

Kinetic investigations concerning selectivity of different Schrock-type carbene complexes

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Abstract

This paper describes investigations concerning the stability, metathesis activity and selectivity of different molybdenum and tungsten Schrock-type carbene complexes. It demonstrates that these catalysts have a limited life time when an acyclic monoolefin is added. Synchronously with decrease of the amount of carbene species olefin isomerization takes place as a catalytic side reaction. The rate of isomerization depends on the concentration and kind of both catalyst and olefin. Catalysts with high metathesis activity also have high activity in these side reactions.

Keywords: Metathesis catalyst; Selectivity; Carbene complexes

1. Introduction

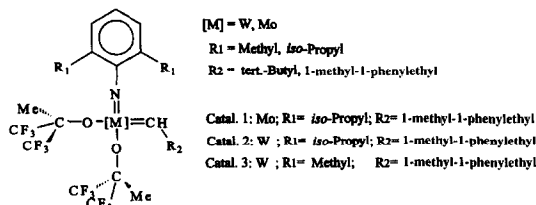
During investigations of intermolecular metathesis polymer degradation using a stable molybdenum Schrock-type carbene complex $\text{Mo}(=\text{CHCMe}_2\text{Ph})(=\text{NAr}^i\text{Pr}_2)[\text{OCMe}(\text{CF}_3)_2]_2$ we found an olefin isomerization as a side reaction [1]. This double-bond shift is well known using classical catalyst systems for α -olefins [2–4] and internal olefins [4–7] but, to the best of our knowledge, unknown in the case of well defined transition metal carbene complexes. Our results showed furthermore that the double bond isomerization occurs when the metathesis reaction has proceeded to an advanced extent.

In order to clarify this preliminary observation kinetic investigations were carried out of

the stability, metathesis activity and selectivity of tungsten and molybdenum carbene complexes in solution with and without added olefin. Scheme 1 shows the structures of the highly active carbene catalysts employed [8].

2. General aspects

The quantitative determination of the carbene species was performed using the Wittig-analogous reaction with an aldehyde, see Fig. 1. In



Scheme 1.

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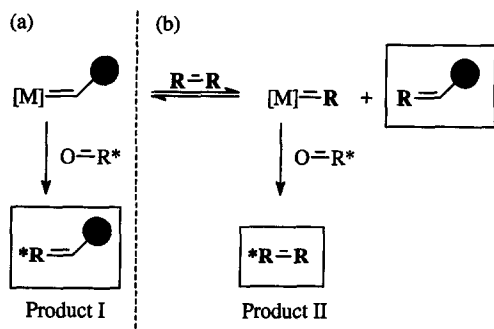


Fig. 1. Wittig-analogous reaction between the active carbene species and an aldehyde without (a) and with addition of monoolefin (a and b).

order to avoid secondary reactions of the coupling product with the substrate the exchange between the carbene species and the aldehyde has to be much faster than the metathesis step. For this reason the employment of ketones failed. Our investigations showed that with propanal and benzaldehyde a fast exchange of the carbene ligand could be achieved. The products obtained were identified by GC/MS and quantitatively determined via GC-analysis.

trans-2-Butene, *trans*-3-hexene and *trans*-5-decene were employed as the olefins. In addition to the expected metathesis reaction products, others, caused by double bond isomerization were also detected. The reaction scheme proposed to explain the observed products for

trans-3-hexene as starting olefin is shown in Scheme 2.

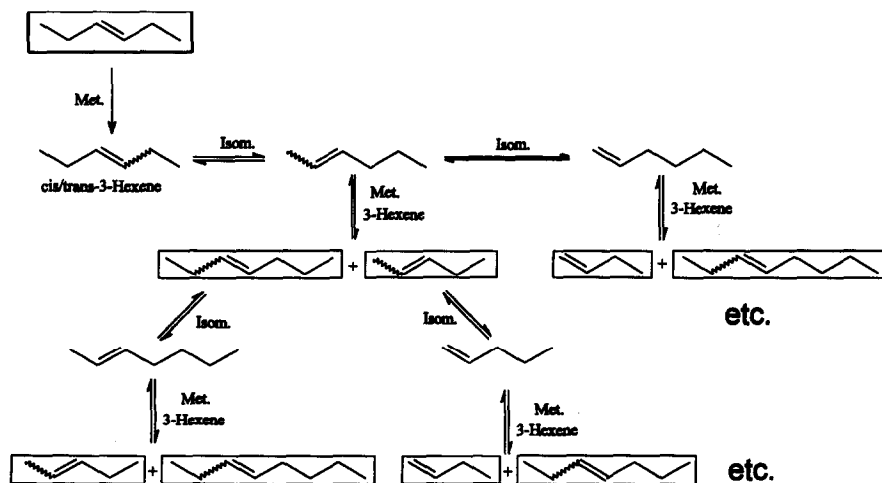
3. Results

3.1. Stability of carbene complexes in solution

The stability of 8 different transition metal carbene complexes using propanal (Fig. 1a; $R^* = CH-CH_2-CH_3$) as quench reagent were investigated. The results demonstrate that all catalysts (with exception of the *neopentylidene*-complexes with a dimethylphenylimido ligand) are stable in solution at room temperature for at least 6 days (Figs. 2 and 3). NMR studies demonstrated that the investigated catalysts are stable for several months [1,9].

3.2. Kinetic investigation of the metathesis product spectra including the active carbene species

The kinetic investigation of the product spectrum during metathesis of commercially available *trans*-5-decene with molybdenum and tungsten carbene complexes was carried out



Scheme 2.

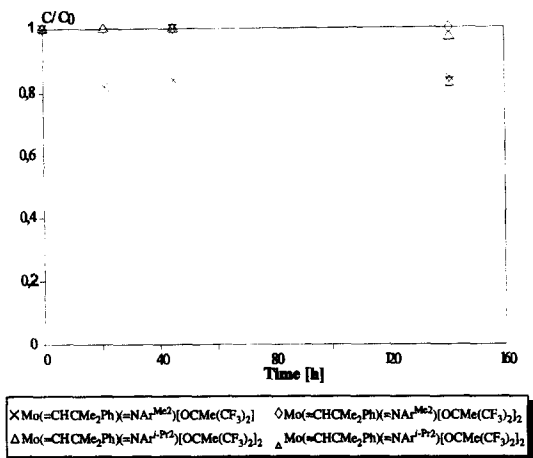


Fig. 2. Time dependent concentration of active tungsten carbene complexes with respect to the initial concentration in methylcyclohexane at room temperature (initial concentration of catalyst, $c_0 = 5\text{--}10\text{ mmol/l}$).

first. Both catalysts contained the same ligands (Scheme 1; catalysts 1 and 2).

When *trans*-5-decene containing 0.25–0.30% 4-decene is employed as starting olefin, 4-nonene and 5-undecene are obtained as well as the *cis/trans*-5-decene. Due to the high excess of 5-decene the formation of 4-octene and 6-dodecene is negligible. In order to investigate the time dependency of the metathesis as well

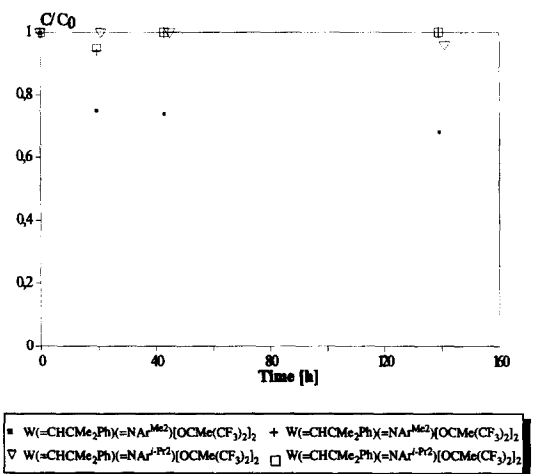


Fig. 3. Time dependent concentration of active molybdenum carbene complexes regarding to the initial concentration in methylcyclohexane at room temperature (initial concentration of catalyst, $c_0 = 5\text{--}10\text{ mmol/l}$).

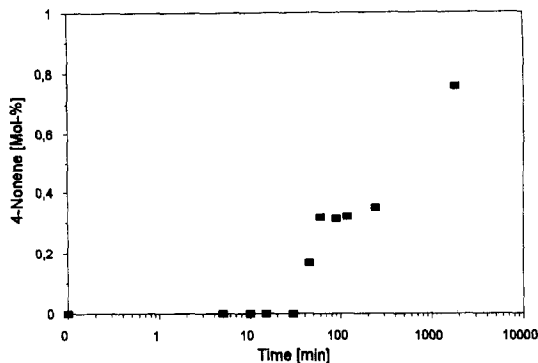


Fig. 4. Time dependent formation of 4-nonene with catalyst 1 (5.47 mmol/l) in presence of *trans*-5-decene (0.48 mol/l) in methylcyclohexane at room temperature.

as the side reaction the formation of 4-nonene was monitored, if only metathesis occurs its amount will be equal to the 4-decene impurity content in the 5-decene used as starting material. Figs. 4 and 5 plot the time dependent amount of *cis/trans*-4-nonene for a molybdenum and tungsten carbene catalysts, respectively.

The results show that in both cases three distinguishable reaction phases exist: firstly an induction period, then metathesis followed by the occurrence of side reactions coupled with metathesis. During the second phase metathesis takes place and equilibrium is established. The amount of 4-nonene is between 0.25 and 0.30 mol% as expected. Furthermore, the figures demonstrate that the metathesis activity of the

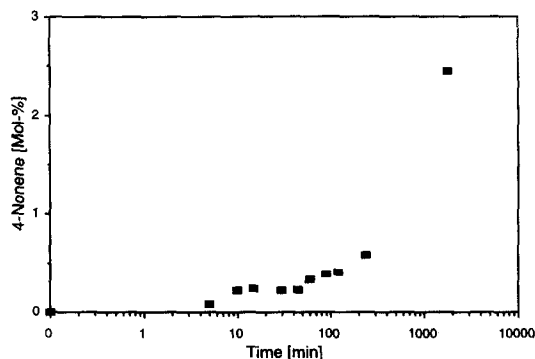


Fig. 5. Time dependent formation of 4-nonene with catalyst 2 (5.90 mmol/l) in presence of *trans*-5-decene (0.48 mol/l) in methylcyclohexane at room temperature.

tungsten carbene complex is higher than that of the molybdenum complex. This is in accordance with some previous results showing that in general tungsten carbene complexes have a higher activity towards *trans* isomers than molybdenum complexes [10].

Results obtained with the tungsten catalyst showed that the formation of 4-nonene in the third reaction phase is caused by a catalytic process, see Fig. 5.

In the experiment with the molybdenum carbene, see Fig. 4, the concentrations of the initial carbene species (Fig. 1, Prod. I), the new carbene with the alkylidene unit of the substrate (Fig. 1, Prod. II) and the sum of both are plotted in Fig. 6. A comparison with Fig. 6 allows the statement that during induction period mainly the initial carbene is present, Synchronously with the metathesis step (the second stage) the exchange of the carbene ligands happens. Additionally the investigations gave us the hint that side reactions occur when the amount of carbene species decreases (see Figs. 4 and 6, $t = 2000$ min).

Next we investigated the tungsten carbene complex **3** in which a dimethylphenylimido replaces the diisopropylphenylimido ligand (see Scheme 1, catal. 3). The concentration of the catalyst was 6.1 mmol/l in cyclohexane, *trans*-

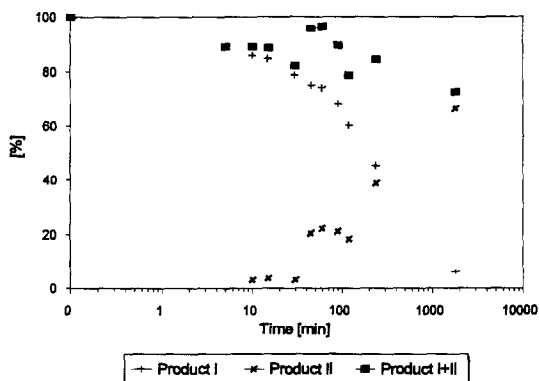


Fig. 6. Time dependent amount of the initial carbene species, the new carbene with the alkylidene unit of the substrate and the sum of both in presence of *trans*-5-decene (0.48 mol/l) in methylcyclohexane (catal. 1; $c_{\text{catal.}} = 5.47$ mmol/l).

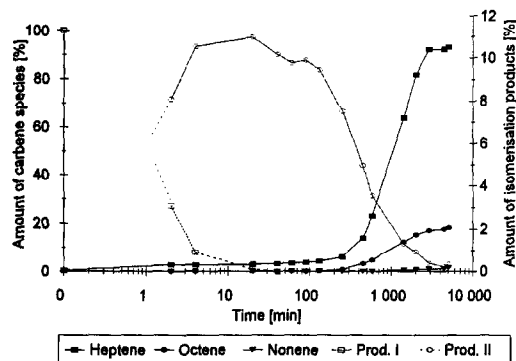
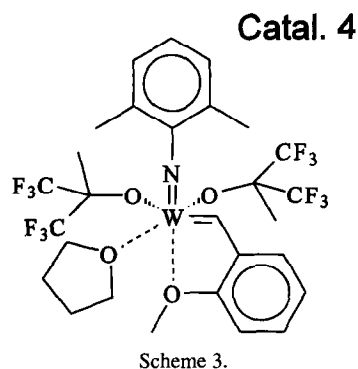


Fig. 7. Time dependent formation of the carbene species and by-products using catalyst **3** in cyclohexane at room temperature ($c_{\text{catal.}} = 6.1$ mmol/l, 3-hexene/catal. = 100:1).

3-hexene containing 0.5% 2-hexene was used as starting monoolefin with benzaldehyde as quench reagent, Fig. 7 summarizes the results.

As expected the induction period of this highly active catalyst could not be observed with the method used. A fast exchange of the initial carbene species with the substrate takes place during the first minutes and the begin of metathesis occurs at the same time.

Formation of by-products occurs synchronously with the decrease of carbene species (see Fig. 7; $t = 200$ –2000 min). This is strong evidence that a product of the metathesis catalyst is responsible for the side reactions. Although in this case by-products are formed also during the main metathesis phase, their amounts remain below 1% during the first 4 hours. Addi-



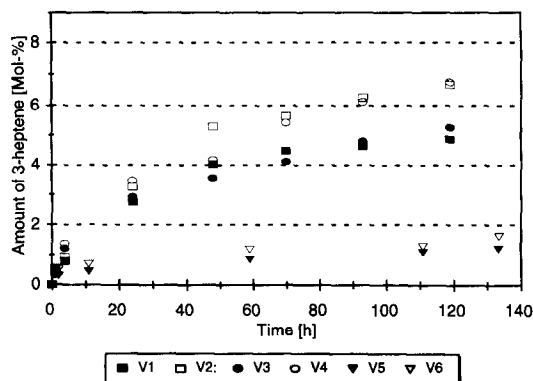


Fig. 8. Time dependent formation of 3-heptene with different catalysts and olefin/catalyst ratios using *trans*-3-hexene as substrate (see Table 1).

tionally we investigated a very stable tungsten carbene complex **4** [11] (Scheme 3).

The results achieved were compared with those obtained with the two tungsten catalysts of high activity (catal. 2 and 3), the catalyst concentration was kept constant whereas the olefin/catalyst ratio was varied. Table 1 summarizes the experimental data.

In Fig. 8 it can be seen, that within the observed time the highly active Schrock-type carbene complexes (catal. 2 and 3) produce much more by-product than the less active methoxy stabilized catalyst 4. Furthermore a higher olefin surplus causes a higher amount of by-products. Investigations comparing different olefins showed that the isomerization reaction rate decreases with growth of chain length [12].

Considering the metathesis activity of the catalysts investigated [1,10,12] it is noted that the catalyst with highest reaction rate in the side reactions also show the highest metathesis turn over rate and vice versa.

3.3. Time dependent UV/vis-spectroscopic measurements of molybdenum carbene complex $\text{Mo}(\text{=CH CMe}_2\text{Ph})(\text{NAr}^{i\text{Pr}})_2(\text{OCMe}(\text{CF}_3)_2)_2$ on addition of olefin

UV/vis-spectroscopy is a powerful tool for investigation of reactions in catalyst systems

Table 1

Reaction conditions for investigations presented in Fig. 8

Exp. No.	Catal. No.	$c_{\text{catal.}}$ (mmol/l)	Olefin/catal.
V1	2	0.83	600:1
V2	2	0.83	200:1
V3	3	0.85	600:1
V4	3	0.85	200:1
V5	4	0.88	600:1
V6	4	0.88	200:1

involving transition metal components. Its suitability for classical metathesis catalysts systems based on WCl_6 and WOCl_4 was demonstrate in our group [13–16].

For a few Schrock-type transition metal carbene complexes UV/vis-spectra are published [17,18], nevertheless no spectroscopic data are known for the $\text{Mo}(\text{=CH CMe}_2\text{Ph})(\text{NAr}^{i\text{Pr}})_2(\text{OCMe}(\text{CF}_3)_2)_2$ complex **1**. Also no UV/vis investigations are published concerning the behaviour of the carbene species on addition of olefin. In this work we deal with the most commonly used Schrock-type carbene **1**. Fig. 9 shows the time dependent spectra of the reaction between catalyst **1** and *trans*-2-butene. The dotted spectrum shows the pure carbene complex **1** in cyclohexane. The main peak at $\lambda = 294$ nm has an absorption coefficient $\epsilon_{294} = 10.5 \text{ l mol}^{-1}\text{cm}^{-1}$, a shoulder at $\lambda = 327$ nm is detected as well, Fig. 10a–d present more details. Analysis of this data can be interpreted in terms of three different phases of reaction.

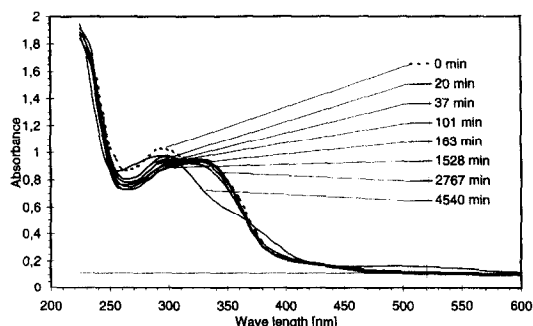


Fig. 9. Time dependent UV/vis-spectra of the reaction of carbene **1** with *trans*-2-butene ($c_{\text{Mo}} = 4.35 \text{ mmol/l}$, $c_{\text{trans-2-butene}} = 0.5 \text{ mol/l}$).

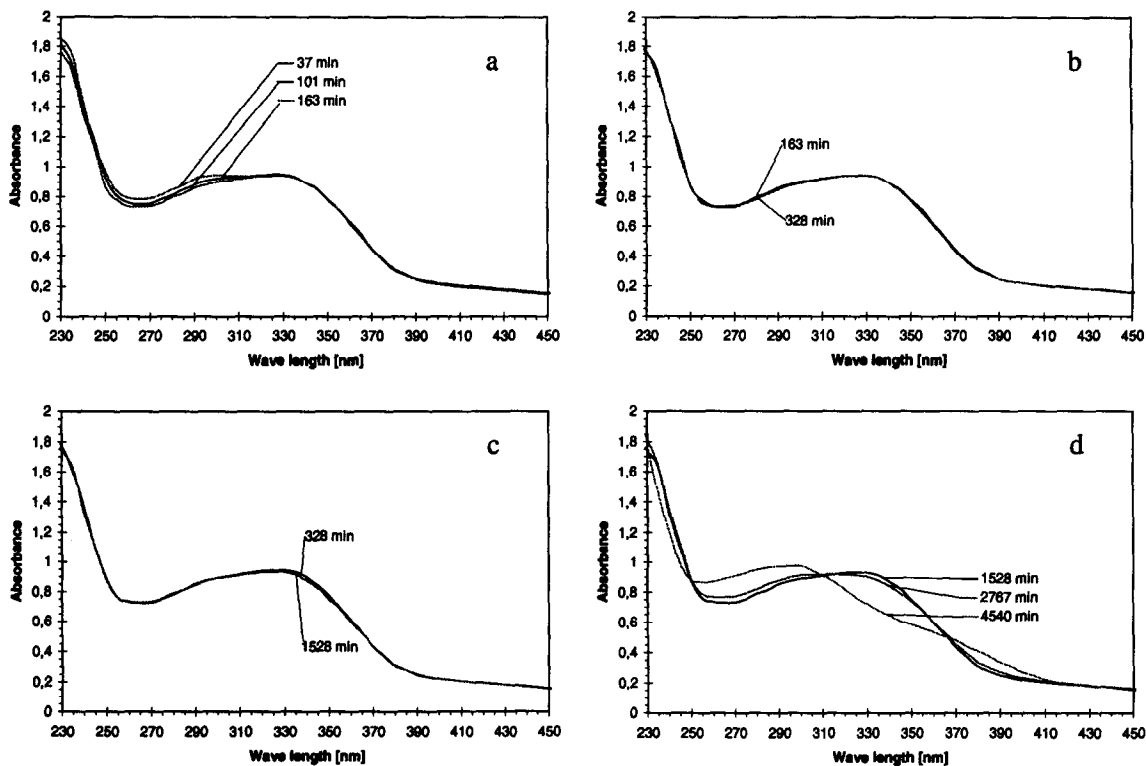


Fig. 10. (a)–(d) Detailed parts of Fig. 9.

During the first stage the main absorbance peak in the UV/vis spectra decrease in intensity and a new band appears as a shoulder at 299 nm (see Fig. 10b). This is due to exchange of the neophylidene ligand of the initial carbene with the substrate *trans*-2-butene and the formation of an ethylidene complex. Under reaction conditions ($c_{\text{Mo}} = 4.35 \text{ mmol/l}$, $c_{\text{2-butene}} = 0.5 \text{ mol/l}$) this exchange occurs mainly during the first 3 hours. In the second phase nearly identical spectra were observed (see Fig. 10b and c). The slight difference in the region of $\lambda = 260\text{--}300 \text{ nm}$ is due to the exchange of the remaining initial carbene ligand, after 1528 min a decrease of the main absorbance ($\lambda \approx 355 \text{ nm}$) is observed. The third stage is characterized by the decrease of the absorption band $\lambda \approx 355 \text{ nm}$ and an increase of the absorbance in the region of $\lambda = 270\text{--}310 \text{ nm}$ (see Fig. 10d). This can be rationalized as the decomposition of the carbene

complex with formation of a new complex. Our GC investigations of the metathesis product spectrum (under same reaction conditions) show that during the third phase double bond isomerization occurs as a side reaction [1]. These results provide evidence, that not the carbene species but its eventual reaction product is responsible for the catalytic side reactions observed.

4. Summary with conclusion

The evidence presented suggests that the selectivity of stable transition metal carbene complexes is high but not unlimited. Synchronously with the decomposition of the carbene species, side reactions take place. Metathesis of high selectivity can be achieved only if the reaction

time is shorter than the life time of the catalyst for the particular system investigated.

Because the catalysts with the highest metathesis activity show also the highest activity towards side reactions, further investigations are necessary to determine the optimal catalyst and optimal metathesis reaction time for each substrate.

5. Experimental

All reactions were carried out under pure argon atmosphere using standard Schlenk technique under rigorous exclusion of water and oxygen (Oxysorb, Fa. Messer Griesheim, Germany). Solvents (cyclohexane, methylcyclohexane) (Fa. Merk, Germany) as well as the olefins (*trans*-3-hexene, *trans*-5-decene) (Fa. Lancaster, GB) were predried over lithium aluminium hydride, distilled, transferred to butyllithium and degassed. The purity of the compounds was checked by gas chromatography. Catalysts were prepared according to literature [8,11]. To quench the catalyst the aldehyde was added in high excess.

GC-analysis was carried out with a Hewlett Packard 5890A GC using a 50 m apolar or polar capillary column. GC-MS were recorded using a Hewlett Packard 5890A GC with a 50 m capillary column coupled to VG analytical 70 SE spectrometer and VAX 2000 data system. UV/vis-spectra were recorded with a Cary 14-spectrometer (Fa. Applied Physics, Monrovia).

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