

# Cross-metathesis of vinyl aromatic heterocycles: comparison of Grubbs catalyst and Schrock catalyst

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Received 15 November 2001

## Abstract

Metathesis of 2-vinyl aromatic heterocycles such as furan and thiophene has been investigated in the presence of a ruthenium-based Grubbs catalyst from a synthetic standpoint. The self-metathesis of 2-vinyl aromatic heterocycles was not successful. However, the cross-metathesis of these aromatic heterocycles with 1-octene occurred efficiently, but the selectivity of cross-metathesis product was very low, below 50%. The origin of the low selectivity of heterodimer formation was elucidated through metallacyclobutane intermediate mechanism, observations of carbenes by *in situ*  $^1\text{H}$  NMR, and the reaction products. The effect of oxygen on the reaction behavior was also examined. Furthermore, the data obtained on the Grubbs catalyst were compared with those on a molybdenum-based Schrock catalyst.

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*Keywords:* Cross-metathesis; Vinylthiophene; Vinylfuran; Styrene; 1-Octene

## 1. Introduction

Various kinds of heterogeneous and homogeneous catalysts have been used for metathesis of a broad range of alkenes [1]. The advent of well-defined transition metal catalysts, especially ruthenium benzylidene catalysts developed by Grubbs et al., and the molybdenum imido alkylidene catalysts developed by Schrock et al., has dramatically increased their application in organic synthesis. They are now extensively used in various kinds of metathesis reactions, such as acyclic diene metathesis (ADMET), ring-closing metathesis, ring-opening metathesis, cross-metathesis, etc. using various kinds of reactants [1]. Thus, the catalysts are very attractive for the synthesis of useful substrates and the metathesis process now represent a powerful

tool in applied organic synthesis due to their versatile areas of application. In general, Schrock catalysts are more active than Grubbs catalyst. However, Schrock catalysts are extremely sensitive to moisture and oxygen, and thus, in order to induce 100% catalytic activity, it is essential to avoid their contamination through careful attentions in handling the catalysts and the use of completely dried experimental apparatus. On the other hand, it has been reported that Grubbs catalysts have remarkable stability towards a wide variety of functional groups [2–13]. The catalysts are stable in common organic solvents even in the presence of water and alcohols [2–4,9,11,12,14], and are moderately stable in air [6,9,13–15], which indicates their ease of handling. However, to the best of our knowledge, there are no reports clarifying the effect of oxygen on the reaction behaviors using the same reactant.

There are several examples related to self- and cross-metathesis of styrene [16–22], however, the self-metathesis reaction of vinyl derivatives of aromatic

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heterocycles such as thiophene, furan, pyrrole, pyridine, etc. and also their cross-metathesis reactions have not been adequately studied, therefore, only limited data dealing with such reactions in the presence of Schrock catalyst can be found in literatures [8,20,21,23]. Wagener et al. [20] succeeded to self-metathesize *N*-methylated pyrrole, and Tuie et al. [21] recently described the ADMET of alkyl substituted 2,5-divinylthiophene with a Schrock catalyst. Crowe and Zhang [16] reported interesting results on selective cross-metathesis between styrene and  $\alpha$ -olefins in the presence of Schrock catalyst [16]. We also have demonstrated that cross-metathesis of styrene and vinyl aromatic heterocycles with 1-octene occurs efficiently and gives cross-metathesis product with very high selectivity in the presence of Schrock catalyst [23]. These results and other ground-breaking studies in the application of cross-metathesis will provide new approaches to the direct synthesis of various interesting olefins containing aromatic moieties. Notwithstanding, the self- and cross-metathesis of aromatic compounds in the presence of Grubbs catalysts have so far not been investigated.

Here we report the study of self-metathesis of 2-vinylfuran and 2-vinylthiophene as aromatic heterocycles, and styrene as a reference sample, and cross-metathesis between these aromatics and 1-octene with a homogeneous well-defined metathesis catalyst, Grubbs catalyst. The objectives of this study are to clarify the possibility of selective synthesis of cross-metathesis product, effect of oxygen on reaction behavior and differences in reaction behaviors, based on Grubbs and Schrock catalysts:

## 2. Experimental

### 2.1. Catalysts and reagents

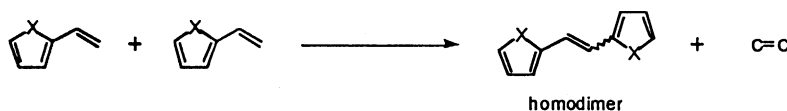
A Grubbs catalyst, bis(tricyclohexylphosphine)benzylidene ruthenium(IV) dichloride was generously donated by Dr. Grubbs and a Schrock catalyst, 2,6-diisopropylphenylimidoneophylidenemolybdenum (VI) bis(hexafluoro-*t*-butoxide) was purchased from Strem Chemicals Inc., and used without further purification.

Vinylthiophene and vinylfuran were prepared in high yield by Wittig reaction according to a modified literature procedure [24–26], and were purified by distillation from Na under nitrogen prior to use. Vinyl pyridine, 1-octene, styrene and all other chemicals were purchased from Tokyo Chemical Industry Co. Ltd. and dried over 5A molecular sieves. Toluene used as a solvent was dried and distilled from Na.

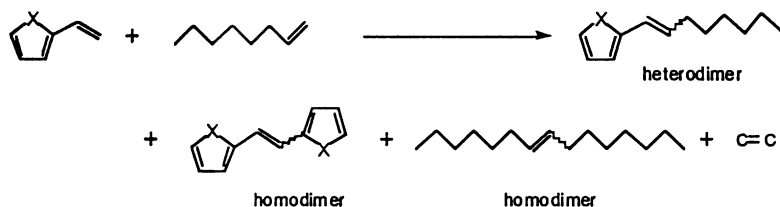
### 2.2. Procedure

All manipulations were performed using standard Schlenk techniques and the reactions were carried out at an atmospheric pressure of nitrogen gas or air. The catalysts were transferred to the Schlenk in a nitrogen atmosphere dry box. All glass wares were fully dried and much attention was paid to ensure the dryness and to avoid contamination by air especially in the case of Schrock catalyst. The typical reaction conditions were as follows: reactant/catalyst molar ratio 100/1 (catalyst ca. 8 mg, 0.01 mmol) for Schrock catalyst and 50/1 (catalyst ca. 12 mg, 0.02 mmol) for Grubbs

#### Self-metathesis



#### Cross-metathesis



where, x is S or O.

catalyst, solvent toluene (ca. 1 ml), temperature 30 °C (Schrock catalyst) and 40 °C (Grubbs catalyst) and reaction time 17 h unless otherwise stated. The reactions to observe carbenes were performed in benzene- $d_6$  (ca. 0.8 ml) at room temperature in an NMR tube using catalyst of ca. 20 mg and reactant/catalyst molar ratio 3. Metathesis products were analyzed by gas chromatography on a Shimadzu GC-12A equipped with an FID and a chemically bonded capillary column HP-5 (30 m  $\times$  0.32 mm). Mass spectroscopy data were obtained with a Shimadzu GCMS-QP5000, gas chromatograph/mass spectrometer, equipped with Shimadzu GC-17A gas chromatograph with a chemically bonded capillary column DB-1 (60 m  $\times$  0.25 mm).  $^1\text{H}$  NMR spectra were recorded on a JEOL JNM-EX270 (270 MHz) spectrometer. Benzene- $d_6$  was used as solvent and tetramethylsilane as the internal standard. Gel permeation chromatography was used to check the formation of oligomer and polymer products.

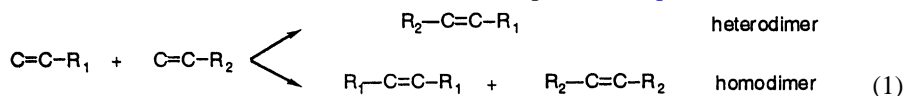
the self-metathesis of styrene and 1-octene. Grubbs catalyst was virtually inactive for the self-metathesis of vinylthiophene and vinylfuran, but Schrock catalyst showed a few activity. It was found that the activity of Grubbs catalyst was lowered in the oxygen atmosphere.

### 3.2. Cross-metathesis

#### 3.2.1. Effect of oxygen on reaction behaviors for Grubbs catalyst

Although it has been reported that Grubbs catalysts are extremely robust, having remarkable stability toward oxygen and moisture, there are no reports clarifying the effect of oxygen on the reaction behaviors using the same reactants. We therefore examined the effect of oxygen on the reaction behaviors in detail.

The simplified cross-metathesis reaction between two  $\alpha$ -olefins is depicted in Eq. (1).



## 3. Results and discussion

### 3.1. Self-metathesis

The self-metathesis of a series of 2-vinylthiophene and 2-vinylfuran, together with 1-octene and styrene used as reference samples was carried out in the presence of Grubbs and Schrock catalysts and the results are summarized in Table 1.

Both catalysts gave self-metathesis product, henceforth referred to as homodimer, as a sole product in

Generally, the reaction proceeds to yield three products, i.e. one cross-metathesis product, henceforth referred to as heterodimer and two homodimers produced by the exchange of alkylidene moieties between the olefins. In the cross-metathesis between olefins with similar structure and reactivity, the product distribution of heterodimer and two homodimers is about 2:1:1, as expected [27–29].

The changes in conversion and distribution of reaction products during the course of reaction in the case of vinylthiophene and 1-octene are shown in Fig. 1 as an example.

Although the self-metathesis of vinylthiophene did not occur, it was surprisingly found that vinylthiophene was converted to heterodimer in the cross-metathesis. The reaction proceeded at a moderate rate and reached a constant at around 15 h under  $\text{N}_2$  atmosphere. On the contrary, catalytic activity under air atmosphere decreased and reached a constant at around 3 h, suggesting that the deactivation occurred in the presence of oxygen. The influence of the atmosphere on the catalytic activity is quite conspicuous as shown in Fig. 1. The catalytic activity is much higher under nitrogen than under oxygen. Under both

Table 1  
Activity (%) of Grubbs and Schrock catalysts in self-metathesis of vinyl compounds

Reactant	Grubbs catalyst		Schrock catalyst
	Under $\text{O}_2$	Under $\text{N}_2$	Under $\text{N}_2$
1-Octene	35.2	65.6	72.8
Styrene	5.3	19.6	47.7
2-Vinylthiophene	0	Trace	2.6
2-Vinylfuran	0	0	4.0

Reaction time: 17 h, activities are shown as conversion.

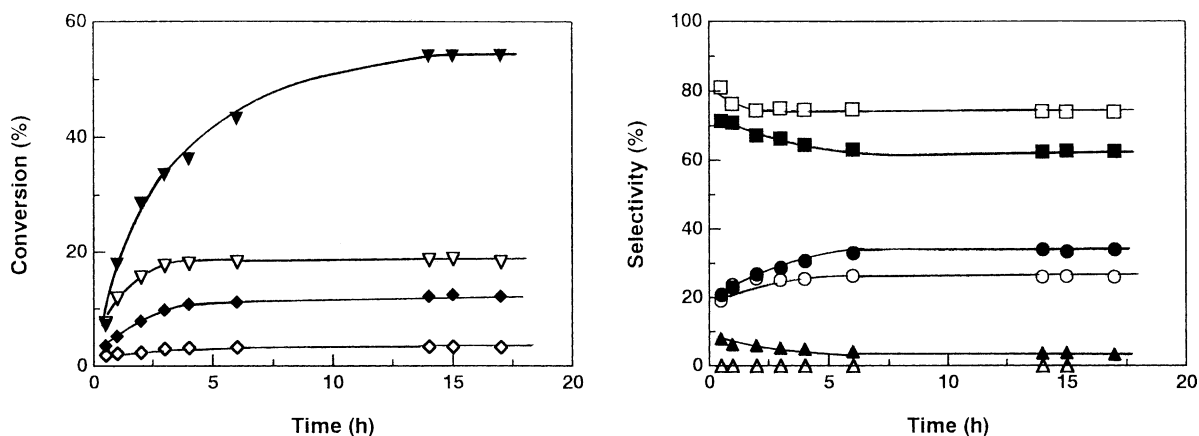


Fig. 1. Effect of an atmosphere of gas in the cross-metathesis of 2-vinylthiophene (VT) and 1-octene ( $C_8'$ ). VT/ $C_8'$  molar ratio, 1.5; VT ( $\blacklozenge$ ,  $\diamond$ ); 1- $C_8'$  ( $\blacktriangledown$ ,  $\triangledown$ ); heterodimer: 1-(2-thiophenyl)-2-heptylethene ( $\bullet$ ,  $\circ$ ); 7-tetradecene ( $\blacksquare$ ,  $\square$ ); 1,2-bis(2-thiophenyl)ethene ( $\blacktriangle$ ,  $\triangle$ ). The data shown in filled and empty symbols mean those obtained under nitrogen and air, respectively.

atmospheres, the reaction products were the heterodimer (1-(2-thienyl)-2-heptylethene) and two homodimers (7-tetradecene and 1,2-bis(2-thienyl)ethene), and side reaction products and oligomers were detected in trace amounts. The effect of atmosphere on selectivity seemed rather little, however, higher selectivity of heterodimer was obtained under the nitrogen atmosphere. Heterodimer selectivity was ca. 35%, which is much smaller than the expected value, 50%. 7-Tetradecene was obtained as the main product and only small amounts (less than 4%) of the homodimer of vinylthiophene was obtained as shown in Fig. 1.

Similar reaction behaviors, i.e. the higher catalytic activity and higher heterodimer selectivity under nitrogen atmosphere than under air were also observed for vinylfuran/1-octene and styrene/1-octene systems.

The effect of oxygen and nitrogen atmosphere on conversion and product distributions was further investigated as a function of reactant molar ratio, and the results in the cross-metathesis of the vinylthiophene and 1-octene are shown in Fig. 2.

Large difference in the catalytic activity based on molar ratio was similarly observed, i.e. the catalytic activity is much higher under nitrogen than under air

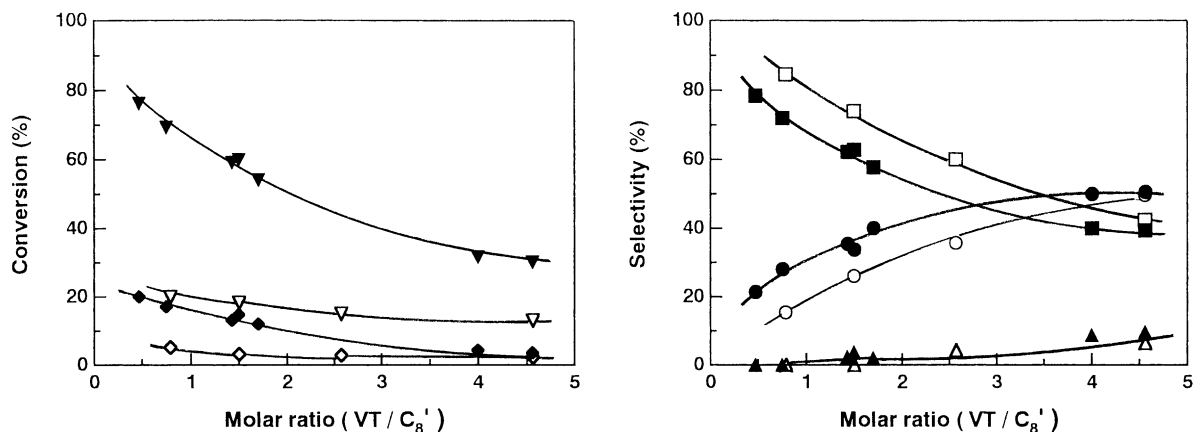


Fig. 2. Effect of an atmosphere of gas in the cross-metathesis of 2-vinylthiophene (VT) and 1-octene ( $C_8'$ ) as a function of reactant molar ratio. VT ( $\blacklozenge$ ,  $\diamond$ ); 1- $C_8'$  ( $\blacktriangledown$ ,  $\triangledown$ ); heterodimer: 1-(2-thiophenyl)-2-heptylethene ( $\bullet$ ,  $\circ$ ); 7-tetradecene ( $\blacksquare$ ,  $\square$ ); 1,2-bis(2-thiophenyl)ethene ( $\blacktriangle$ ,  $\triangle$ ). The data shown in filled and empty symbols mean those obtained under nitrogen and air, respectively.

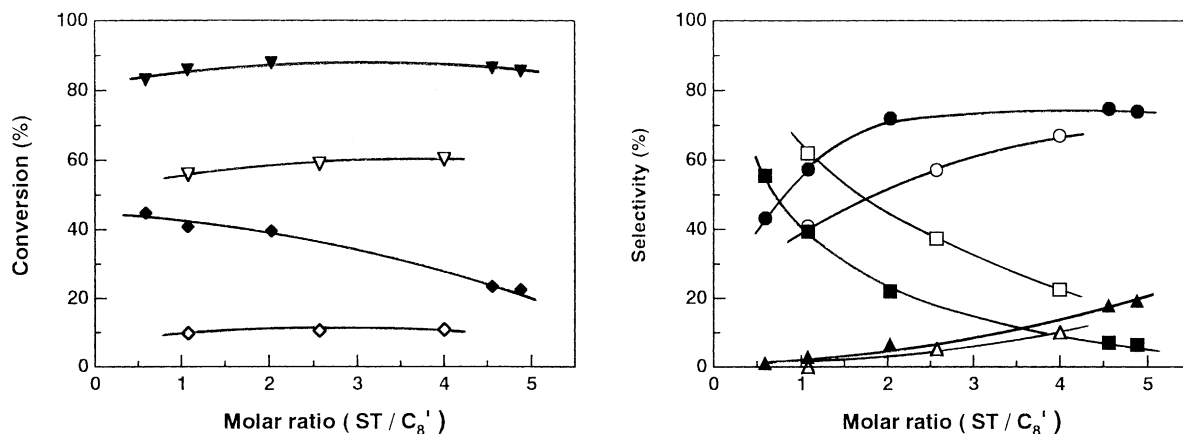


Fig. 3. Effect of an atmosphere of gas in the cross-metathesis of styrene (ST) and 1-octene ( $C_8^1$ ) as a function of reactant molar ratio. ST ( $\blacklozenge$ ,  $\diamond$ ); 1- $C_8^1$  ( $\blacktriangledown$ ,  $\triangledown$ ); heterodimer: 1-phenyl-2-heptylethene ( $\bullet$ ,  $\circ$ ); 7-tetradecene ( $\blacksquare$ ,  $\square$ ); stilbene ( $\blacktriangle$ ,  $\triangle$ ). The data shown in filled and empty symbols mean those obtained under nitrogen and air, respectively.

at each molar ratio. The selectivity of the heterodimer increased gradually with an increase in vinylthiophene molar ratio and reached to ca. 50%. The selectivity of the homodimer of vinylthiophene also increased with an increase of the vinylthiophene molar ratio, but it was always less 10%. On the other hand, the yield of the homodimer of 1-octene decreased with the increase of the vinylthiophene molar ratio. Similar reaction behaviors were observed in the cross-metathesis of vinylfuran with 1-octene.

Similarly, the cross-metathesis of 1-octene with styrene that was used as a reference was investigated and the results are shown in Fig. 3. The results indicate higher catalytic activity for styrene as compared to thiophene and furan, and also higher heterodimer selectivity were observed. The selectivity of heterodimer (1-phenyl-2-heptylethene) under  $N_2$  atmosphere reached 75% more than the expected value of 50% and the homodimer selectivities at styrene molar ratio of 4.6 were stilbene 23% and 7-tetradecene 7%, respectively. It is clear that the presence of oxygen decreased greatly the catalytic activity and lowered the heterodimer formation.

### 3.2.2. Comparison of Schrock catalyst and Grubbs catalyst

It becomes clear that it is essential to carry out the metathesis under nitrogen gas atmosphere when using Grubbs catalyst, as the activity and the heterodimer

selectivity were lowered in the presence of oxygen. The effects of the Schrock and Grubbs catalysts on catalytic activity under nitrogen atmosphere and the reaction behavior were investigated in order to make clear the differences in both catalysts.

Activity changes as a function of reaction time in the metathesis of vinylthiophene and 1-octene system are shown for both Schrock and Grubbs catalysts in Fig. 4. The activity of Schrock catalyst is very high and reached a constant within 2 h, but that of Grubbs is very low. The Schrock catalyst showed much higher heterodimer selectivity (84%) as compared to Grubbs catalyst (34%).

Furthermore, the effects of reactant molar ratio on reaction behaviors for the both catalysts were investigated and their comparisons were made for vinyl thiophene, vinylfuran or styrene with 1-octene system. The results are shown in Figs. 5–7.

It becomes clear that heterodimer selectivity in the cross-metathesis of vinyl heteroaromatics with 1-octene in the presence of the Grubbs catalyst is lower than 50% of the expected value, differing greatly from selective heterodimer formation in the presence of the Schrock catalyst as summarized in Table 2.

### 3.3. Reaction mechanism

We have discussed the high selectivity of heterodimer formation in the presence of the Schrock

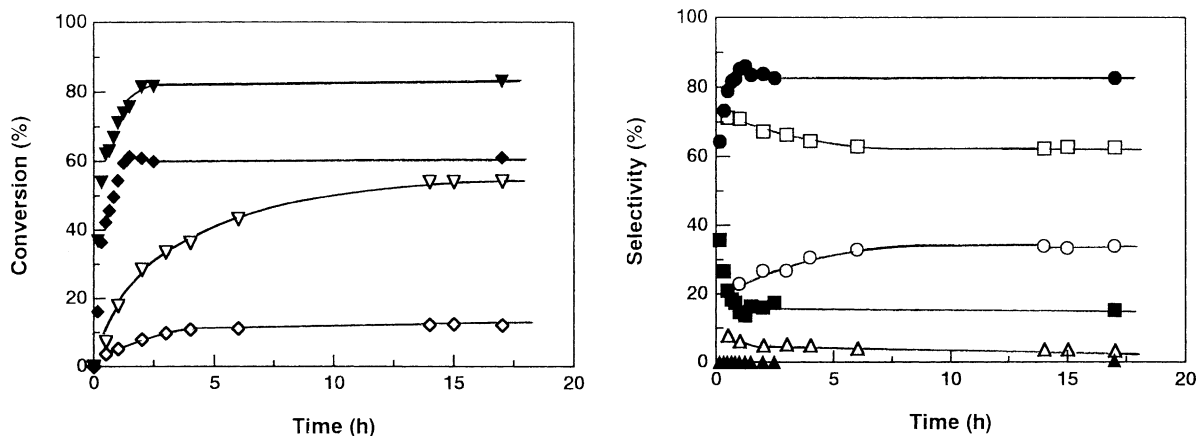


Fig. 4. Changes in activity and selectivity for Grubbs and Schrock catalysts in the cross-metathesis of 2-vinylthiophene (VT) and 1-octene ( $C_8^1$ ). VT ( $\blacklozenge$ ,  $\diamond$ );  $1-C_8^1$  ( $\blacktriangledown$ ,  $\triangledown$ ); heterodimer: 1-(2-thiophenyl)-2-heptylethene ( $\bullet$ ,  $\circ$ ); 7-tetradecene ( $\blacksquare$ ,  $\square$ ); 1,2-bis(2-thiophenyl)ethene ( $\blacktriangle$ ,  $\triangle$ ). The data shown in filled and empty symbols mean those obtained for Schrock and Grubbs catalysts, respectively.

catalyst and proposed the plausible mechanism [23]. It is of interest to clarify the reasons why the self-metathesis of 2-vinyl aromatic heterocycles such as furan, thiophene did not proceed with appreciable rate and, on the contrary, the cross-metathesis of these 2-vinyl aromatic heterocycles with 1-octene proceeded to yield corresponding one heterodimer and two homodimers. The reasons why heterodimer selectivity is lower than 50% in the presence of the Grubbs catalyst could be explained as follows.

The observations of carbenes in the reaction solution by *in situ*  $^1H$  NMR spectroscopy were carried out at room temperature. When vinylthiophene was added to the catalyst solution, only thiophenylidene carbene (**A**, see Fig. 9) was found and the amount was almost constant during the observation of 48 h. 1-Octene was added to the solution after 48 h reaction, but new carbene peaks were not observed except thiophenylidene carbene (**A**). When the mixture of vinylthiophene and 1-octene was added to the catalytic solution, only

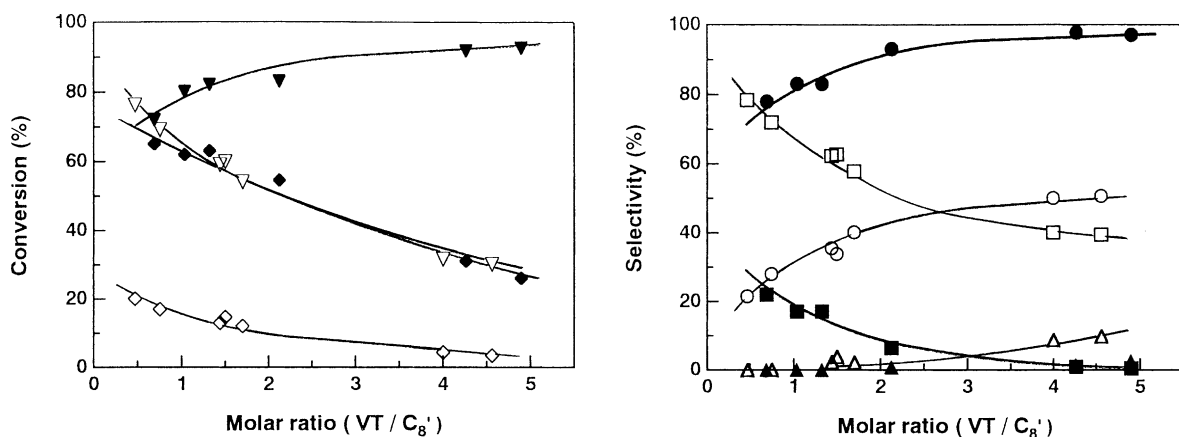


Fig. 5. Comparison in activity and selectivity for Grubbs and Schrock catalysts in cross-metathesis of 2-vinylthiophene (VT) and 1-octene ( $C_8^1$ ) as a function of reactant molar ratio. VT ( $\blacklozenge$ ,  $\diamond$ );  $1-C_8^1$  ( $\blacktriangledown$ ,  $\triangledown$ ); heterodimer: 1-(2-thiophenyl)-2-heptylethene ( $\bullet$ ,  $\circ$ ); 7-tetradecene ( $\blacksquare$ ,  $\square$ ); 1,2-bis(2-thiophenyl)ethene ( $\blacktriangle$ ,  $\triangle$ ). The data shown in filled and empty symbols mean those obtained for Schrock and Grubbs catalysts, respectively.

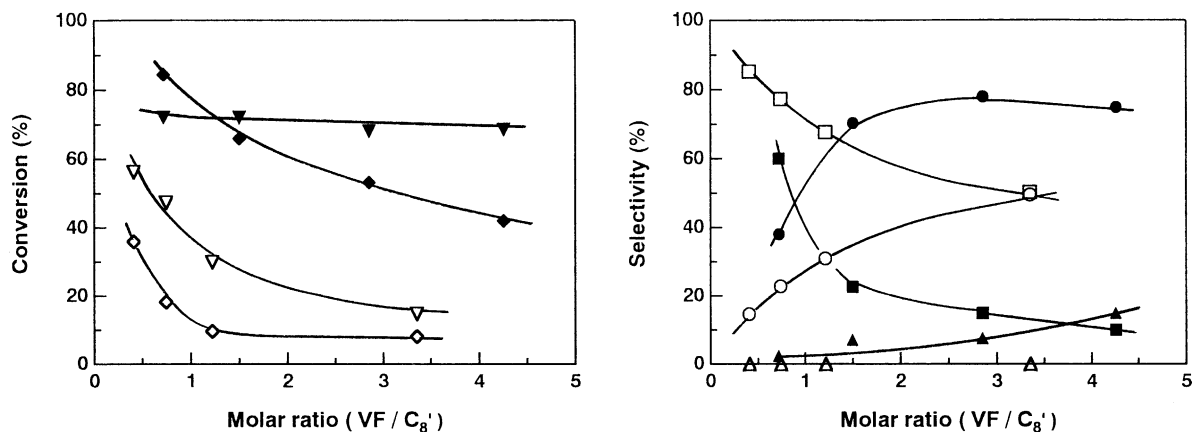


Fig. 6. Comparison in activity and selectivity for Grubbs and Schrock catalysts in the cross-metathesis of 2-vinylfuran (VF) and 1-octene ( $C_8^v$ ) as a function of reactant molar ratio. VF ( $\blacklozenge$ ,  $\diamond$ ); 1- $C_8^v$  ( $\blacktriangledown$ ,  $\triangledown$ ); heterodimer: 1-(2-furanyl)-2-heptylethene ( $\bullet$ ,  $\circ$ ); 7-tetradecene ( $\blacksquare$ ,  $\square$ ); 1,2-bis(2-furanyl)ethene ( $\blacktriangle$ ,  $\triangle$ ). The data shown in filled and empty symbols mean those obtained for Schrock and Grubbs catalysts, respectively.

thiophenylidene carbene (A) was observed throughout the reaction period of 20 h. This suggests that thiophenylidene carbene (A) is formed with ease and is very stable in comparison with the heptylidene carbene (B). On the other hand, heptylidene carbene (B) and methylenidene carbene (C) were found by adding 1-octene to the catalyst solution, and heptylidene carbene (B) decreased and methylenidene carbene (C) increased with increasing reaction time as shown in 8-1-8-3 of Fig. 8. Upon the addition of thiophene to

the solution after 240 min reaction, thiophenylidene carbene (A) was observed and the amount was increased with reaction time. On the contrary, methylenidene carbene (C) decreased and heptylidene carbene (B) disappeared in a few minutes after the addition of thiophene as shown in 8-4-8-6 of Fig. 8.

The relation between the amount of carbenes and the distribution of the three dimers can also be explained through the carbene mechanisms shown in Fig. 9. Let us consider the mechanism of

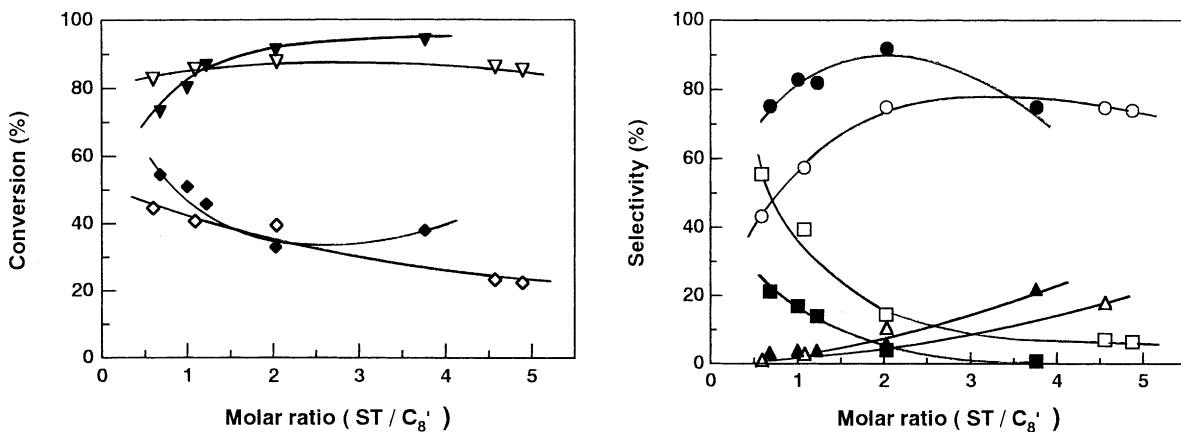


Fig. 7. Comparison in activity and selectivity for Grubbs and Schrock catalysts in the cross-metathesis of styrene (ST) and 1-octene ( $C_8^s$ ) as a function of reactant molar ratio. ST ( $\blacklozenge$ ,  $\diamond$ ); 1- $C_8^s$  ( $\blacktriangledown$ ,  $\triangledown$ ); heterodimer: 1-phenyl-2-heptylethene ( $\bullet$ ,  $\circ$ ); 7-tetradecene ( $\blacksquare$ ,  $\square$ ); stilbene ( $\blacktriangle$ ,  $\triangle$ ). The data shown in filled and empty symbols mean those obtained for Schrock and Grubbs catalysts, respectively.



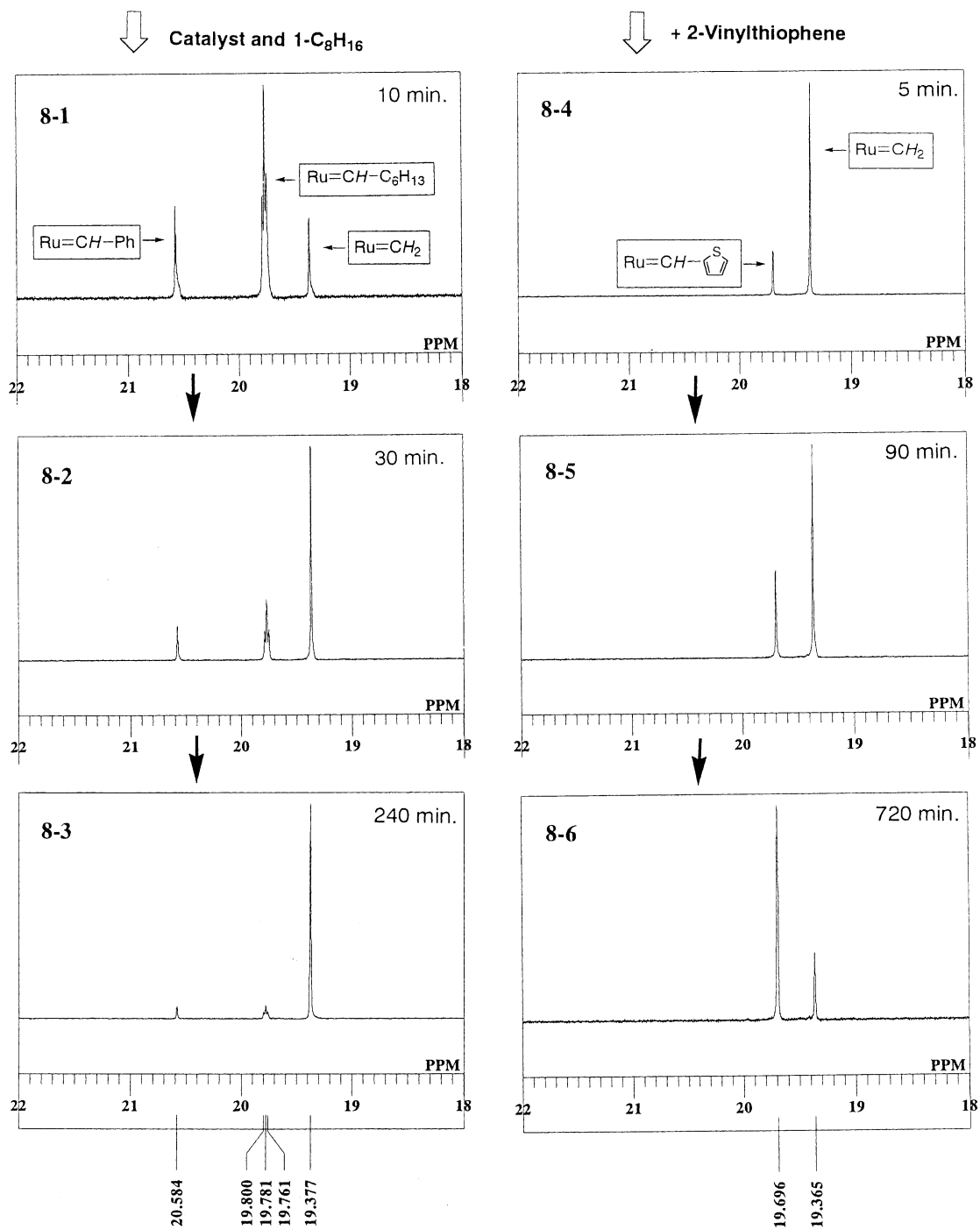


Fig. 8. Observation of carbenes by  $^1\text{H}$  NMR in the metathesis of 2-vinylthiophene (VT) and 1-octene ( $\text{C}_8$ ). Solvent:  $\text{C}_6\text{D}_6$ ; reactants/catalyst: 3; temperature:  $25^\circ\text{C}$ ; VT/ $\text{C}_8$  molar ratio: 1. The times shown are reaction times after the addition of reactant. Literature data of  $^1\text{H}$  NMR in  $\text{CD}_2\text{Cl}_2$  [15,30];  $\text{Ru}=\text{CH}_2$  18.94 (s),  $\text{Ru}=\text{CH-Ph}$  20.10 (s),  $\text{Ru}=\text{CH-}n\text{-C}_4\text{H}_9$  (t,  $^3J_{\text{HH}} = 5.1$ ).



Table 2  
Data of maximum selectivity on cross-metathesis

Substrate	Product	Grubbs catalyst		Schrock catalyst
		Under O <sub>2</sub>	Under N <sub>2</sub>	Under N <sub>2</sub>
Styrene	Heterodimer	67	75	92
	7-Tetradecene	23	14	4
2-Vinylthiophene	Stilbene	10	11	4.1
	Heterodimer	50	51	98
	7-Tetradecene	42	40	0.9
	Homodimer of vinylthiophene	7.8	9.8	1.4
2-Vinyfuran	Heterodimer	–	50	78
	7-Tetradecene	–	50	14
	Homodimer of vinyfuran	–	–	7.8

Styrene/1-C<sub>8</sub> molar ratio: 1; 2-vinylthiophene/1-C<sub>8</sub> molar ratio: 1.6; reaction temperature: RT; reaction time: 60 min; reactants/catalyst molar ratio: 5; solvent: toluene.

cross-metathesis of vinylthiophene and 1-octene system as an example. It has been reported that secondary reaction of stilbene with 1-octene does not occur and the reaction of styrene with 7-tetradecene is slow enough to influence reaction product ratio in the cross-metathesis of styrene and 1-octene [16].

The methyldiene carbene (**C**) formed after producing a dimer reacts competitively with vinylthiophene and 1-octene, and the corresponding carbenes (**A**) and (**B**) are formed. Thiophenylidene carbene (**A**) is stable due to the polarizable, electron-rich metal–carbon bond [16] and is formed easier than heptylidene

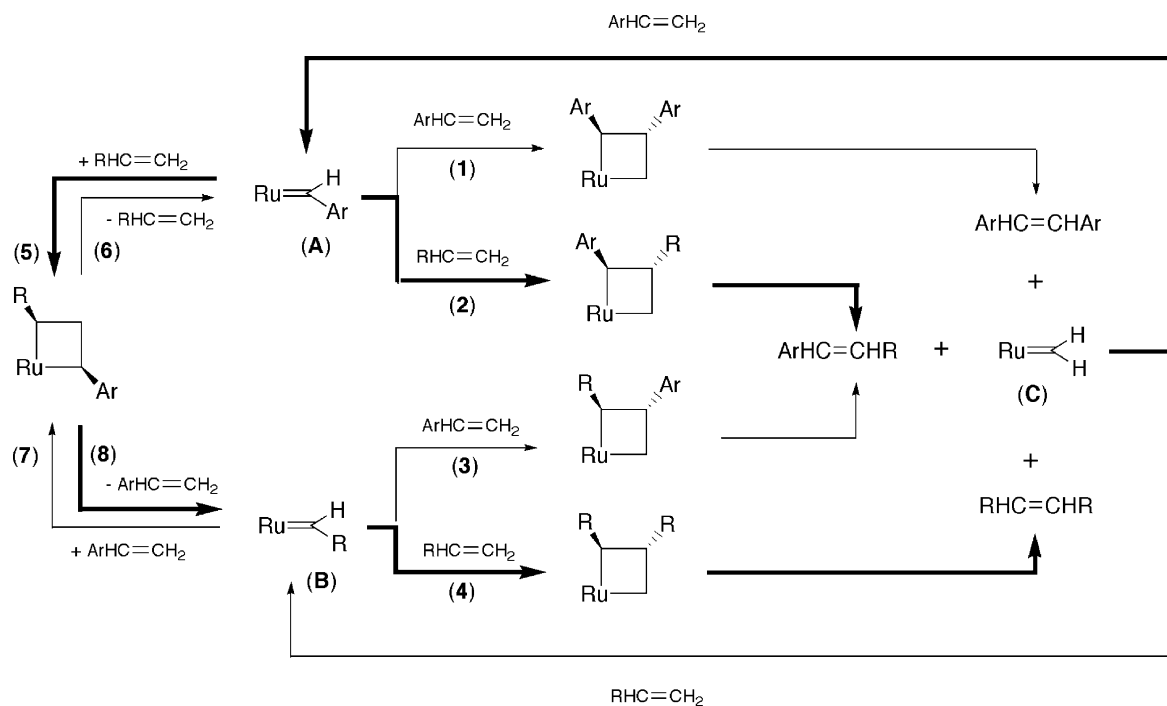


Fig. 9. Plausible reaction mechanism. Ar: phenyl, thienyl, or furanyl; R: hexyl.

carbene (**B**), as confirmed by  $^1\text{H}$  NMR observation. Heptylidene carbene (**B**) can be formed via two routes: (i) reaction of methylidene carbene (**C**) with 1-octene, and (ii) interconversion of thiophenylidene carbene (**A**) through reactions (5) and (8) (see Fig. 9). Interconversion between two carbenes (**A**) and (**B**) via  $\alpha,\alpha'$ -disubstituted metallacycle is much faster than other reactions (1)–(4) to form  $\alpha,\beta$ -disubstituted metallacycles due to steric hindrance. Since heptylidene carbene (**B**) was not observed during observation of carbenes in the reaction solution of vinylthiophene and 1-octene system, the reactivity of heptylidene carbene (**B**) with reactants must be fast. The reaction (4) of heptylidene carbene (**B**) with 1-octene which has stronger basicity and smaller steric hindrance must be faster than that of heptylidene carbene (**B**) with thiophene which has larger molecular size and weaker basicity [16,23] as confirmed by distribution of dimer formation. These strongly suggest that heptylidene carbene (**B**) will be formed via interconversion of thiophenylidene carbene (**A**) through reactions (5) and (8). The reaction (1) between the thiophenylidene carbene (**A**) with vinylthiophene occurs slowly, as can be judged from lack of formation of the homodimer of vinylthiophene in the competitive system with 1-octene and in the self-metathesis of vinylthiophene. Heterodimer can be obtained by the reactions (2) and/or (3). However, it was suggested that the rate of reaction (2) is much faster than that of reaction (3) by considering the basicity and steric hindrance of coming olefins [23,30].

Thus, it was found that most heterodimer was produced through the reaction (2) and that the contribution of the reaction (3) was minor. By increasing vinyl aromatics molar ratio, the contribution of the reaction (2) will be increased, resulting in the higher yield of heterodimer, in accordance with experimental data.

Conclusively, the main pathways to produce heterodimer and homodimer are indicated by bold arrows. However, further studies on the reactivities of carbenes with reactants are needed to enhance deeper profound understanding of the reaction mechanism.

#### 4. Summary

2-Vinylfuran and 2-vinylthiophene as aromatic heterocycles, and styrene were applied to self-metathesis

and cross-metathesis reactions with terminal olefin, i.e. 1-octene in the presence of Grubbs catalyst. The results were compared with those of Schrock catalyst. The results of this study can be summarized as follows:

1. It is essential to carry out the metathesis reaction in the use of Grubbs catalyst under nitrogen atmosphere. The activity and the heterodimer selectivity decreased greatly under oxygen atmosphere.
2. The self-metathesis of 2-vinyl aromatic heterocycles in the presence of both catalysts was not successful due to steric hindrance in the formation of  $\alpha,\beta$ -disubstituted metallacycles.
3. The cross-metathesis of 2-vinyl aromatic heterocycles and styrene with 1-octene proceeded easily in the presence of Grubbs catalyst. The main reaction is homodimer formation of 7-tetradecene. The low heterodimer formation was attributed to low reactivity of stable hetero aromatic carbene (**A**).
4. The reaction behaviors were elucidated through the metallacyclobutane intermediate mechanism, as well as the observation of carbenes by in situ  $^1\text{H}$  NMR and the reaction products. The following key steps are clarified:
  - 4.1. The reactivity of methylidene carbene with aromatic heterocycles is much faster in comparison with 1-octene.
  - 4.2. The reactivity of heteroaromatic carbenes with aromatic heterocycles is extremely slow, yielding small amount of heteroaromatic homodimers.
  - 4.3. The reaction of heteroaromatic carbenes with 1-octene is faster than that with aromatic heterocycles, resulting in heterodimer formation.
  - 4.4. The reaction of heptylidene carbene with aromatic heterocycles proceeds with slower rate as compared to that of heteroaromatic carbenes with 1-octene.
  - 4.5. The main route to produce 7-octadecene as a main product is the reaction between 1-octene and heptyridene carbene (**B**) formed via interconversion of heteroaromatic carbenethiophenylidene (**A**) through reactions (5) and (8).
5. The heterodimer selectivity was much lower compared with the Schrock catalyst, indicating that the Grubbs catalyst is inadequate for the synthesis of heterodimer.

## Acknowledgements

This work was supported by Grant-in-Aid for Science Research from the Ministry of Education, Science, Sports and Culture, Japan (No. 10650773).

## References

- [1] K.J. Ivin, J.C. Mol, *Olefin Metathesis and Metathesis Polymerization*, Academic Press, London, 1997.
- [2] H.E. Blackwell, D.J. O'Leary, A.K. Chatterjee, R.A. Washenfelder, D.A. Bussmann, R.H. Grubbs, *J. Am. Chem. Soc.* 122 (2000) 58–71.
- [3] S. Kanaoka, R.H. Grubbs, *Macromolecules* 28 (1995) 4707–4713.
- [4] C. Fraser, R.H. Grubbs, *Macromolecules* 28 (1995) 7248–7255.
- [5] R.H. Grubbs, S.J. Miller, G.C. Fu, *Acc. Chem. Res.* 28 (1995) 446–452.
- [6] A.J. Phillips, A.D. Abell, *Aldrichim. Acta* 32 (3) (1999) 75–89.
- [7] S. BouzBouz, J. Cossy, *Org. Lett.* 3 (10) (2001) 1451–1454.
- [8] Y.J. Miao, G.C. Bazan, *Macromolecules* 30 (1997) 7414–7418.
- [9] D.M. Lynn, S. Kanaoka, R.H. Grubbs, *J. Am. Chem. Soc.* 118 (1996) 784–790.
- [10] G.C. Fu, S.T. Nguyen, R.H. Grubbs, *J. Am. Chem. Soc.* 115 (1993) 9856–9857.
- [11] S.T. Nguyen, L.K. Johnson, R.H. Grubbs, *J. Am. Chem. Soc.* 114 (1992) 3974–3975.
- [12] D.M. Lynn, B. Mohr, R.H. Grubbs, *J. Am. Chem. Soc.* 120 (1998) 1627–1628.
- [13] E.L. Dias, S.T. Nguyen, R.H. Grubbs, *J. Am. Chem. Soc.* 119 (1997) 3887–3897.
- [14] S.T. Nguyen, R.H. Grubbs, *J. Am. Chem. Soc.* 115 (1993) 9858–9859.
- [15] P. Schwab, M.B. France, J.W. Ziller, R.H. Grubbs, *Angew Chem. Int. Ed. Engl.* 34 (18) (1995) 2039–4116.
- [16] W.E. Crowe, Z.J. Zhang, *J. Am. Chem. Soc.* 115 (1993) 10998.
- [17] H.H. Fox, R.R. Schrock, R. O'Dell, *Organometallics* 13 (1994) 635.
- [18] W.E. Crowe, D.R. Goldberg, Z.J. Zhang, *Tetrahedron Lett.* 37 (1996) 2117.
- [19] E. Thorn-Csanyi, P. Kraxner, *J. Mol. Catal. A: Chem.* 115 (1997) 21.
- [20] K.B. Wagener, J.M. Boncella, J.G. Nel, R.P. Duttweiler, M.A. Hillmyer, *Makromol. Chem.* 191 (1990) 365.
- [21] B. Tuie, K.B. Wagener, J.R. Reynolds, *Polym. Prep.* 40 (1999) 790.
- [22] C. Piertraszuk, B. Marciniak, H. Fischer, in: *Proceedings of the 13th International Symposium on Olefin Metathesis and Related Chemistry (ISOM'99)*, The Netherlands, 1999, p. 29 (Abstract).
- [23] T. Kawai, M. Komaki, T. Iyoda, *J. Mol. Catal.*, accepted for publication.
- [24] J. Arekion, M. Delmas, A. Gaset, *Biomass* 3 (1983) 59.
- [25] J.W. Van Reijendam, G.H. Heeres, M.J. Janssen, *Tetrahedron* 26 (1970) 1291.
- [26] C.G. Overberger, A. Wartman, J.C. Salamone, *Organ. Prep. Procedures* 1 (1969) 117.
- [27] R. Spronk, *J. Mol. Appl. Catal.* 70 (1991) 295.
- [28] T. Kawai, N. Maruoka, M. Goke, T. Ishikawa, *J. Mol. Catal.* 49 (1989) 261.
- [29] T. Kawai, H. Goto, Y. Yamazaki, T. Ishikawa, *J. Mol. Catal.* 46 (1988) 157.
- [30] P. Schwab, R.H. Grubbs, J.W. Ziller, *J. Am. Chem. Soc.* 118 (1996) 100–110.