

Structure/property relationship of Schrock-type alkylidene complexes based on tungsten and molybdenum

Emma Thorn-Csányi*, Jörg Ulrich Zilles

Institute of Technical and Macromolecular Chemistry, University of Hamburg, Bundesstrasse 45, D-20146 Hamburg, Germany

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Abstract

The structure/property relationship of Schrock-type alkylidene complexes with tungsten and molybdenum as central atoms was investigated. Terminal and, *E* and *Z* internal olefins as well as double bond substituted and unsubstituted unsaturated polymers served as metathesis substrates. According to the results obtained, it is possible to choose the optimal catalyst depending on the metathesis substrate and temperature, the central atom plays a decisive role. Examples concerning equilibrium polymerization demonstrate the practical utilization.

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1. Introduction

Our interest in olefin metathesis focuses on three fields, like analysis of tyres [1,2], synthesis of polyconjugated compounds for the use in the opto-electronics [3–5] and study of the chain growth (ROMP, ADMET)/chain degradation equilibrium [6–10]. All these examples represent difficult metathesis conversions thus they require highly selective catalysts with good activity and stability.

Classical systems cannot be used, their stability, selectivity and tolerance towards hetero atoms is not satisfactory [11]. But among the Schrock-type alkylidene complexes we found such catalysts, which are suitable. So our interest in Schrock-type catalysts began. A fine review about these well-defined complexes

of molybdenum and tungsten has been published by Schrock in 1998 [12].

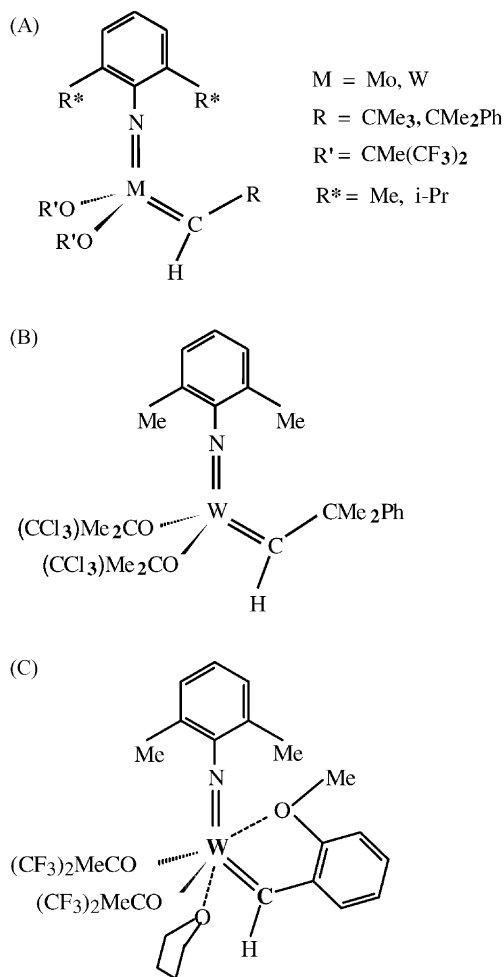
To determine the structure/property relationship, we synthesized several Schrock-type alkylidene complexes [13,14] (Scheme 1, A) by varying the central atom (tungsten and molybdenum), the substituent at the phenylimido ligand (R^* = methyl and isopropyl) and the alkylidene group (R = neopentylidene and neophylidene). In order to obtain high activity, hexafluoroalkoxo ligands were chosen, with one exception (Scheme 1, B). Additionally, a very stable Schrock-type tungsten-based catalyst (first described by Grubbs et al. [15]; Scheme 1, C) was synthesized.

As metathesis substrates terminal and, *E* and *Z* internal olefins were used as well as polymers with substituted and unsubstituted double bonds (polyisoprenes resp. polybutadienes). In this paper, results concerning catalyst structure/property relationship will be presented together with a few selected examples from the field of polymerization/depolymerization equilibrium

* Corresponding author. Tel.: +49-40-42838-3166;

fax: +49-40-42838-6008.

E-mail address: thorn@uni-hamburg.de (E. Thorn-Csányi).



Scheme 1.

(like thermodynamically controlled ROMP) which demonstrate practical applications.

2. Results

2.1. Stability and selectivity

Results concerning catalyst stability and selectivity were published [16], thus only a summary will be given here:

- The catalysts investigated are very stable in an inert atmosphere, in solid state and also in solution (toluene and methyl cyclohexane were used). The catalysts have limited life time when an olefin is added.
- Important finding is furthermore that synchronously with the decrease of the amount of the alkylidene species, double bond shifting takes place as side reaction.

As conclusion, it may be stated that highly selective course of metathesis can be achieved only if the reaction time is shorter than the life time of the catalyst in the particular system investigated.

The great advantage of the Schrock-type catalysts in comparison to classical systems is their long time stability. Therefore side reactions mostly do not occur at all. But they have to be taken into account if the metathesis is hampered and therefore a long reaction time is required.

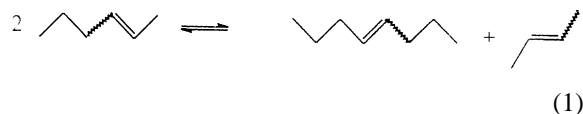
Table 1

Conversion rate at 50% of the equilibrium conversion ($[\Delta(X/X_{\text{Eq}})/\Delta t]_{X=0.5X_{\text{Eq}}}$ in min^{-1}) of 2-hexenes and the induction period (t_{ind} in min) of homo-metathesis of Z- resp. E-2-hexene (1 mol l^{-1}) using four molybdenum and four tungsten-based alkylidene complexes (2 mmol l^{-1}), in methyl cyclohexane at room temperature

Catalyst	Z-2-Hexene		E-2-Hexene	
	t_{ind} (min)	$[\Delta(X/X_{\text{Eq}})/\Delta t]_{X=0.5X_{\text{Eq}}}$ (min^{-1})	t_{ind} (min)	$[\Delta(X/X_{\text{Eq}})/\Delta t]_{X=0.5X_{\text{Eq}}}$ (min^{-1})
Mo(NPh ^{Me2})(neoP)(OR _F) ₂	–	≥0.418	–	0.253
Mo(NPh ^{Me2})(neoPh)(OR _F) ₂	–	≥0.384	–	0.248
Mo(NPh ^{iPr2})(neoP)(OR _F) ₂	1	0.180	13	0.074
Mo(NPh ^{iPr2})(neoPh)(OR _F) ₂	3	0.174	15	0.065
W(NPh ^{Me2})(neoP)(OR _F) ₂	–	≥0.426	–	≥0.407
W(NPh ^{Me2})(neoPh)(OR _F) ₂	–	≥0.393	–	≥0.399
W(NPh ^{iPr2})(neoP)(OR _F) ₂	–	0.250	1	0.230
W(NPh ^{iPr2})(neoPh)(OR _F) ₂	1	0.225	3	0.220

2.2. Metathesis of internal olefins

The course of metathesis of internal monoolefins was investigated in dependence on the double bond configuration and the length of the alkylidene groups:



Results of homo-metathesis (Eq. (1)) of Z- resp. E-2-hexene are shown in Table 1. As catalysts four molybdenum and four tungsten-based alkylidene complexes were used (see Scheme 1, A). In order to obtain a quick comparative information about the reaction courses two characteristic features were determined, the reaction rate at 50% of the equilibrium conversion and the induction period (see Table 1). Additionally, the time dependent conversion of Z- and E-2-hexene during the cross-metathesis reaction with

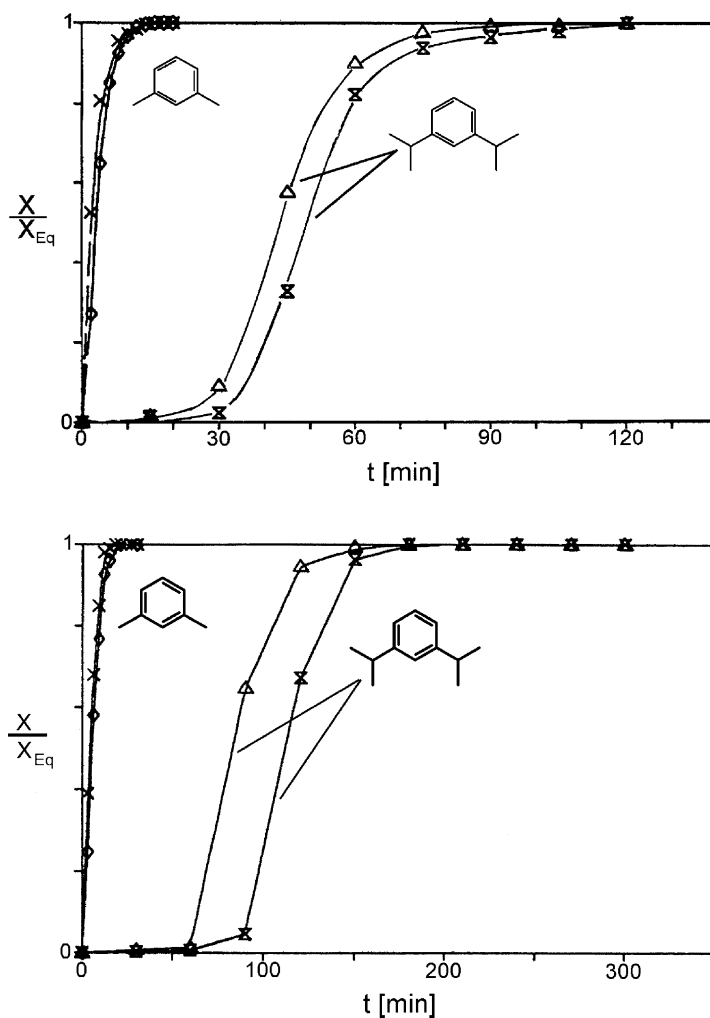


Fig. 1. Time dependent conversion of 2-hexenes (X/X_{Eq}), starting with Z-2-hexene (at the top) resp. E-2-hexene (at the bottom) via cross-metathesis with E-3-hexene by varying the ligands at the molybdenum-based alkylidene complexes; $c_{\text{catalyst}} = 2 \text{ mmol l}^{-1}$, $c_{\text{Z-(resp. E)-2-hexene}} = 100 \text{ mmol l}^{-1}$, $c_{\text{E-3-hexene}} = 900 \text{ mmol l}^{-1}$, in methyl cyclohexane at room temperature: (x) $\text{Mo}(\text{NPh}^{\text{Me}_2})(\text{neoP})(\text{OR}_F)_2$; (\diamond) $\text{Mo}(\text{NPh}^{\text{Me}_2})(\text{neoPh})(\text{OR}_F)_2$; (\triangle) $\text{Mo}(\text{NPh}^{\text{iPr}_2})(\text{neoP})(\text{OR}_F)_2$; (\times) $\text{Mo}(\text{NPh}^{\text{iPr}_2})(\text{neoPh})(\text{OR}_F)_2$.

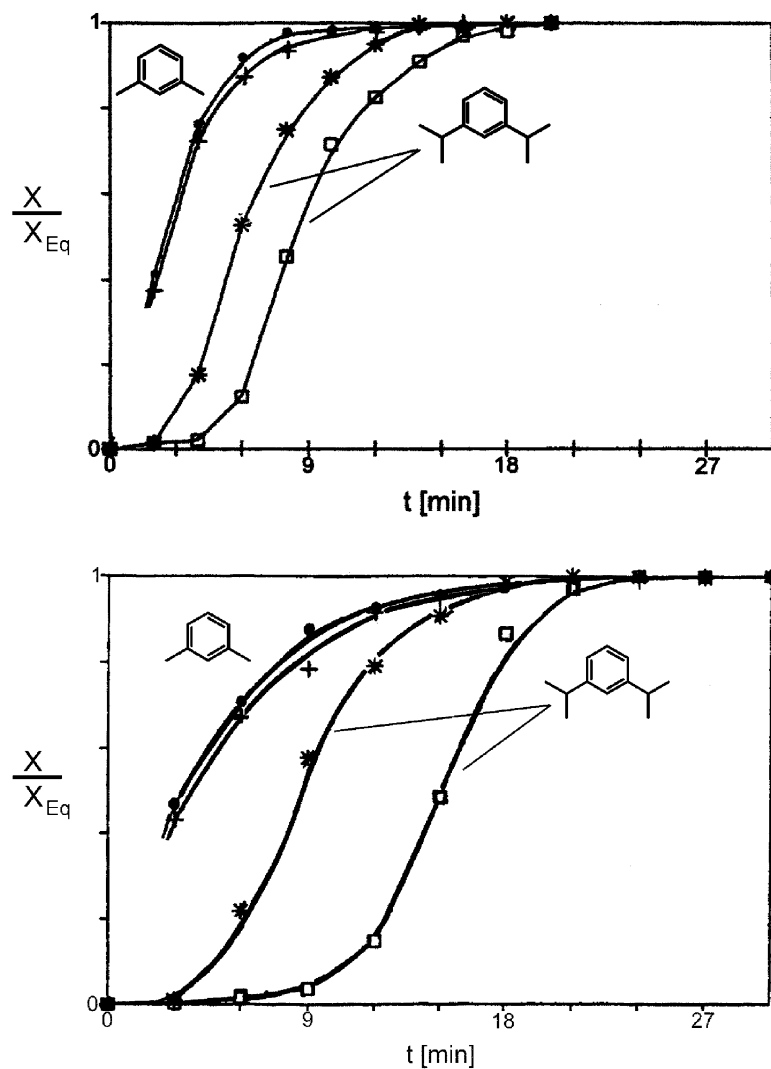


Fig. 2. Time dependent conversion of 2-hexenes (X/X_{Eq}), starting with Z-2-hexene (at the top) resp. E-2-hexene (at the bottom) via cross-metathesis with E-3-hexene by varying the ligands at the tungsten-based alkylidene complexes; $c_{catalyst} = 2 \text{ mmol l}^{-1}$, CZ-(resp. E-)2-hexene = 100 mmol l^{-1} , CE-3-hexene = 900 mmol l^{-1} , in methyl cyclohexane at room temperature: (●) $W(NPh^{Me_2})(neoP)(ORF)_2$; (+) $W(NPh^{Me_2})(neoPh)(ORF)_2$; (*) $W(NPh^{iPr_2})(neoP)(ORF)_2$; (□) $W(NPh^{iPr_2})(neoPh)(ORF)_2$.

E-3-hexene (2-hexene:3-hexene = 1:9) is illustrated in Figs. 1 and 2; the equilibrium conversion X_{Eq} is normalized to 1.

Results of the homo-metathesis and cross-metathesis investigations will be presented concerning the influence of:

- the substituent at the phenylimido ligand,
- the alkylidene species,

- the central atom,
- the solvent.

2.2.1. The substituent on the phenylimido ligand

The substituent on the phenylimido ligand influences the induction period as well as the metathesis activity. The occurrence of the induction period is a characteristic feature of the internal olefin metathesis. Among the investigated tungsten and molybdenum

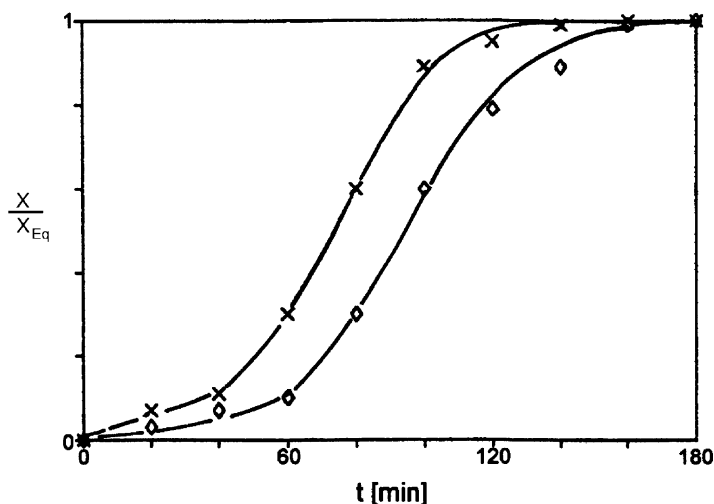


Fig. 3. Time dependent metathesis conversion of *E*-/*Z*-2-pentene (X/X_{Eq}), using (2,6-dimethylphenyl)-imido-molybdenum complexes with neopentylidene and neophylidene ligands at -78°C in methyl cyclohexane; $c_{\text{catalyst}} = 1 \text{ mmol l}^{-1}$, $c_{E-/Z-2\text{-pentene}} = 1 \text{ mol l}^{-1}$: (×) $\text{Mo}(\text{NPh}^{\text{Me}_2})(\text{neoP})(\text{OR}_F)_2$; (\diamond) $\text{Mo}(\text{NPh}^{\text{Me}_2})(\text{neoPh})(\text{OR}_F)_2$.

complexes, only catalysts with isopropyl substituent at the phenylimido ligand show a distinct induction period at room temperature. Especially, in the case of the metathesis conversion of *trans*-configured olefins with molybdenum complexes very long induction periods were observed.

The existence of induction time for catalysts with methyl-substituted phenylimido ligands was proven at low temperatures of 0°C for tungsten-based catalysts and at -78°C for molybdenum complexes (Fig. 3). The time dependent product analysis was carried out in intervals of 3 min and the first sample was taken 3 min after the catalyst was added. Under these conditions, for the dimethyl-substituted phenylimido molybdenum complexes (using *Z*- and *E*-2-pentene as substrate in methyl cyclohexane) an induction period could not be proven even at -40°C .

Time dependent determination of the alkylidene ligands (via an analogous Wittig reaction, by adding propanal) demonstrates that the transalkylidene of the originally used alkylidene by the substrate also shows an induction period. It starts synchronously with (slightly in advance of) the metathesis conversion.

It is remarkable that the influence of the sterically demanding substituent (isopropyl vs. methyl) on the metathesis course is much more distinct in the case of

molybdenum-based catalysts. Results in Figs. 1 and 2 illustrate clearly the existence of two separated regions depending on the substituent, methyl resp. isopropyl, employing molybdenum as central atom.

2.2.2. The alkylidene species

The alkylidene ligand has a strong influence on the induction time. The exchange of neopentylidene for neophylidene group resulted in a strong increase in the induction period but the metathesis conversion rate remains the same, under conditions used. For substrates investigated, this observation is independent of the reaction temperature, of the central atom and is valid for methyl as well as for isopropyl-substituted phenylimido alkylidene complexes (Figs. 1 and 2).

2.2.3. The central atom

Tungsten and molybdenum influence the course of the metathesis reaction differently in dependence on substrate double bond configuration. Using tungsten as central atom *E*- and *Z*-2-hexene are converted with approximately equal reaction rates. But, with molybdenum-based catalysts the metathesis of *E*-isomer is hampered in comparison to the *Z*-olefin. The difference between the metathesis courses of *Z*- and *E*-olefin is modest using molybdenum catalysts with dimethyl-substituted imido

ligand. But, it is very distinct if the phenylimido ligand is di-isopropyl-substituted. The metathesis reaction rate is lower and above all the induction time is much longer for the *E*-isomer (Table 1). To elucidate the reason for this fact, additional time and temperature dependent $^1\text{H-NMR}$ investigations were performed in toluene d_8 starting at -70°C , using *E*- resp. *Z*-2-pentene as substrate and $\text{Mo}(\text{NPh}^{i\text{Pr}_2})(\text{CHMe}_2\text{Ph})[\text{OCMe}(\text{CF}_3)_2]_2$ as catalyst (in a molar ratio of 1:5) [17]. Results obtained give an additional evidence that the conversion of the *E*-configured

olefin is strongly disadvantaged. Already, the formation of the first intermediate (preliminary step of the transalkylidenation) is greatly delayed, employing *E*-pentene. Furthermore, stable intermediates are formed. Detailed investigations are in progress to identify the structure of the intermediates exactly [18].

2.2.4. The solvent

To determine the *solvent effect*, the metathesis of *Z/E*-2-pentene was investigated in toluene and methyl cyclohexane at 0°C (Fig. 4) and 20°C . As catalysts

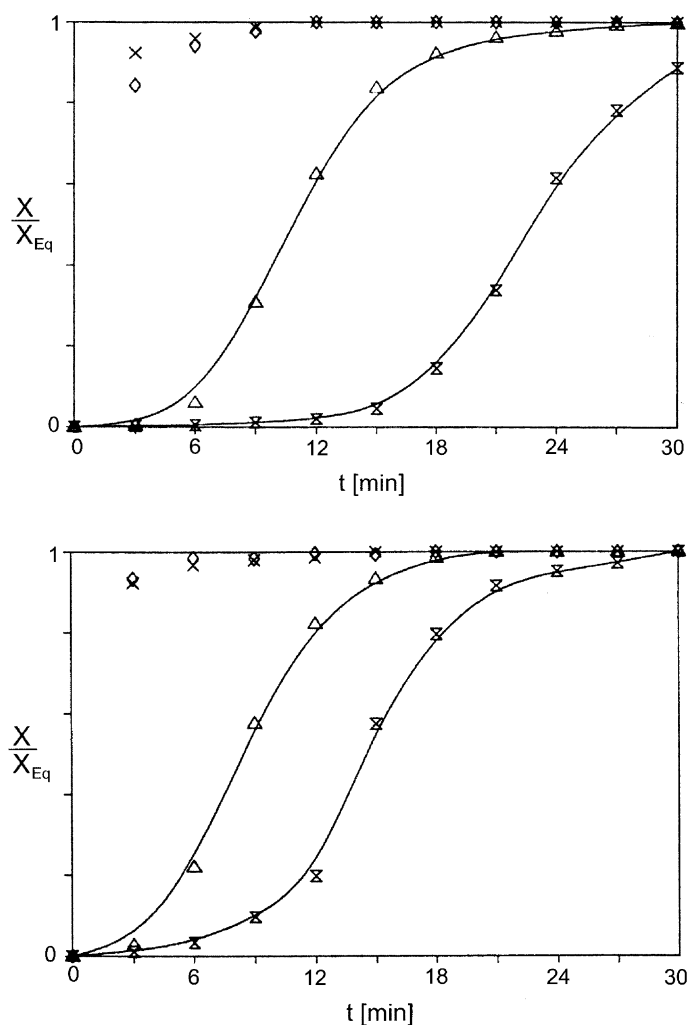


Fig. 4. Time dependent metathesis conversion (X/X_{Eq}) of *E*-*Z*-2-pentene (containing 0.61% 1-pentene), using four molybdenum-based catalysts at 0°C in methyl cyclohexane (at the top) resp. toluene (at the bottom); $c_{\text{catalyst}} = 1 \text{ mmol l}^{-1}$, $c_{E-Z-2\text{-pentene}} = 1 \text{ mol l}^{-1}$: (\times) $\text{Mo}(\text{NPh}^{\text{Me}_2})(\text{neoP})(\text{OR}_F)_2$; (\diamond) $\text{Mo}(\text{NPh}^{\text{Me}_2})(\text{neoPh})(\text{OR}_F)_2$; (\triangle) $\text{Mo}(\text{NPh}^{i\text{Pr}_2})(\text{neoP})(\text{OR}_F)_2$; (\boxtimes) $\text{Mo}(\text{NPh}^{i\text{Pr}_2})(\text{neoPh})(\text{OR}_F)_2$.

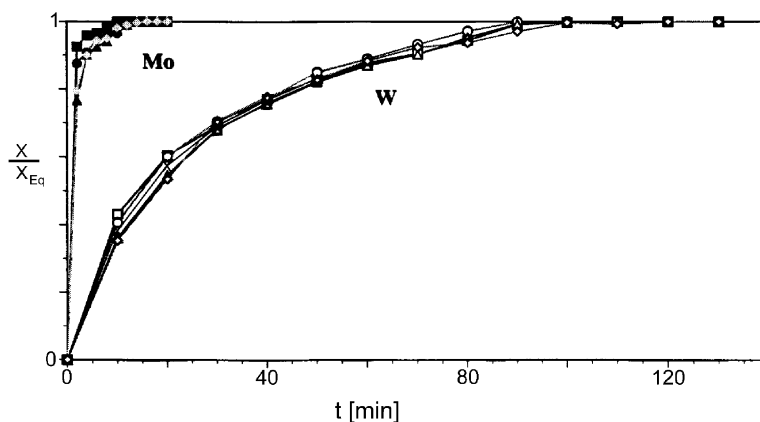
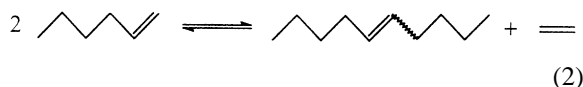


Fig. 5. Time dependent metathesis conversion of 1-hexenes, using four molybdenum and five tungsten-based catalysts $c_{\text{catalyst}} = 2 \text{ mmol l}^{-1}$, $c_{1\text{-hexenes}} = 1 \text{ mol l}^{-1}$, in methyl cyclohexane: (■) $\text{Mo}(\text{NPh}^{\text{Me}_2})(\text{neoP})(\text{OR}_F)_2$; (□) $\text{W}(\text{NPh}^{\text{Me}_2})(\text{neoP})(\text{OR}_F)_2$; (●) $\text{Mo}(\text{NPh}^{\text{Me}_2})(\text{neoPh})(\text{OR}_F)_2$; (○) $\text{W}(\text{NPh}^{\text{Me}_2})(\text{neoPh})(\text{OR}_F)_2$; (▲) $\text{Mo}(\text{NPh}^{\text{iPr}_2})(\text{neoP})(\text{OR}_F)_2$; (△) $\text{W}(\text{NPh}^{\text{iPr}_2})(\text{neoP})(\text{OR}_F)_2$; (⊙) $\text{Mo}(\text{NPh}^{\text{iPr}_2})(\text{neoPh})(\text{OR}_F)_2$; (◇) $\text{W}(\text{NPh}^{\text{iPr}_2})(\text{neoPh})(\text{OR}_F)_2$; (×) $\text{W}(\text{NPh}^{\text{Me}_2})(\text{neoPh})(\text{OCMe}_2\text{Cl}_3)_2$.

served four molybdenum-based complexes. Results obtained reveal that the induction time is shorter for toluene in comparison to methyl cyclohexane, but between the metathesis reaction rates a significant difference does not exist. This finding demonstrates that the induction time is more sensitive to slight differences in solvent polarities than the reaction rate of the metathesis.

2.3. Metathesis of terminal olefins

The metathesis course of a conventional terminal olefin (1-hexene, Eq. (2)) using the catalysts presented in Scheme 1 (A and B), is illustrated in Fig. 5:



The results show three characteristic features:

- An induction period cannot be observed.
- The central atom has a strong influence upon the reaction rate; in principle, molybdenum complexes show a high and tungsten complexes a low activity.
- Among the investigated molybdenum resp. tungsten catalysts, different ligands have only a very modest resp. no influence on the metathesis conversion of 1-hexene. Even the tungsten catalyst with

trichloroalkoxo ligands, which hardly catalyzed internal olefin metathesis, reacts as fast as the hexafluoroalkoxo alkylidene complexes. Using 2 mol l^{-1} *E*-2-hexene and 2 mmol l^{-1} chloroalkoxo tungsten catalyst only 20% conversion was achieved within 120 min, in methyl cyclohexane at room temperature.

The strongly hindered α -olefin metathesis using tungsten-based complexes is of consequence for metathesis of internal olefins, if α -olefins are present in the reaction mixture, even in traces. As Fig. 6 demonstrates, the induction period vanishes and the time dependent conversion is strongly hindered, like the conversion of α -olefins.

The hampered metathesis of internal olefins in the presence of α -olefins is a characteristic feature of all tungsten-based catalysts regardless of the ligand sphere. Degrading butadiene rubbers using the classical catalyst system, tungsten hexachloride/tetraethyltin/diethylether, we also found a strong decrease in the conversion rate of internal double bonds (1,4-butadiene units) if additional 1,2-units (terminal double bonds) were present [19].

Decreasing the temperature, the influence of α -olefin traces upon metathesis reaction rate of internal olefins (using tungsten catalysts!) grows strongly. As Fig. 7 demonstrates the metathesis conversion rate decreases dramatically.

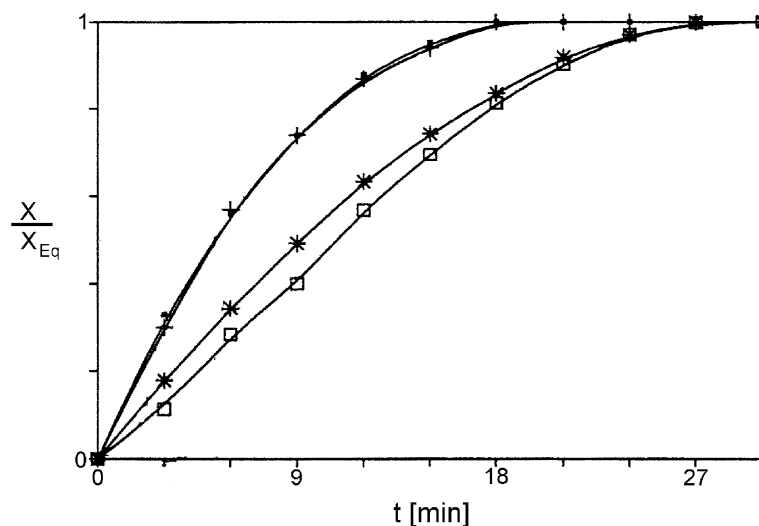


Fig. 6. Metathesis course of *E*-/*Z*-2-pentene containing 0.61% 1-pentene using four tungsten-based catalysts, at room temperature $c_{\text{catalyst}} = 1 \text{ mol l}^{-1}$, $c_{\text{substrate}} = 1 \text{ mol l}^{-1}$, in methyl cyclohexane: (●) $\text{W}(\text{NPh}^{\text{Me}_2})(\text{neoP})(\text{OR}_F)_2$; (+) $\text{W}(\text{NPh}^{\text{Me}_2})(\text{neoPh})(\text{OR}_F)_2$; (*) $\text{W}(\text{NPh}^{i\text{Pr}_2})(\text{neoP})(\text{OR}_F)_2$; (□) $\text{W}(\text{NPh}^{i\text{Pr}_2})(\text{neoPh})(\text{OR}_F)_2$.

In accordance with the results shown in Figs. 6 and 7 is the finding that using tungsten-based catalysts, with rise in temperature the conversion rate of α -olefins increases strongly, basic requirement is a high temperature stability of the catalyst. While

at room temperature, molybdenum-based catalysts show much higher activities towards α -olefins than the tungsten alkylidene complexes do (Fig. 5), for metathesis conversions at higher temperatures (e.g. 80–150 °C), the very stable tungsten alkylidene

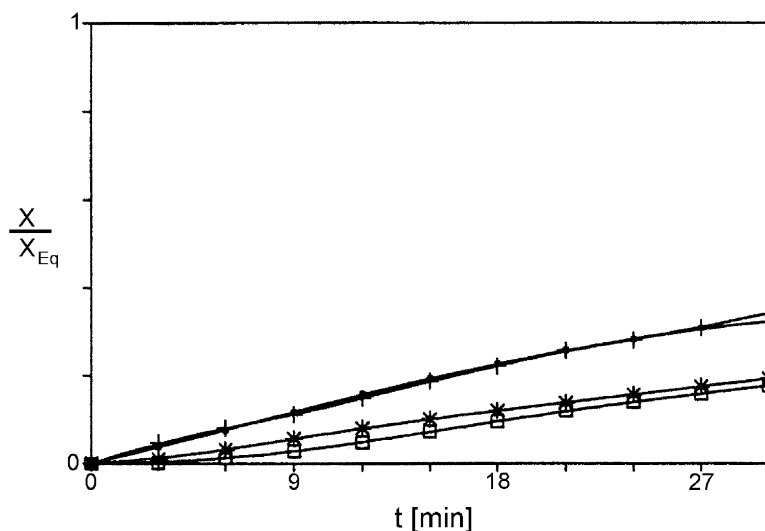
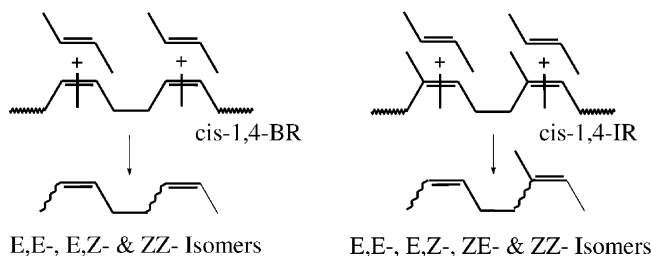


Fig. 7. Metathesis course of *E*-/*Z*-2-pentene containing 0.61% 1-pentene using four tungsten-based catalysts, at 0 °C, $c_{\text{catalyst}} = 1 \text{ mol l}^{-1}$, $c_{\text{substrate}} = 1 \text{ mol l}^{-1}$, in methyl cyclohexane: (●) $\text{W}(\text{NPh}^{\text{Me}_2})(\text{neoP})(\text{OR}_F)_2$; (+) $\text{W}(\text{NPh}^{\text{Me}_2})(\text{neoPh})(\text{OR}_F)_2$; (*) $\text{W}(\text{NPh}^{i\text{Pr}_2})(\text{neoP})(\text{OR}_F)_2$; (□) $\text{W}(\text{NPh}^{i\text{Pr}_2})(\text{neoPh})(\text{OR}_F)_2$.



Scheme 2.

complex $W(\text{CHPh}^{o\text{-MeO}})(\text{NPh}^{\text{Me}_2})[\text{OCMe}(\text{CF}_3)_2]_2$ (THF) is the best suited of the catalysts investigated (Scheme 1) [5].

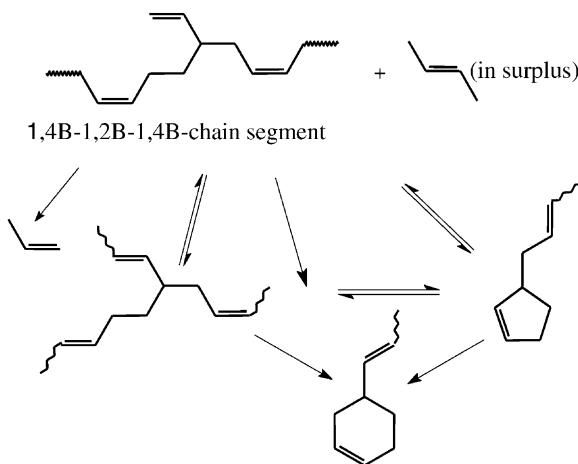
In contrary to the conversion of conventional α -olefins (like 1-hexene), the influence of different ligands is noticeable when sterically demanding substrates are used and it is considerable in the case of sterically bulky derivatives [20].

2.4. Metathesis of olefins with substituted double bonds

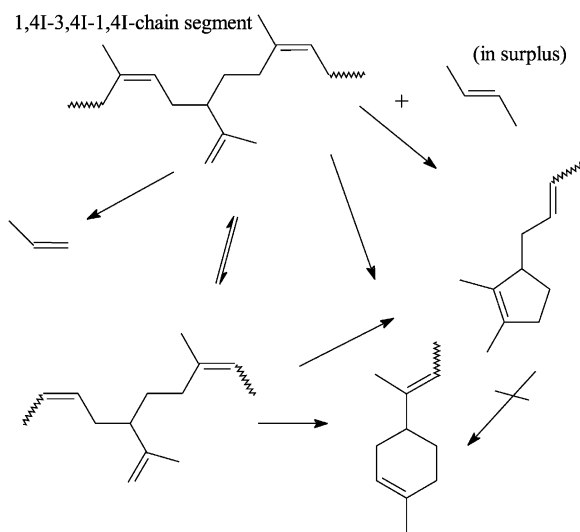
Degrading butadiene and isoprene rubbers, with different tungsten and molybdenum-based catalysts, by adding or without adding a monoolefin, the substituent effect could be studied extensively [21–23]. Summing up the results obtained, it may be stated that a similarity exists between the conversion rate of *trans*-configured olefins (from 2-pentene upwards) and of polyenes with methyl-substituted double bonds. Whereas among the tungsten-based complexes all four are well suited for the splitting of methyl-substituted double bonds, in the case of molybdenum complexes only those with (2,6-dimethylphenyl)-imido ligand can be used. The molybdenum catalysts with isopropyl substituents on the phenylimido ligand show a strongly hampered reaction course due to the substituent on the double bond. To demonstrate this, kinetic results of metathesis degradation of a *cis*-1,4-butadiene-resp. *cis*-1,4-isoprene rubber by adding *E*-2-butene in surplus are described, employing the best known and most frequently used Schrock-type catalyst $\text{Mo}(\text{NPh}^{i\text{Pr}_2})(\text{CHMe}_2\text{Ph})[\text{OCMe}(\text{CF}_3)_2]_2$. The products investigated were Ziegler polymers, Nd–BR with 0.6% 1,2-units resp. Ti–IR with 0.5% 3,4-units. Reaction conditions were: $c_{\text{BR resp. IR}} = 56 \text{ mmol l}^{-1}$,

$c_{\text{cat}} = 1.6 \text{ mmol l}^{-1}$, $c_{2\text{-butene}} = 1.9 \text{ mol l}^{-1}$ in cyclohexane at room temperature [21]. The characteristic chain segments and the corresponding degradation products are presented in Schemes 2–4.

According to the results obtained, the cross-metathesis degradation of polybutadiene with *E*-2-butene is already complete within 5 min (time of the first sampling). On the contrary, the degradation of polyisoprene required several days. Furthermore, when degrading polybutadiene, not only the final product distribution, but also their thermodynamically predicted configuration is reached within 5 min. When degrading polyisoprene, much more time is needed to establish the configuration equilibrium, but it was reached earlier (within 1 day) than the final product distribution. It should be noted that the formation of *E,E'*- and *E,Z'*-isomers of 3-methyl-2,6-octadiene (Scheme 2) is kinetically preferred. Their amount at the early stage of the reaction is much higher than



Scheme 3.



Scheme 4.

thermodynamically predicted [21]. This finding shows that the threefold substituted double bonds are at first predominantly *trans*-configured.

The 1,2-butadiene resp. of 3,4-isoprene units of the Nd–BR resp. Ti–IR are mainly isolated, according to our results [22]. Schemes 3 and 4 illustrate that from the chain segments with isolated 1,2-butadiene or 3,4-isoprene units the configuration isomers of four degradation products (two acyclic components and two cyclic derivatives) are generated.

As shown by our kinetic examinations, the number of fragments belonging to one sequence can be reduced by shifting the reaction towards the thermodynamically stable compounds. Chain segments with isolated 1,2-butadiene units yield configurational isomers of a cyclohexene derivative as metathesis end products. Already after 5 min reaction time, only the final products, the *E*- and *Z*-isomers of 4-(propen-2-yl)-cyclohexene, were observed employing $\text{Mo}(=\text{NPh}^{i\text{Pr}_2})(\text{CHMe}_2\text{Ph})[\text{OCMe}(\text{CF}_3)_2]_2$ as catalyst. For comparison, using the classical catalyst system $\text{WCl}_6/\text{SnEt}_4/\text{EtOEt}$, it takes a long time to reach the final ring distribution (~ 1 day), the cyclopentene ring formation is kinetically strongly preferred. Consequently, the ring closing reaction described can be exploited for the synthesis of the cyclopentene or the cyclohexene component on preparative scale [24].

When degrading polyisoprenes, much more time is needed to reach the final product spectrum of isolated 3,4-isoprene units. From 1,4I-3,4I-1,4I-chain segments, not only the thermodynamically most stable cyclohexene product but also the cyclopentene derivative (Scheme 4) are obtained. The metathetic ring closure yielding the cyclopentene product is an irreversible process, because the tetrasubstituted double bond formed is sterically hindered and therefore not accessible to the catalyst.

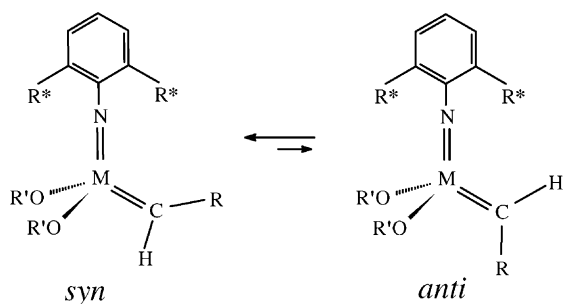
Concerning the determination of the sequence length distribution of 3,4-isoprene units we found that Schrock-type alkylidene complexes are generally excellent catalysts regarding the synthesis of tetrasubstituted double bonds via ring closing. Even the sterically demanding catalyst $\text{W}(\text{CHPh}^{o\text{-MeO}})(\text{NPh}^{\text{Me}_2})[\text{OCMe}(\text{CF}_3)_2]_2$ (THF) (Scheme 1, C) is able to produce successfully the cyclopentene derivative presented (see Scheme 4) [25].

Our investigations revealed the tungsten-based alkylidene complexes with dimethyl-substituted phenylimido ligand (Scheme 1, A) to be the best catalysts for the degradation of isoprene rubbers [21–23]. Working with *E*-3-hexene as monoolefin, for example, a quantitative degradation of polyisoprene to the smallest chain fragments including the achievement of the thermodynamically predicted product spectrum was obtained within half an hour. The reaction conditions were: $\text{W}(\text{CHCMe}_2\text{Ph})(\text{NPh}^{\text{Me}_2})[\text{OCMe}(\text{CF}_3)_2]_2$ as catalyst, $c_{1,4\text{-IR}} = 60 \text{ mmol}(\text{C}_5\text{H}_8)^{-1}$, $c_{\text{catalyst}} = 0.6 \text{ mmol l}^{-1}$, monoolefin/polymer double bond ratio = 15/1, in cyclohexane at room temperature [22].

3. Discussion

3.1. Metathesis conversion of internal olefins

Changing the imido substituents from 2,6-dimethylphenyl to 2,6-di-isopropyl-phenyl in the catalyst, strongly influences the metathesis course of olefins with internal double bonds. The induction time increases and the reaction rate of the metathesis decreases. The influence of the sterically demanding isopropyl substituent is especially distinct in the case of molybdenum-based catalysts. This result can be explained considering that two $\text{M}=\text{CHR}'$ rotamers



Scheme 5.

(Scheme 5) of the catalyst exist, *syn* and *anti*, from which the *syn* form is the most stable (and vice versa, the *anti* form the most reactive).

The *syn* rotamer can convert into the more active *anti* form either by rotation of the alkylidene about the M=C bond, or as a consequence of reaction with an olefin in a metathesis step. According to Osakam and Schrock [26,27], for molybdenum catalysts $\text{Mo}(\text{CHCMe}_2\text{Ph})(\text{NPhR}^*)(\text{OR})_2$ ($\text{R}^* = \text{Me}$ or *i*Pr), the rate of interconversion of *syn* and *anti* rotamers is fast for *t*-butoxide complexes ($k_{s/a} \approx 1 \text{ s}^{-1}$ at 298 K) but slow for hexafluoro-*t*-butoxide complexes ($k_{s/a} \approx 10^{-5} \text{ s}^{-1}$ at 298 K). Furthermore, only a little difference exists between the rates of alkylidene ligand rotation that contain (2,6-isopropyl-phenyl)-imido or (2,6-dimethylphenyl)-imido ligands. Thus, the *syn/anti* conversion alone cannot be responsible for the observed differences in catalyst activity. Additionally, we have to take into account, that the activity of the *syn* rotamer in complexes with 2,6-dimethyl-substituted phenylimido ligands is much less hampered than with 2,6-isopropyl-substituted, which sterically interact with the alkylidene substituent [28].

Among the catalysts and substrates investigated, changing the alkylidene ligand from neopentylidene to neophylidene has a strong influence on the induction time, but not on the metathesis reaction rate. This result can be explained, taking into account that the conversion rate of the *syn* into the more active *anti* rotamer is lower for the sterically demanding neophylidene group and that the same alkylidene group is responsible for the course of metathesis.

We found an analogy between the *central atom dependent metathesis* behavior of *trans*-configured olefins (from 2-pentene upwards) and of polyenes

with methyl substituents on the double bonds. In general, for the conversion of sterically demanding internal olefins, tungsten catalysts are the better suited. Among the tungsten-based complexes, catalysts with (2,6-dimethylphenyl)-imido as well as with (2,6-di-isopropyl-phenyl)-imido ligand show good activities, but in the case of molybdenum complexes only those with (2,6-dimethylphenyl)-imido ligand are suited.

To explain our experimental results, electronic as well as sterical effects should be taken into account [29].

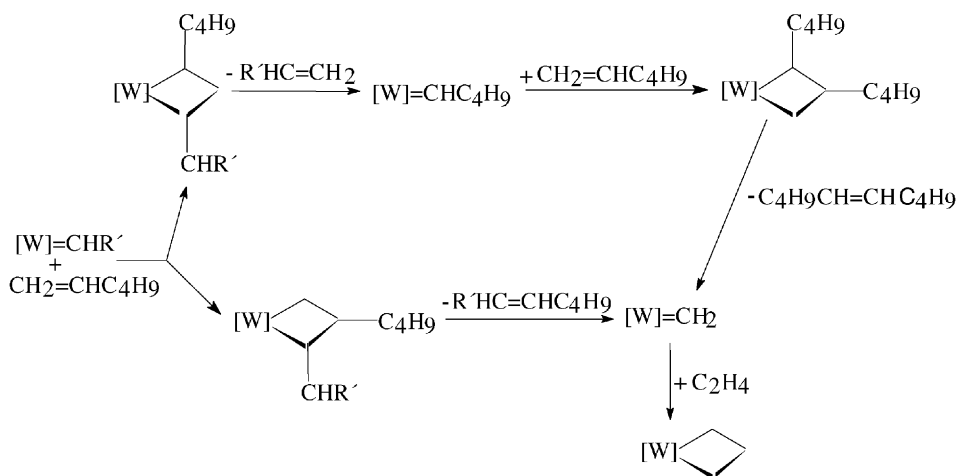
In course of the olefin attack, the approaching olefin donates an electron pair to the central atom of the catalyst. Hence the imido ligand becomes less important as π -donor and it pulls back the nitrogen “free” electron pair. The ligand twists back and thus makes place for the olefin, which can now change its position in the coordination sphere, reach the M=C and react with it (formation of a metallacyclobutane). If the olefin–metal interaction in the olefin–catalyst adduct (π -complex) is weak, then the imido ligand twist angle is expected to be small and vice versa, stronger interactions resulted in a larger imido ligand twist angle. Thus, results obtained can be explained by means of the assumption that the electron affinity of the tungsten central atom is higher. Consequently, molybdenum complexes are more sensitive against sterically demanding substrates and sterically demanding ligands than the analogous tungsten catalysts.

A measure for the olefin \rightarrow metal σ -bond strength in the π -complex is the electron affinity of the metal. Tungsten indeed has a higher electron affinity (78.6 kJ/mol) than molybdenum (71.9 kJ/mol) (both affinity values refer to the 0-valent atoms, however) [30].

The higher electron affinity of tungsten is in accordance with the observation that a base is more strongly bound to the central atom in the case of tungsten in comparison with molybdenum [12].

3.2. Terminal olefins

As demonstrated, the central atom has a strong influence upon the metathesis reaction rate of α -olefins; in principle, molybdenum complexes show a high and tungsten complexes a low activity. It has to be emphasized that the reactivity of the terminal olefins



Scheme 6.

towards tungsten complexes also is very high, according to our results. The formation of the first metallacyclobutane complexes and their consecutive reactions occur quickly (Scheme 6). The rate limiting step of the α -olefin conversion is the consecutive reaction of the unsubstituted tungstacyclobutane intermediate. It is generated from an intermediate methyldiene tungsten complex and the product ethene. This trigonal-bipyramidal tungstacyclobutane ring can be proven via NMR spectroscopy, even at room temperature [31,32].

The much higher reactivity of the terminal in comparison to internal olefins towards tungsten complexes on the one hand, and the high stability of the formed unsubstituted tungstacyclobutane intermediate on the other hand, are responsible for the observation that the metathesis of internal olefins is hampered if α -olefins are present in the reaction mixture, even in traces.

Decreasing the reaction temperature, the stability of the tungstacyclobutane intermediate increases strongly and as a consequence, the rate of the metathesis conversion decreases dramatically. This finding shows that tungsten-based catalysts are not suitable for metathesis at low temperatures if α -olefins are present, and vice versa that higher temperatures are needed to increase the reaction rate of α -olefin metathesis.

In contrary to tungsten-based alkylidene complexes, using molybdenum catalysts only the alkylidene complex can be observed on $^1\text{H-NMR}$ scale at

room temperature, during metathesis conversion of a conventional terminal olefin. In case of the sterically strongly demanding substrates 2,5-diheptyl-1,4-divinylbenzene, for the first time, a molybdenacyclobutane complex could also be detected (-0.3 ppm H_β (TBP) and -1.2 ppm $\text{H}_{\beta'}$ (TBP) of $\text{Mo}(\text{CH}(p\text{-styryl})\text{CH}_2\text{CH}_2)(\text{NPh}^{\text{Me}_2})[\text{OCMe}(\text{CF}_3)_2]_2$) [33].

4. Application of olefin metathesis that only became possible by applying Schrock-type alkylidene complexes: study of the metathesis chain growth/chain degradation equilibrium

Taking into account the results obtained concerning temperature and substrate dependent stability, selectivity and activity of Schrock-type catalysts investigated, substantial improvement was achieved in all three fields of our research (see Section 1). In this paper, the most important results concerning the study of the metathesis chain growth/chain degradation equilibrium will be presented. This topic was chosen due to high relevance of metathesis equilibrium polymerization (like ROMP and ADMET) for the olefin metathesis in general and because of the great importance of results obtained for the polymer chemistry as well as organic chemistry in particular.

Basic requirement for the extensive study of the metathesis chain growth/chain degradation

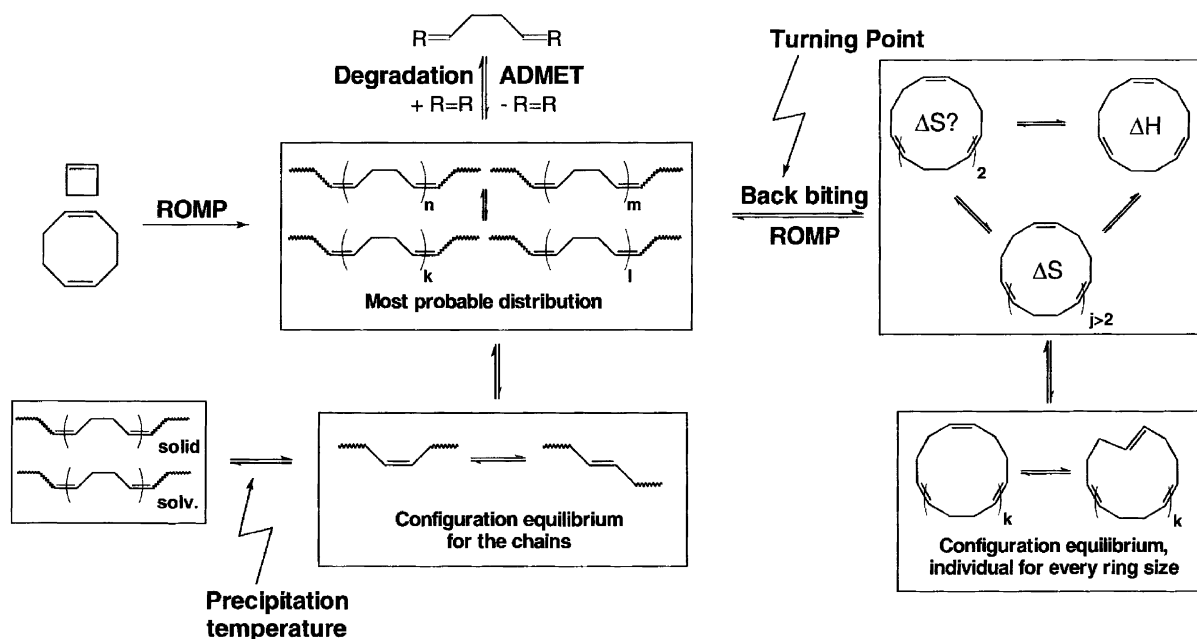


Fig. 8. Metathesis polymerization/depolymerization equilibrium for the 1,4-polybutadiene (resp. cyclobutene) system.

equilibrium is the availability of highly active and selective catalysts in a broad temperature range, taking into account the results obtained this condition was fulfilled. In this context, it should be mentioned that also considering the new developments on the field of Ru-based catalysts high as well as low reaction temperatures remain until now a domain of the Schrock-type catalysts.

4.1. Quantitative description of the metathesis polymerization/depolymerization equilibrium in the 1,4-polybutadiene and 1,4-polyisoprene system

At first, the polybutadiene (resp. cyclobutene) system was investigated, as a function of the feed concentration, of the temperature and of the solvent. Results obtained demonstrate that we succeeded for the first time in reaching [6] and quantitatively describing [8–10] the metathesis chain growth/chain degradation equilibrium (including all sub-equilibria).

ROMP of 1Z,5Z-cyclooctadiene, 1E,5E,9E- and 1Z,5E,9E-cyclododecatriene as well as ADMET of 1,5-hexadiene (by removal of ethene) and degrading 1,4-polybutadienes (*cis*-, and *trans*-configured)

intramolecularly all resulted in the very same complex product spectrum.

As Fig. 8 demonstrates, the whole equilibrium consists of several coupled sub-equilibria, like the polymerization/depolymerization equilibrium between ROMP of cyclic oligomers (from trimers upwards) and back-biting of 1,4-polybutadiene resp. between ADMET and degradation of 1,4-polybutadiene by adding monoolefin. Furthermore, an equilibrium exists between rings of different sizes, one between the chains of different length, a configuration equilibrium for the chains and other also for every individual ring size. Additionally, our results reveal the existence of a solution/precipitation equilibrium at lower temperatures [9].

An important finding is furthermore, the chain growth proceeds endothermically, in the solution region. To our knowledge, this is the first example in the field of hydrocarbon chemistry that higher temperatures are needed to increase the polymer yield. Decreasing the temperature the oligomer yield increases. Responsible for the unusual temperature dependence of the total ring concentration is the main component within the rings, the all-*trans*-configured

cyclic trimer. Its formation in the back-biting reaction is an exothermic process.

Due to the existence of the solution/precipitation equilibrium the whole equilibrium system must be divided into two sub-systems, a solution region which is dominated by the exothermic formation of the all-*trans* cyclic trimer and a heterogeneous region with polymeric chains precipitated (highly crystalline *trans*-1,4-polybutadiene, a product with memory shape effect) as determinant.

Based on the results obtained, a great number of hitherto not available, for the organic as well as polymer chemistry valuable thermodynamic data was determined [8,9] and for the first time the polybutadiene/solvent interaction exactly quantified [10]. Finally, it has to be mentioned that by means of the reaction scheme described, the product spectrum can be controlled qualitatively as well as quantitatively.

Based on the results obtained, we investigated the 1,4-polyisoprene (resp. 1-methylcyclobutene) system and found that in analogy to the unsubstituted system the all-*trans*-configured cyclic trimer is dominant within the rings [7]. It is a valuable compound for the synthesis of fragrances and pheromone derivatives [34,35].

Recently, we began with the investigations regarding quantitative description of the thermodynamically controlled chain growth/chain degradation reaction in the polyisoprene system. In contrary to rings with butadiene units (COD, CDTs) cyclic isoprene oligomers with high regularity are commercially not available, thus polymers (especially the natural products) served as feed-compound. In this context, it has to be mentioned that the intramolecular degradation of 1,4-polyisoprenes proceeds more hampered than the intermolecular degradation by adding a monoolefin (see Section 2.3). Above all, it is exceedingly difficult to achieve the equilibrium product spectrum. Using the highly active tungsten-based Schrock-type alkylidene complexes, above all those with methyl-substituted phenylimido ligand, recently we succeeded for the first time, to establish the thermodynamically predicted product spectrum and to determine the turning point including the ring saturation concentration. The results obtained will be published in detail [23], thus in this contribution the most important results will be summarized, only.

The overall equilibrium consists of the same coupled sub-equilibria as observed in the polybutadiene system, with one exception. A solution/precipitation equilibrium could not be observed. Likewise the chain formation is an endothermic process! and the all-*trans*-configured cyclic trimer the dominant compound within the rings. But the ring saturation concentration and the configuration equilibrium of chains (as well as of rings which are controlled entropically) differ strongly.

4.2. Is the existence of the solution/precipitation equilibrium a peculiarity of the cyclobutene system only?

Taking into account results obtained investigating the cyclobutene and the methylcyclobutene system we were interested in the question: Is the existence of the solution/precipitation equilibrium a peculiarity of the cyclobutene system, exclusively?

Despite of numerous publications on the field of ROMP of conventional cyclic olefins in general and about the ring-chain equilibrium in particular [11], we did not find any evidence (or hint) about the existence of a solution precipitation equilibrium. Therefore, we widened our studies to further ring systems, like cyclopentene, cycloheptene and cyclooctene [17]. In the following only the most important results will be summarized.

In the cyclopentene system a solution/precipitation equilibrium could not be found, the investigations were carried out within a temperature region between 20 and -60°C , using methyl cyclohexane as solvent.

In contrary, the cycloheptene as well as the cyclooctene system include a solution/precipitation sub-equilibrium. In both cases, working within the temperature region below the precipitation point highly crystalline products with a *trans* amount = 95% were obtained, in analogy to the cyclobutene system. Knowing the solvent dependent precipitation point it is possible to control the product spectrum.

Finally, it should be mentioned that the polymerization reaction is an exothermic reaction, in all three cases, as expected. The endothermic course remains a peculiarity of the C4 (cyclobutene and methylcyclobutene) systems. Responsible for this is the all-*trans*-configured cyclic trimer, which is not a conventional ring, according to our results [36].

5. Conclusion

To sum up the results presented, it may be stated that there does not exist an optimal Schrock-type metathesis catalyst for all substrates investigated. For conversion of terminal olefins and for reactions which should be carried out at low temperatures molybdenum catalysts are more suitable. But for the metathesis of substrates which are sterically demanding (like *trans*-configured olefins with long alkylidene chains or bulky alkylidene groups and polyenes with substituted double bonds) the tungsten catalysts are the best choice.

Despite the suitability of Schrock-type alkylidene complexes (especially with the dimethyl-substituted phenylimido ligands) for a great number of valuable metathesis reactions, their practical applicability is limited, at the moment. The reasons are the expensive chemicals needed and above all the time spent on the multi-stage synthesis. Therefore, the use of these metathesis catalysts can only be suggested for basic investigations, analytical applications and for the synthesis of specialties, e.g., of high tech products like substituted PPVs.

Finally, it has to be mentioned that in the case of α -olefin conversion the replacement of the Schrock-type alkylidene complexes by the commercially available, highly active ruthenium-based Grubbs' catalyst (it contains a 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene ligand) [37] fails if very high selectivities are needed, according our preliminary results [38].

6. Experimental

The catalysts with hexafluoroalkoxo ligands were prepared according to the literature [13–15].

The new tungsten complex $W(=NAr^{Me})(=neoPh)[OCMe_2CCl_3]_2$ was synthesized analogously to $W(=NAr^{Me})(=neoPh)[OCMe(CF_3)_2]_2$. For the crystallization, a 1:2 mixture of diethylether/hexane was used instead of pure hexane, due to lower solubility of the chloroalkoxo derivative in hexane. The product yield was 56.2% of the theoretical value. IR (Nujol, KBr), ν (cm^{-1}): 567 (w), 696 (w), 790 (s), 854 (s), 931 (m), 998 (s), 1095 (w), 1155 (s), 1193 (w), 1307 (w), 1345 (s). 1H -NMR in C_6D_6 , δ (ppm): 1.47 (s, 6, $(CH_3)_2ArC-CH=$), 1.53 (s, 6, $=CMe_2aCCl_3$), 1.56

(s, 6, $=CMe_2bCCl_3$), 2.30 (s, 6, Me_2Ar-N), 6.89–7.38 (m, 8, $H-Ar$), 8.74 (s, 1, $(CH_3)_2ArC-CH=$); $J_{HW} = 13.16$ Hz ($(CH_3)_2ArC-CH=$).

The metathesis conversions were carried out under rigorous exclusion of water and oxygen in argon atmosphere (it was additionally purified via Oxysorb, Fa. Messer Griesheim, Germany) using standard Schlenk technique. Reaction vessels were annealed by flame at Hg diffusion pump vacuum. Solvents (methyl cyclohexane and toluene) (Merck) as well as the olefins (*E,Z*-2-pentene, 1-hexene (Aldrich), *E*-2-pentene, *E*-2-hexene, *Z*-2-hexene (Fluka), *E*-3-hexene (Lancaster)) were predried over lithium aluminum hydride, distilled, degassed after the addition of pure butyllithium, by freeze–pump–thaw cycles and condensed subsequently. The purity of the chemicals was checked by gas chromatography. The commercially available *E*-2-hexene was purified from traces of 2-hexene via split-tube distillation.

The concentrations used were 1 or 2 $mmol\ l^{-1}$ for the catalyst and 1 $mol\ l^{-1}$ for the monoolefin. The standard deviation of the kinetic results was $\pm 1.5\%$ if solvent, substrate as well as catalyst in each case came from the same charge, and $\pm 3.5\%$ for experiments with a feed composition originated from different charges. To determine the catalyst activity and selectivity, time dependent investigations of the product spectrum were carried out by means of gas chromatography, in situ and externally. The catalyst intermediates were investigated via NMR spectroscopy. The kind and amount of the alkylidene species and the product spectrum were determined kinetically by means of gas chromatography. For this reason, the reaction was quenched by the addition of propanal or benzaldehyde in high excess.

The investigated polymers were commercially available products, a high *cis*-1,4-polybutadiene with ca. 0.6% 1,2-units (Nd-BR, Bayer AG) and a high *cis*-1,4-polyisoprene containing 0.5% 3,4-units (Ti-IR, Goodyear Tire and Rubber).

For the Headspace-GC analysis a Perkin Elmer, PE 900A equipped with a 3m/ $d_i = 0.2$ cm column (Porapak Q) was used. The GC analysis of the liquid samples was performed using a Hewlett Packard 5890A GC with a 50 m fused silica column (SE-52-DF-0.5).

GC–MS measurements were recorded using a Hewlett Packard 5890A GC with the same 50m

capillary column coupled to a VG analytical 70 SE spectrometer and a VAX 2000 data system.

Due to different distributions of the reaction components between liquid and vapor phase, calibrations by means of mixtures of known composition were carried out.

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