

# Cross-metathesis of vinyl aromatic heterocycles with 1-octene in the presence of a Schrock catalyst

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## Abstract

Metathesis of 2-vinyl aromatic heterocycles such as furan, thiophene, pyrrole and pyridine in the presence of a molybdenum-based Schrock catalyst has been investigated from a synthetic point of view. The self-metathesis of 2-vinyl aromatic heterocycles was not successful. However, in cross-metathesis of thiophene, furan and styrene with 1-octene, the cross-metathesis product, heterodimer, was readily obtained selectively, together with only small amounts of the two corresponding self-metathesis products. The origin of the surprisingly high selectivity of heterodimer formation was elucidated through metallacyclobutane intermediate mechanism, observations of carbenes by in situ  $^1\text{H}$  NMR, and reaction products.

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## 1. Introduction

Numerous studies have been reported on the metathesis of a broad range of alkenes for various kinds of heterogeneous and homogeneous catalysts [1]. The advent of well-defined transition metal catalysts, especially the ruthenium benzylidene complexes developed by Grubbs et al., and the molybdenum imido alkylidene complexes 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 and cross-metathesis [1]. These catalysts are also applied to various kinds of reactants, not only simple hydrocarbons such as alkene

and alkadiene, but also functionalized olefins containing ethers, thioethers, ketones, amines, carbonates, silane, siloxanes, esters and so on. The metathesis processes now represent a powerful tool in applied organic synthesis due to the aforementioned versatile areas of applications.

A number of articles on cross-metathesis reactions between acyclic compounds have been reported, however, only a few examples were reported between aromatic compounds and acyclic compounds [1–6]. In cross-metathesis between two olefins with similar structure and reactivity, the product distribution of cross-metathesis product, hereinafter described as heterodimer and two self-metathesis products, hereinafter described as homodimers is about 2:1:1, as expected [7–9], which might be the reasons for the limited studies on cross-metathesis. Cross-metathesis will become powerful tool for the synthesis of complex organic molecules if it occurs selectively. There are several examples of self- and cross-metathesis

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of styrene [2,6,10,11], however, the self-metathesis reaction of vinyl derivatives of aromatic heterocycles such as thiophene, furan, pyrrole, pyridine, etc. and also their cross-metathesis reactions have not been adequately studied. Wagener et al. succeeded to self-metathesize *N*-methylated pyrrole with a Schrock catalyst [12]. Recently, Tuie et al. described the ADMET of alkylsubstituted 2,5-divinylthiophene with a Schrock catalyst [13]. Also Crowe and Zhang has reported interesting results on selective cross-metathesis between styrene and  $\alpha$ -olefins in the presence of a Schrock catalyst [2]. However, the application of cross-metathesis to the synthesis of complex organic molecules is limited. The success of application of metathesis to the chemistry of vinyl aromatic heterocycles will provide new approaches to the direct synthesis of various kinds of interesting olefin containing aromatic heterocycles.

This paper reports the study of self-metathesis of 2-vinyl aromatic heterocycles such as furan, thiophene and pyrrole, and cross-metathesis between these 2-vinyl aromatic heterocycles and 1-octene in the presence of a homogeneous well-defined Schrock metathesis catalyst.

## 2. Experimental

### 2.1. Catalysts and reagents

A Schrock catalyst, 2,6-diisopropylphenylimido-neophylidene molybdenum(VI) bis(hexafluoro-*t*-butoxide) was purchased from Strem Chemicals Inc. and used without further purification. Vinylthiophene, vinylfuran, vinylpyrrole and 1-aryl-1,3-butadiene were prepared in a high yield by Wittig reaction according to a modified literature procedure [14–16], and were purified by distillation from Na under nitrogen prior to use. Vinylpyridine, 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 under an atmosphere of nitrogen.

The catalysts were transferred to the Schlenk in a nitrogen atmosphere dry box. All glasswares were fully dried and much attention was paid to ensure the dryness and to avoid contamination by air.

The reactions were carried out at an atmospheric pressure of nitrogen gas. The typical reaction conditions were as follows unless otherwise indicated; reactant/catalyst molar ratio 100:1 (catalyst: ca. 8 mg, 0.01 mmol), solvent toluene (ca. 1 ml), temperature 30 °C and reaction time 72 h. The reactions to observe carbenes were performed in benzene- $d_6$  (ca. 0.8 ml) at room temperature in an NMR tube using ca. 20 mg catalyst and reactant/catalyst molar ratio 3. The reactions were monitored by *in situ*  $^1\text{H}$  NMR.

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 with 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 oligomers and polymers.

## 3. Results and discussion

### 3.1. Self-metathesis

The self-metathesis of a series of 2-vinyl aromatic heterocycles, together with 1-octene and styrene used as reference samples was carried out and the results are summarized in Table 1.

Table 1  
Self-metathesis of vinyl compounds

Substrate	Conversion (%)	Metathesis selectivity (%)
1-Octene	72.8	100
Styrene	47.7	100
2-Vinylthiophene	2.4	100
2-Vinylfuran	5.0	100
2-Vinylpyrrole	95.0	0
2-Vinylpyridine	0	–

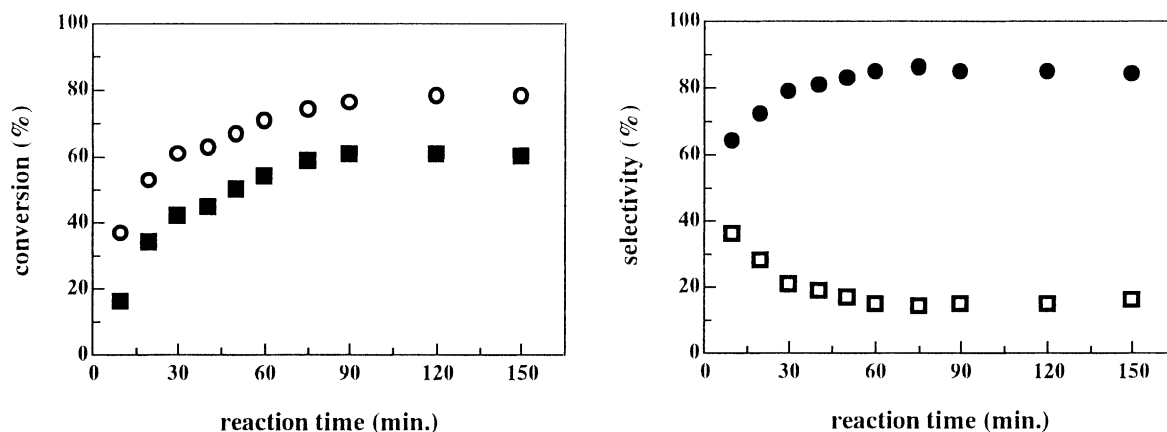
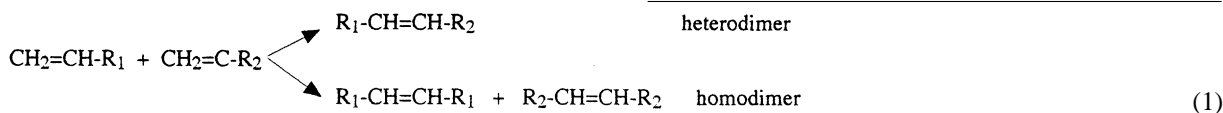


Fig. 1. Cross-metathesis of 2-vinylthiophene (VT) and 1-octene (C<sub>8</sub>). VT/C<sub>8</sub> molar ratio 1.13, (○) 1-C<sub>8</sub>, (■) VT, (●) heterodimer: 1-(2-thiophenyl)-2-heptylethene, (□) 7-tetradecene. The amounts of 1,2-bis(2-thiophenyl)ethene formed is less than 1%.

The self-metathesis of styrene and 1-octene occurred with high selectivity. Vinylthiophene and vinylfuran gave homodimer, but their reactivity was extremely low. In the metathesis of vinylpyrrole, homodimer did not form at all, but various kinds of unmetathesis reaction products together with oligomers and polymers were formed instead. In the metathesis of vinylpyridine no products were detected. As *N*-methylated pyrrole, 1-methyl-2-(1-propenyl)pyrrole, is metathesized with a tungsten-based Schrock catalyst [12], *N*-alkylated pyrrole may be metathesized with a molybdenum-based Schrock catalyst. Unreactivity of vinylpyridine resulted from a stable adduct formation with a molybdenum-based Schrock catalyst [17].

### 3.2. Cross-metathesis of 2-vinylthiophene and 2-vinylfuran with 1-octene

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



where, R<sub>1</sub> and R<sub>2</sub> are, e.g. alkyl groups.

Three kinds of dimer products, i.e. one heterodimer and two homodimers, are produced by the exchange of alkylidene moieties between the olefins.

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. The reaction proceeded at a moderate rate and reached an equilibrium within 90 min. A selectivity of 86% for the heterodimer 1-(2-thiophenyl)-2-heptylethene and 14% for 7-tetradecene were obtained, while only a negligible amounts of homodimer (1,2-bis(2-thiophenyl)ethene) of vinylthiophene was detected.

Since self-metathesis of vinylthiophene did not occur, it was surprising to find that vinylthiophene efficiently converted to heterodimer with very high selectivity in cross-metathesis. Similar reaction behaviors were observed for vinylfuran–1-octene and styrene–1-octene systems.

The effect of reactant molar ratio on conversion and product distributions was further investigated and the results of the cross-metathesis reaction of vinylthiophene and 1-octene are shown in Fig. 2.

The reaction products were the heterodimer and two homodimers. No side reaction products and oligomers

were detected. The selectivity of the heterodimer increased greatly with an increase in vinylthiophene molar ratio and reached up to 98%. The selectivity of the homodimer of vinylthiophene also increased with increasing the vinylthiophene molar ratio, but it was always less than 2%. On the other hand, the yield of

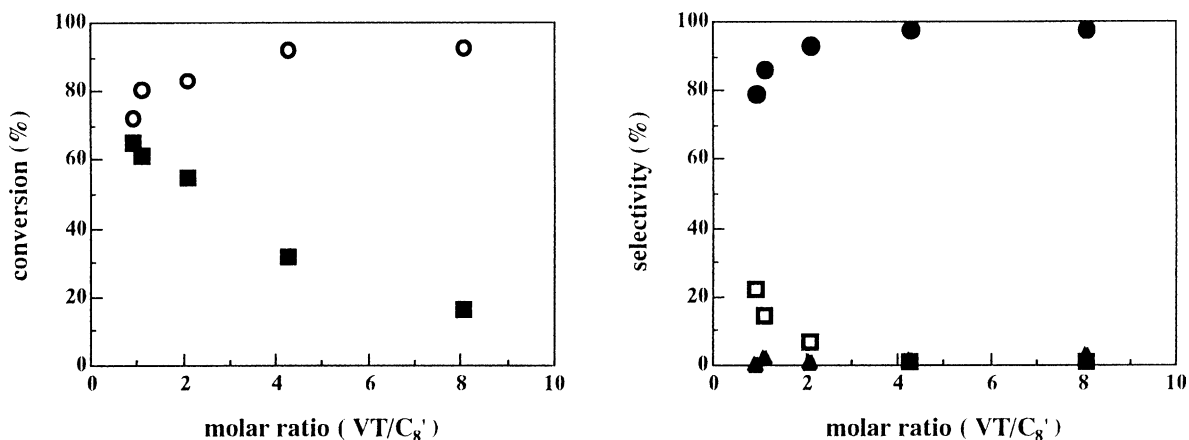


Fig. 2. Effect of molar ratio on conversion and selectivity of reaction products in the cross-metathesis of 2-vinylthiophene (VT) and 1-octene (C<sub>8</sub>'). (○) 1-C<sub>8</sub>', (■) VT, (●) heterodimer: 1-(2-thiophenyl)-2-heptylethene, (□) 7-tetradecene, (▲) 1,2-bis(2-thiophenyl)ethene.

the homodimer of 1-octene decreased steeply with the increase of the vinylthiophene molar ratio.

Similarly, the cross-metathesis of 2-vinylfuran with 1-octene was investigated and the results are shown in Fig. 3. The reaction products were the heterodimer 1-(2-furanyl)-2-heptylethene and two homodimers, (7-tetradecene and 1,2-bis(2-furanyl)ethene) and no side reaction products were formed. The heterodimer selectivity was 77%, i.e. lower than in the case of vinylthiophene.

In order to clarify the reaction behavior of aromatic heterocycles, styrene was used as the reference reac-

tant in the cross-metathesis, and the results are shown in Fig. 4.

The selectivity of heterodimer (1-phenyl-2-heptylethene) reached 92% and the homodimer selectivities were 4% stilbene and 4% 7-tetradecene at styrene molar ratio of 2.1, respectively. The values are in fair agreement with the data reported [2]. The decrease in heterodimer selectivity at higher molar ratio of styrene (3.8) is attributed to the increase in stilbene produced by the self-metathesis of styrene.

The cross-metathesis between a series of 2-vinyl aromatic heterocycles with styrene were investigated.

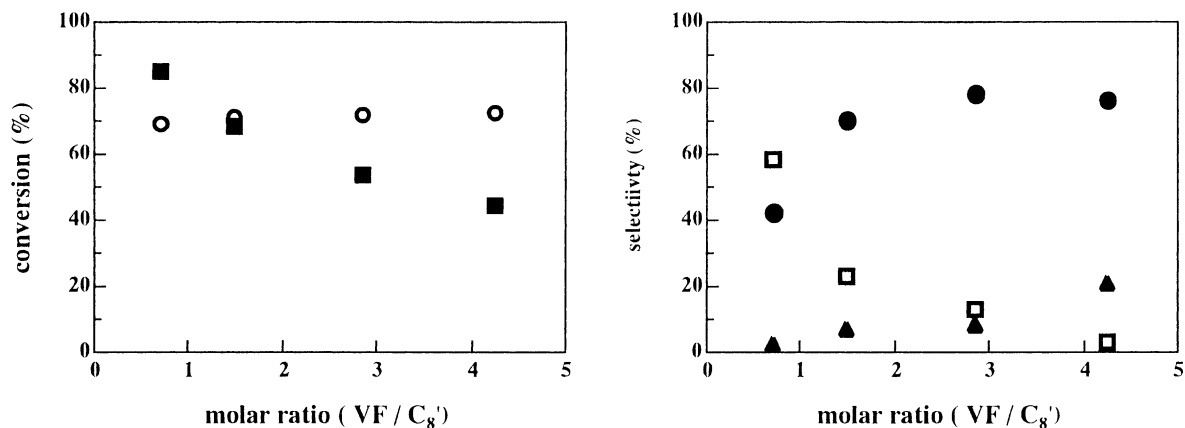


Fig. 3. Effect of molar ratio on conversion and selectivity of reaction products in the cross-metathesis of 2-vinylfuran (VF) and 1-octene (C<sub>8</sub>'). (○) 1-C<sub>8</sub>', (■) VF, (●) heterodimer: 1-(2-furanyl)-2-heptylethene, (□) 7-tetradecene, (▲) 1,2-bis(2-furanyl)ethene.

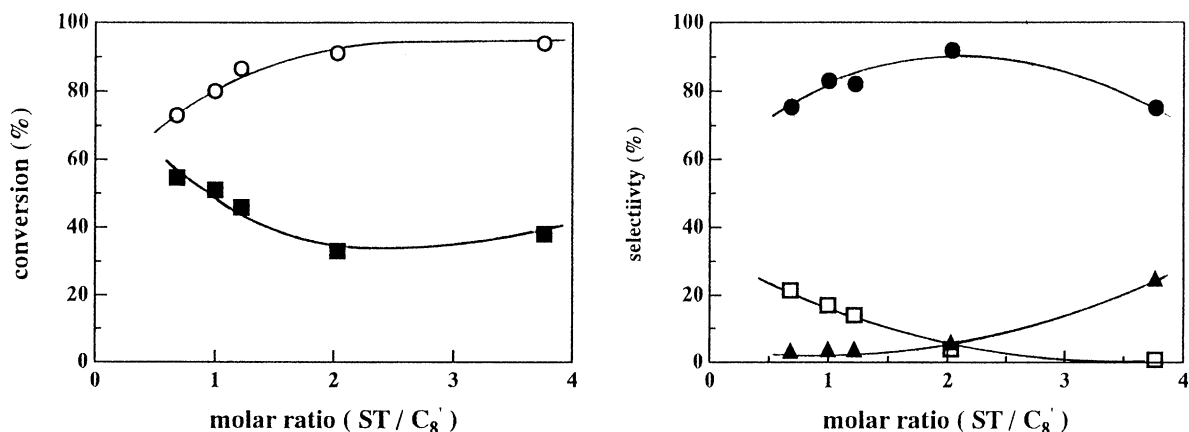


Fig. 4. Effect of molar ratio on conversion and selectivity of reaction products in cross-metathesis of styrene (ST) and 1-octene (C<sub>8</sub>). (○) 1-C<sub>8</sub>, (■) ST, (●) heterodimer: 1-phenyl-2-heptylethene, (□) 7-tetradecene, (▲) stilbene.

In the cross-metathesis of styrene and vinylthiophene, the ratio of products, heterodimer(1-phenyl-2-(2-thiophenyl)ethene): stilbene: 1,2-bis(2-thiophenyl)ethene was 39:32:29. Also in the cross-metathesis of styrene and vinylfuran, the ratio of products, heterodimer (1-phenyl-2-(2-furanyl)ethene): stilbene: 1,2-bis(2-furanyl)ethene, was 50:44:6. These data indicate that the selective formation of heterodimer is difficult for the system consisting of two different kinds of aromatic compounds.

### 3.3. Reaction mechanism

It is of interest to clarify the reasons why the self-metathesis of 2-vinyl aromatic heterocycles such as furan, thiophene did not proceed at appreciable rate and, on the contrary, the cross-metathesis of these 2-vinyl aromatic heterocycles with 1-octene proceeded easily to yield the heterodimer with high selectivity, yielding only small amounts of the corresponding homodimers.

The observations of carbenes in the reaction solution by in situ <sup>1</sup>H NMR spectroscopy were carried out at room temperature. The spectrum obtained for the styrene and 1-octene system, with molar ratio of 1, and after 60 min reaction is shown in Fig. 5.

Similar <sup>1</sup>H NMR spectra were obtained for cross-metathesis reactions between 2-vinyl aromatic heterocycles with 1-octene. The amount of carbenes

and the distribution of reaction products are summarized in Table 2.

It was found from the amount of carbenes present in the reaction solution that the tolyliden and thiophenyliden carbenes are formed with ease as compared to the formation of the heptyliden carbene.

The relation between the amount of carbenes and the distribution of the three dimers might be also explained through the carbene mechanisms. The expected carbene cycle is shown in Fig. 6.

Let us consider the mechanism of cross-metathesis of styrene 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 [2]. The methylidene carbene **C** formed after producing a dimer reacts competitively with styrene and 1-octene and the corresponding carbenes **A** and **B** are formed. 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. However, judging from the experimental data, the reactions (5)–(7) mostly occurred and the reaction (8) occurred lesser. If the heptyliden carbene is formed in appreciable amount, the homodimer of 1-octene increases and the selectivity of heterodimer lowers. It was found from the observation of carbenes by <sup>1</sup>H NMR that the methylidene carbene **C** reacted

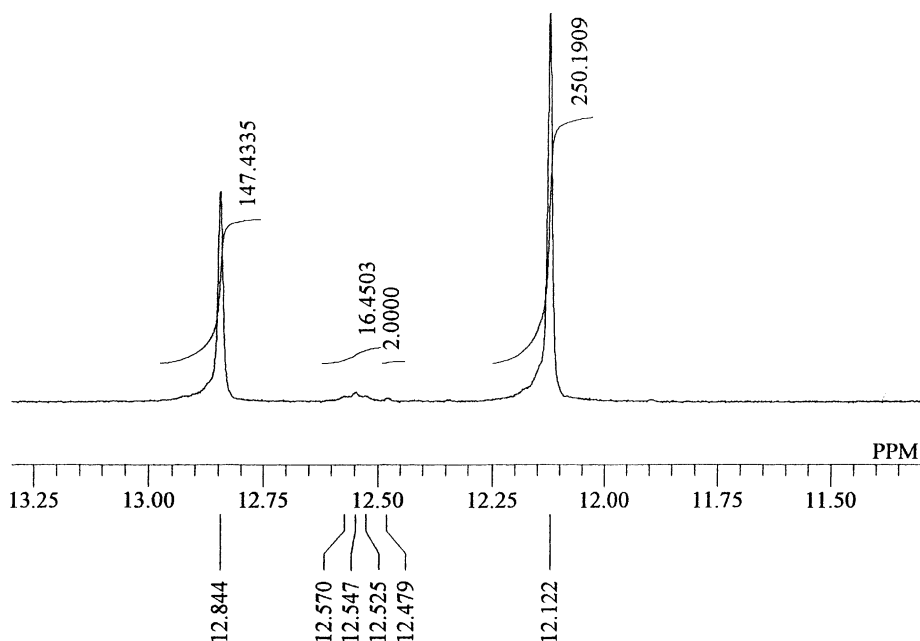


Fig. 5. Observation of carbenes in cross-metathesis of styrene (ST) and 1-octene ( $C_8^1$ ). Solvent:  $C_6D_6$ , reactants/catalyst: 3, temperature: 25 °C, ST/ $C_8^1$  molar ratio: 1.

with styrene much faster than with 1-octene, leading to the high concentration of the toluylidene carbene **A** (ca. 90%). This is attributed to the stability of aryl carbene due to the polarizable, electron-rich metal-carbon bond [2]. The reaction (1) between the toluylidene carbene **A** with styrene occurs slowly, owing to the lack of formation of stilbene in the competitive system with 1-octene. In the self-metathesis of styrene, fair amount of stilbene is produced, suggesting that the reactions (2) and/or (3) are very fast. On the other hand,

methylidene carbene **C** reacts with 1-octene to yield heptylidene carbene **B** 10%. The rate of the reaction (3) between the heptylidene carbene **B** and styrene might be similar to that (2) between toluylidene carbene **A** and 1-octene, because the similar structures of metallacyclobutane intermediates are formed by their combinations. However, by considering the basicity and steric hindrance of coming olefins, the rate of reaction (2) must be much faster than that of reaction (3). The reaction (4) is fast due to the least steric

Table 2  
Product distribution and amount of carbene complexes

	Ratio of carbenes			Selectivity (%)		
	M=CHAr <sup>a</sup>	M=CHC <sub>6</sub> H <sub>5</sub> <sup>a</sup>	M=CH <sub>2</sub> <sup>a</sup>	Heterodimer	Homodimer of 1-octene	Homodimer of arene
Styrene	147.4	16.5	1.00	81.0	16.6	2.4
2-Vinylthiophene	41.1	0.95	1.00	87.6	10.4	2.0

Styrene/1- $C_8^1$  molar ratio: 1, 2-vinylthiophene/1- $C_8^1$  molar ratio: 1.6, reaction temperature: rt, reaction time: 60 min, reactants/catalyst molar ratio: 5, solvent:  $C_6D_6$ .

<sup>a</sup> Mo=CHPh:  $\delta$  12.84 ppm, s ( $\delta$  12.44 ppm [18] ( $C_6D_6$ )); Mo=CHC<sub>4</sub>H<sub>9</sub>S:  $\delta$  12.81 ppm, s; Mo=CH-CMe<sub>2</sub>Ph:  $\delta$  12.12 ppm, s ( $\delta$  12.2 ppm [19] ( $C_6D_6$ ),  $\delta$  12.87 ppm [20] (toluene- $d_8$ )); Mo=CHC<sub>6</sub>H<sub>13</sub>:  $\delta$  12.54 ppm, t, <sup>3</sup> $J_{HH}$  = 6.2 (Mo=CH<sub>2</sub>Et,  $\delta$  12.44 ppm, t, <sup>3</sup> $J_{HH}$  = 6.2 [18]); Mo=CH<sub>2</sub>,  $\delta$  12.48 ppm, s.

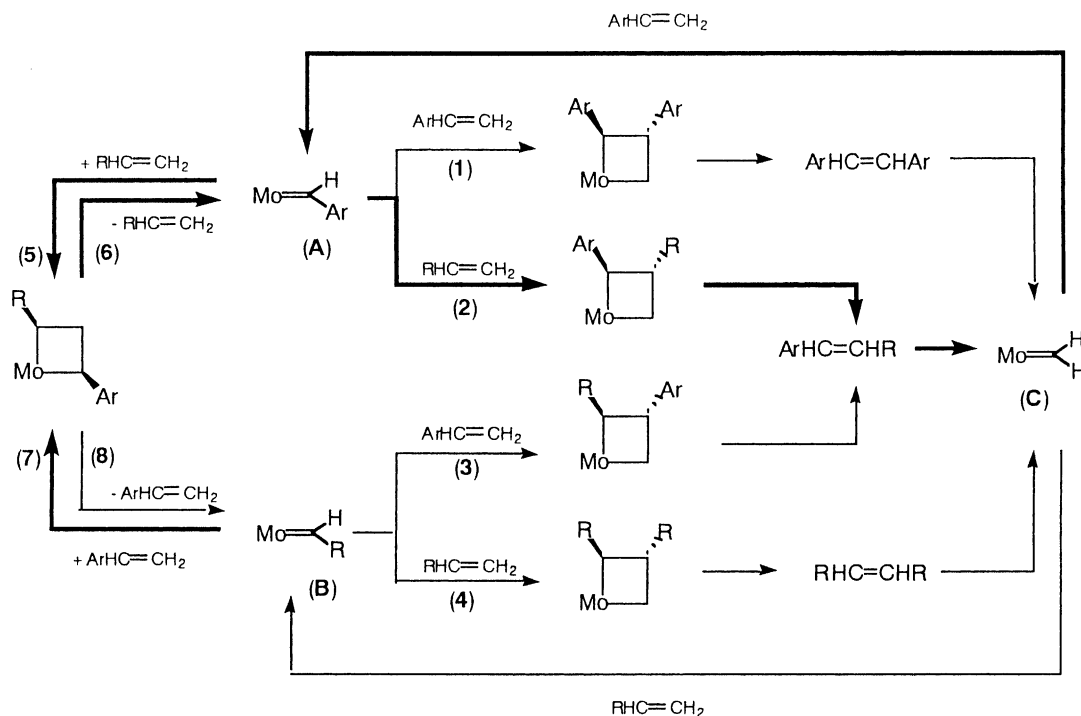


Fig. 6. Plausible reaction mechanism.

effect and the high basicity of incoming 1-octene, although the contribution to homodimer, 7-tetradecne, is few because of the small amount of heptylidene carbene **B**.

Thus, it was found that most heterodimer was produced through the reaction (2) and that the contribution of the reaction (3) was insignificant. By increasing the styrene molar ratio, the amount of tolylidene carbene **A** will increase and this enhances the reaction (2) and the contribution of the reaction (3), resulting in the higher yield of heterodimer, in accordance with experimental data shown in Fig. 4. Conclusively, the main pathways to produce heterodimer are indicated by bold arrows. Similarly, the cross-metathesis of vinylthiophene with 1-octene was investigated by  $^1\text{H}$  NMR and the data are summarized in Table 2. It was clarified that the heterodimer is produced with much higher selectivity in an analogous mechanism to the system of styrene and 1-octene.

However, further studies on the reactivities of carbenes with reactants are needed in order to obtain the

more profound understandings of the reaction mechanisms.

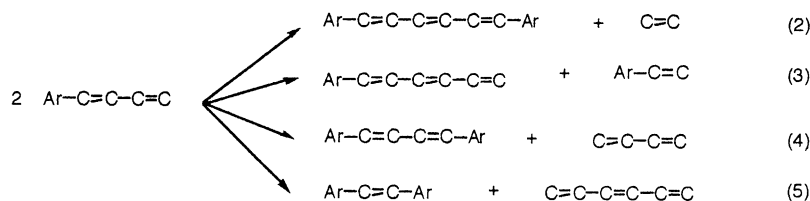
In cross-metathesis of two different kinds of vinylarene, we could not get heterodimer with high selectivity more than 50%. This must be attributed to the low selectivities in the arene carbene formation and in reactions of arene carbene with vinylarene.

### 3.4. Metathesis of aromatic compounds with 1,3-butadienyl group

The reaction rate in metathesis depends greatly on the structure of reactant and the rate decreased with increase in the steric hindrance. We have reported the relative rate shown in parenthesis as follows: 1-heptene (1.24) > 5-methyl-1-hexene (1.00) > 4-methyl-1-hexene (0.72) > 3-methyl-1-hexene (0.08) [8]. The reactivity of vinylthiophene and vinylfuran in self-metathesis was very low, but the cross-metathesis of these vinyl aromatic heterocycles with 1-octene occurred with ease and gave heterodimers

selectively. The findings suggest that formation of the  $\alpha,\beta$ -disubstituted metallacyclobutane intermediate to give homodimer is difficult due to steric hindrance.

1,3-Butadienyl aromatic compounds are interesting examples in clarifying this suspicion. The following metathesis reactions are expected for the self-metathesis:



where Ar means thiophenyl, furanyl or phenyl group.

In the case of 2-(1,3-butadienyl)thiophene, 1,6-bis(2-thiophenyl)-1,3,5-hexatriene was obtained with 34.8% yield as a sole product by Eq. (2). The reaction products attributed to Eqs. (3)–(5) were not formed. Similarly, 2-(1,3-butadienyl)furan and 1,3-butadienyl benzene gave 1,6-bis(2-franyl)-1,3,5-hexatriene and 1,6-diphenyl-1,3,5-hexatriene as a sole product, respectively. These strongly show that the low reactivity in self-metathesis of 2-vinyl heteroaromatics results in the difficulty of formation of  $\alpha,\beta$ -disubstituted metallacyclobutane due to steric hindrance.

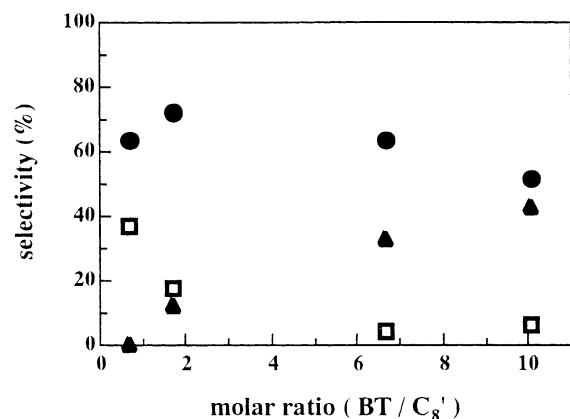
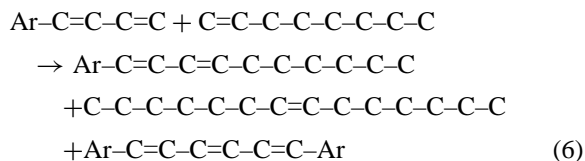


Fig. 7. Effect of molar ratio on selectivity of reaction products in cross-metathesis of 2-(1,3-butadienyl)thiophene (BT) and 1-octene (C<sub>8</sub>). (●) Heterodimer: 1-(2-thienyl)-1,3-decadiene, (□) 7-tetradecene, (▲) 1,6-dithienyl-1,3,5-hexatriene.

Cross-metathesis of 1,3-butadienyl aromatic compounds with 1-octene was further investigated.



In 2-(1,3-butadienyl)thiophene and 1-octene system, both reactants reacted to a reasonable extents for example, 52% for 2-(1,3-butadienyl)thiophene and 70% for 1-octene at molar ratio 5.7. The expected one heterodimer and two homodimers were formed, and the product distributions as a function of molar ratio are shown in Fig. 7. Heterodimer was obtained as a major product, but the selectivity was less than 71%. In 2-(1,3-butadienyl)furan and 1-octene, and 1,3-butadienyl benzene and 1-octene systems, the highest heterodimer selectivity was 49% and 73%, respectively. The decrease in heterodimer formation might be caused by the increase in formation of homodimer of 1,3-butadienyl aromatic compounds due to the decrease in steric hindrance.

#### 4. Summary

Not only styrene, but also 2-vinyl aromatic heterocycles such as furan, thiophene were successfully applied to cross-metathesis reactions with terminal olefin, and it appeared to be a promising method for the direct synthesis of various kinds of interesting molecules. The results of this study can be summarized as follows.

1. The self-metathesis of 2-vinyl aromatic heterocycles such as furan and thiophene was not successful due to steric hindrance in the formation of  $\alpha,\beta$ -disubstituted metallacycles. On the other hand, the self-metathesis of 1,3-butadienyl



aromatic compounds proceeded with ease and 1,6-diarenyl-1,3,5-hexatriene was formed as a sole product. This is caused by the decrease in steric hindrance to form  $\alpha,\beta$ -disubstituted metallacycles.

2. The cross-metathesis of 2-vinyl aromatic heterocycles (furan and thiophene) and styrene with 1-octene proceeded easily and the heterodimers were synthesized with high selectivity by using a 2–4-fold excess of aromatic heterocycles.
3. The origin of the high selectivity for heterodimer formation was 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 followings are the key steps to govern the high selectivity for heterodimer formation.
  - (1) The reactivity of methylenide carbene with aromatic compounds is much faster in comparison with 1-octene.
  - (2) The reactivity of aromatic carbenes with aromatic compounds are extremely slow, resulting in small amount of aromatic homodimers.
  - (3) The reaction of aromatic carbenes and 1-octene is fast, resulting in the high selectivity of heterodimer formation.
  - (4) The reaction of heptylidene carbene with aromatic compounds proceeds in somewhat more slower rate compared to that of aromatic carbenes with 1-octene.

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