to the factors described above, there is another important factor affecting the rate of ROMP. This factor is determined by a possible interaction between the active ruthenium complex and the monomer itself. It is obvious that single polymerization with specific components is a special case that requires separate consideration. But still, some studies exist for monomers, including those contain functional groups. In a study of Moore (Rule & Moore, 2002) the low rate of polymerization of endo-dicyclopentadiene (DCPD) versusexo-DCPD and norbornene on the Grubbs I catalyst is explained by the existence of an intramolecular complex between active ruthenium and the double bond of endo-DCPD (Fig. 4a). The existence of the complex is assumed on the basis of low activation energy of endo-DCPD in comparison with an equivalent molecule of dicyclopentadiene without double bond.

A paper by Weck (Pollino *et al.,* 2003) is devoted to the investigation of ROMP of the norbornenecarboxyl ester isomers with Grubbs first and second generations catalysts. The study shows that exo-isomers have a higher polymerization rate than a mixture of endo- and exo-isomers.

Kenwright and Khosravi (Haigh *et al.,* 2005; Czelusniak *et al.,* 2008) studied in detail the formation of intramolecular complexes between active ruthenium and oxygen-containing norbornene derivatives.
Their conclusions are based on the spectral information obtained by NMR spectroscopy.

An additional shift of the proton of the Ru=CH bond is observed in a high-frequency region (18...20 ppm) as a result of the Ru-O bond formation. It was found that 7-alkoxynorbornenes form an intramolecular complex similar to the five-membered ring (Fig.4, b).

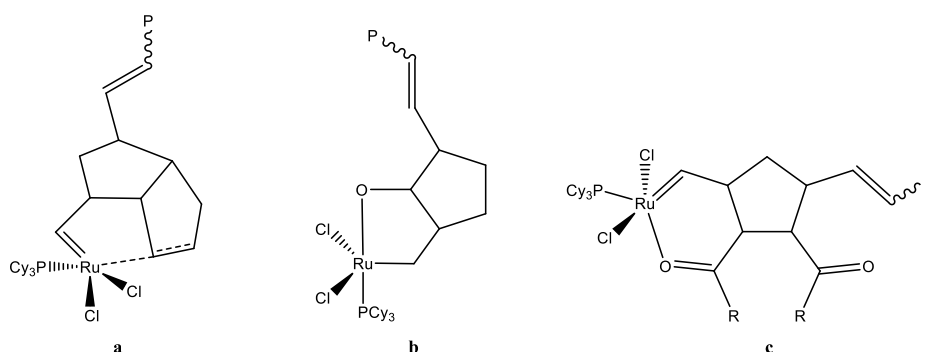**Figure 4.** Known intramolecular complexes at the end of a growing polymer chain (Rule & Moore, 2002; Pollino *et al.,* 2003; Lyapkov *et al.,* 2018; Haigh *et al.,* 2005)

They perform a resonance at a lower frequency than exo and endo-2,3-disubstituted norbornenes forming six-membered complexes. The intramolecular 16-electron complexes shown at the Fig.4, stabilize the active ruthenium intermediate. The resulting

complex does not perform any catalytic activity and requires activation through the functional group decoordination and formation of the 14-electron structure.

7.   Stereochemical aspects of ROMP

Alongside its molecular-weight distribution, the structure of a polymer is the main factor affecting its physical, mechanic and performance properties (Bicerano, 2002). The evolution of 'well-defined' catalysts allowed to study thoroughly the ROMP system and promoted understanding of the structure of polymers acquired as a result of this process. Consequently, this brought the possibility of monitoring the structure of the polymers via changing the catalyst structure (Keitz *et al.,* 2012; Schrock, 2011; Flook *et al.,* 2001; Flook *et al.*, 2009). There are two structural peculiarities typical of repeating units of ROMP. The first one is the spatial structure of double bond which determines the instance of cis- and trans-fragments of polymers. The other structural peculiarity is the tacticity typical of structural blocks with a chiral atom of carbon (e.g. asymmetrical 2,3-disubstituted norbornenes). The tacticity of a polymer is determined by the mutual arrangement of analogous chiral atoms of carbon in the adjacent fragments of the polymer.

Recently, scientists have been solving the problem of obtaining high-stereoregular polymers with a well-defined structure of the polymer chain and spatial ordering of monomer units with respect to one another. The main condition necessary for the dominance of one type of connection and spatial interrelation of the monomer units is the ratio of the rates of the target and side processes. To obtain the stereoregular polymers, the rate of the main stereoselective reaction should exceed at least 20-fold all possible ways of chain growth (Schrock, 2011; Breslow, 1993). For instance, the quantitative ratio of cis- and trans-fragments in a macromolecule would be determined according to the kinetic and energy parameter of polymerization. So, the formation of trans-fragments for cyclopentene is more beneficial by 4 kJ·mole^{-1} than that of cis-fragments. This difference increases up to 6 kJ·mole^{-1} in the case of cycloheptene (Cherednichenko, 1978). The difference in the Gibbs energy would depend on how easily metal-cyclobutane intermediate evolves.

Despite the fact of the use a ruthenium catalyst complex, the interpretation of the formation of ROMP polymer chain is similar to the formation of using molybdenum catalysts, for which there are two main reasons. The first one is that as of now, molybdenum catalysts are used in many studies discussing stereochemical peculiarities of ROMP issuing on the instance of disubstituted norbornenes. The second reason is that mainly under the ruthenium-containing catalysts, non-stereoregular polymers evolve, that is why there are a few studies describing the stereoselective synthesis of polymers in ROMP under ruthenium-based catalysts. A group of scientists led by Robert Grubbs obtained cis-selective catalysts based on ruthenium only in 2012 (Keitz *et al.,* 2012). It is known that imido-alkylidene catalyst complexes, containing W and Mo of the first generation, can exist in two varying forms (Scheme 10). The transition from one form to another at room temperature is quite slow at $k_{syn/anti} = 10^{-5}$ s^{-1} and varies by an order of magnitude in different solvents, while the *syn*-form of the catalyst prevails over the *anti*-form (Oskam & Schrock,1992; Oskam & Schrock, 1993):
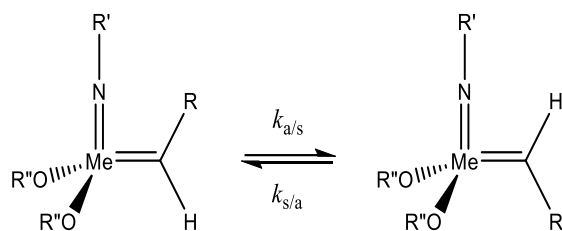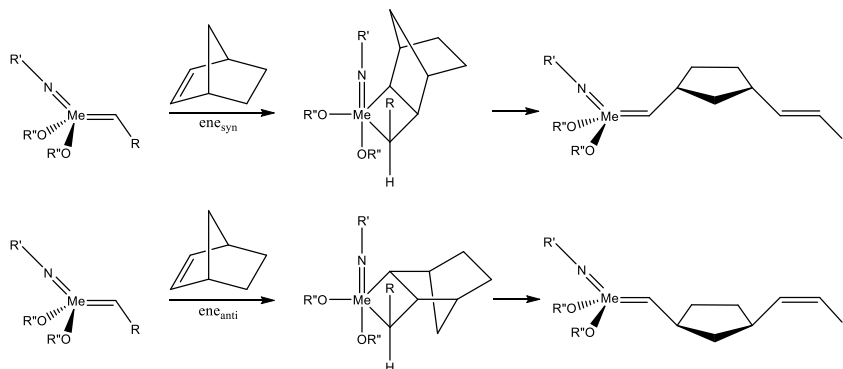
Scheme 10.

The demonstrated catalyst forms are the basis for understanding the way monomer molecules shape the polymer chain.

R.R. Schrock (Schrock, 2011) describes at length the mechanism in which the appearance of the trans- and cis- structures depends on two possible orientation of the monomer molecule in the metal-cyclobutane complex. The norbornene molecule (Scheme 11) with its external side of the double bond is attached to the back surface of CNO, while the norbornene ring can be positioned with an orientation towards the imido-group of ene$_{syn}$ or away from it ene$_{anti}$.
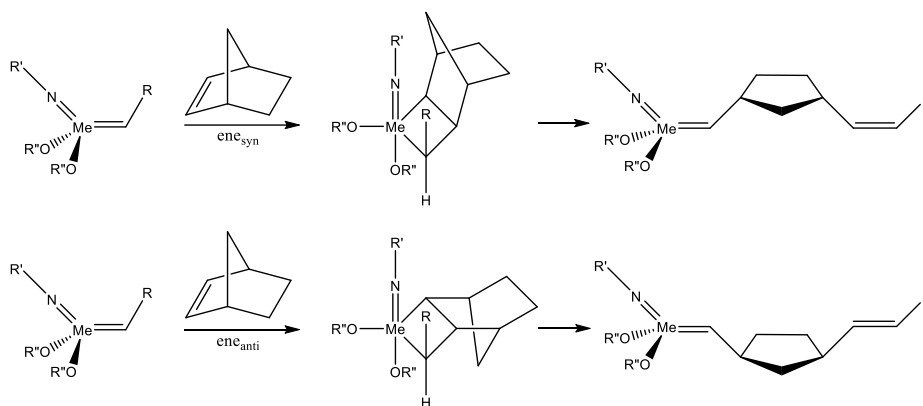
Scheme 11.

At the same time, the transitional state has a trigonal bipyramidal structure, determined by the dislocation of imido and alkoxide groups into an axial position. The decay of the transitional state would lead to the formation of cis- and trans-fragments. Anti-isomer may also attach ene$_{syn}$ and ene$_{anti}$ norbornene (Scheme 12).

Scheme 12.

In the discussed cases, there are four energetically distinguishable ways of initiation resulting in four varying products. Trans-configuration can be obtained via anti/ene$_{syn}$ and syn/ene$_{anti}$, and cis- via anti/ene$_{anti}$ and syn/ene$_{syn}$. With the following attachment of a monomer, the number of possible initiation ways may increase up to eight. Nonetheless, the given transformations result in four types of regular structures (Fig. 5). The formation of a polymer with high tacticity of the units is more possible if one way of chain growth prevails. The preference of one possible structure will depend on both the monomer structure and the structure of the catalyst complex. Currently, the studies (Keitz *et al*., 2012; Flook *et al.,* 2011; Flook *et al.,* 2009) discuss Mo and Ru catalyst complexes which initiate the polymerization of 2,3-disubstitutednorbornenes, resulting in the formation of highly cis-tactic polymers.
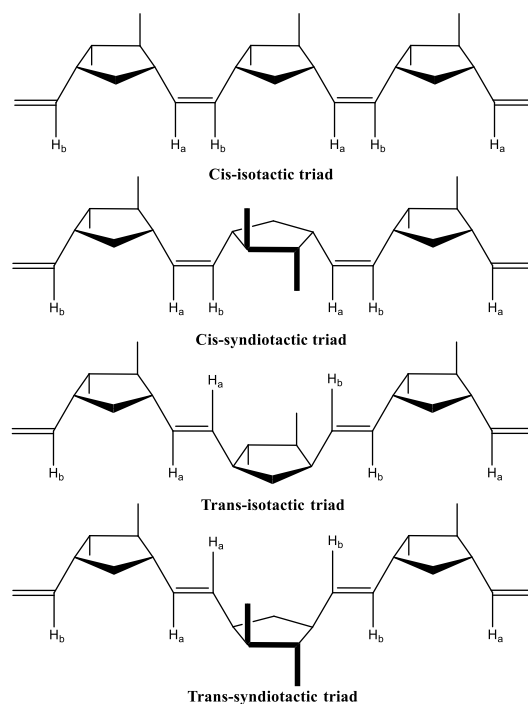

Figure 5. Possible structures in the polymerization of 2,3-disubstituted norbornene
(O'Dell, 1994; Delaude *et al*., 2003)

The paper by Schrock et al. (O'Dell *et al*., 1994) demonstrates the way to differentiate among the four potential polymer structures using ^{1}H homonuclear correlation NMR-spectroscopy (COSY). However, this is only possible with the use of chiral norbornene derivatives. Using the principles of symmetry of organic molecules, the authors demonstrated that the protons of the double bond would differ from one another. So, *cis*-isotactic olefinic polymer protons will be unequal and positioned on different sides of the same double bond. In a COSY spectrum, they will appear as two resonances with a spin-spin coupling constant. In a *cis*-syndiotactic triad, a couple of equivalent protons is positioned on each double bond which would cause two resonances not connected with one anotherinthe COSY spectrum of such polymer. If the same approach is applied to *trans*-isotactic and syndiotactic structures, then the COSY spectrum would demonstrate the appearance of two resonances without a spin-spin coupling constant for a trans-isotactic triad, and in the case of trans-isotacticone, similar protons would have a spin-spin interaction.

A common approach to study tactic structures is based only on the use of COSY spectra. In the case of polymerization of prochiral molecules, an additional element of the symmetry would appear in the discussed structures. Each of these structures would have a medium plane spreading through the middle of cyclopentene ring. This would lead to all protons of double bonds becoming equivalent and, using the COSY technique, it would be impossible to distinguish between syndio- and iso-tactic structures. However, it would be possible to distinguish *cis-* and *trans-*fragments using one-dimensional ^{1}H NMR spectra (Petasis & Fu, 1993; Kiselev *et al.,* 2016) or NMR spectra on ^{13}C nuclei (Brumaghim & Girolami, 1999; Al-Samak *et al*., 1996).

8. Conclusion

Ring Opening Metathesis Polymerization is one of the main types of metathesis, which is currently an area of broad interests, both in the scientific and industrial fields. The rapid development of catalysts for metathesis polymerization allows expanding the range of monomers used for the synthesis of functionalized polymers. Of all the catalysts of metathesis polymerization currently known, the most active and resistant to oxygen and moisture in the air, as well as to most of the functional groups of monomers, are ruthenium catalysts of the Hoveyda-Grubbs type II.

To summarize, it is necessary to note that metathesis polymerization with cycle opening has proved to be a powerful method of synthesizing polymers. Materials obtained with this method possess fair exploitation characteristics and have already proved effective on the market of polymer goods (Bozhenkova *et al.,* 2017).

Largely, the polymerization rate is defined by the structure of catalyst and monomer. The activity of ruthenium catalyst complexes is well studied and apart from the structure of the complex itself, it depends on a number of external factors including temperature, solvent polarity, the presence of acceptor or donor compounds and etc. The structure of monomer also affects polymerization rate.

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