Novel Synthesis of π-Conjugated Molecules by Cross-Metathesis of Vinylarene and Vinylferrocene with a Schrock Catalyst

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Abstract: The novel synthesis of π-conjugated molecules by the cross-metathesis reaction of vinylferrocene with a series of vinylarenes has been investigated with a molybdenum-based Schrock catalyst $(CHCMe_2Ph)Mo(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)[OCMe(CF_3)_2]_2$. The cross-metathesis product, a heterodimer, was readily obtained selectively, and only small amounts of the respective homodimers were formed. The origin of the high selectivity of heterodimer formation was elucidated through the metallacyclobutane intermediate mechanism, the observation of carbenes by *in situ* ^{1}H NMR, and the reaction products.

Keywords: chemoselectivity; conjugation; cross-metathesis; molybdenum; vinylarene; vinylferrocene

Introduction

Numerous studies on the metathesis of a broad range of alkenes in the presence of various kinds of heterogeneous and homogeneous catalysts have been reported.[1] The advent of well-defined transition metal catalysts, especially ruthenium-benzylidene complexes developed by Grubbs et al.,[2] and molybdenum imidoalkylidene complexes developed by Schrock et al.,[3] have dramatically increased their application in organic synthesis. They are now extensively used in various kinds of metathesis reactions, such as acyclic diene metathesis (ADMET),[1,4] ring-closing metathesis,[1,5] ring-opening metathesis,[1,6] and cross-metathesis[1,7] using various kinds of reactants, not only simple hydrocarbons such as alkenes and alkadienes, but also functionalized olefins containing ethers, thioethers, ketones, amines, carbonates, silanes, siloxanes, esters, and so on.[8–15]

Cross-metathesis reactions can be classified into the following four types by the combination of two reactants.

Equations (1), (2), and (3)[16,17] are easier routes by which to obtain heterodimers selectively than Equation (4).[18-22] Equation (4) seems to be the most difficult way to obtain heterodimers selectively. In the cross-metathesis reaction between two olefins with similar structures and reactivities, the product distribution of the heterodimer and the two homodimers is about 2:1:1, as expected.[18-20] However, Crowe et al. reported interesting results on selective cross-metathesis to produce heterodimers between styrene and α-olefins in the presence of a Schrock catalyst.[23] We have also demonstrated that cross-metathesis of styrene and vinylaromatic heterocycles such as vinylthiophene and vinylfuran with 1-octene occurs efficiently and produces the cross-metathesis product with very high selectivity in the presence of a Schrock catalyst.[21] On the other hand, the heterodimer in the cross-metathesis reaction cannot be obtained selectively with the Grubbs catalyst, bis(tricyclohexylphosphine)benzylidineruthenium(IV) dichloride.[22]

Not only the self-metathesis reactions of vinylarenes, but also their cross-metathesis reactions, have much less studied, and only limited data can be found in the literature.[1,21–26] Recently, we have presented the first examples of cross-metathesis between vinylferrocene and vinylarenes using a Schrock catalyst.[26] The successful application of metathesis to the chemistry of vinylarenes will provide new approaches to the direct

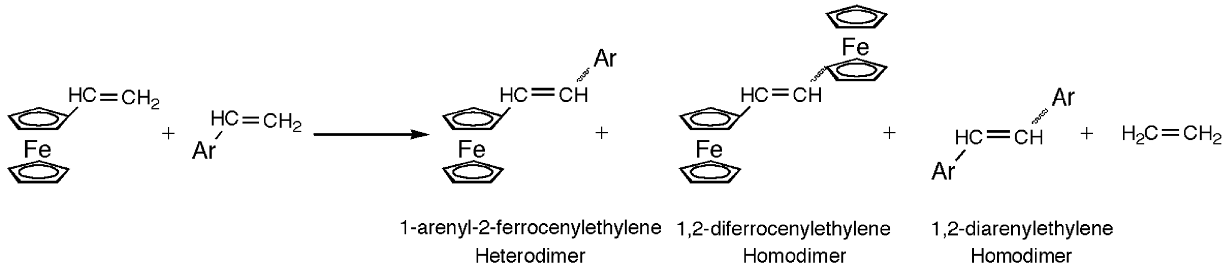
$$R^1HC{=}CHR^1 + R^2HC{=}CHR^2 \longrightarrow 2\ R^1HC{=}CHR^2 \qquad (1)$$

$$H_2C{=}CHR^1 + R^2HC{=}CHR^2 \longrightarrow R^1HC{=}CHR^2 + H_2C{=}CHR^2 + R^1HC{=}CHR^1 + H_2C{=}CH_2 \qquad (2)$$

$$H_2C{=}CR^1R^2 + H_2C{=}CHR^3 \longrightarrow R^2R^1C{=}CHR^3 + R^3HC{=}CHR^3 + H_2C{=}CH_2 \qquad (3)$$

$$H_2C{=}CHR^1 + H_2C{=}CHR^2 \longrightarrow R^1HC{=}CHR^1 + R^1HC{=}CHR^2 + R^2HC{=}CHR^2 + H_2C{=}CH_2 \qquad (4)$$

Scheme 1. Various cross-metathesis reactions.



Scheme 2. Cross-metathesis of vinylferrocene and vinylarene.

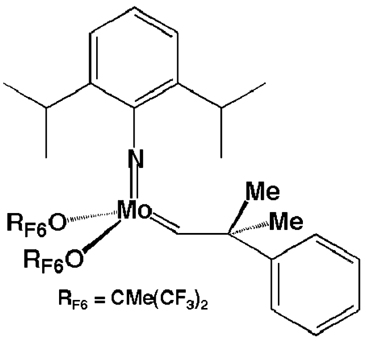


Figure 1. Schrock catalyst.

synthesis of valuable materials, and this will result in the development of new fields.

Here we report a detailed study on the cross-metathesis reaction between vinylferrocene and a series of vinylarenes (Scheme 2) to synthesize a series of interesting π-conjugated molecules with a homogeneous well-defined metathesis Schrock catalyst, as shown in Figure 1.

Ferrocene is a typical redox-active molecule and has been widely utilized in functional molecules such as dendrimers,[27] C-T complexes with TCNQ,[28] diferrocenes, to demonstrate mixed-valence properties,[29] and so on. In the present work, we focus upon a series of π-conjugated compounds due to their unique properties, including non-linear, magnetic, and electrical properties.

Results and Discussion

Self-Metathesis and Cross-Metathesis of Vinylarenes and Vinylferrocene

The self-metathesis and cross-metathesis of vinylferrocene and a series of styrenes were carried out in an NMR tube to observe the reaction behavior *in situ*. The changes in yield during the course of self- and cross-metathesis are shown in Figure 2.

The reaction proceeded at a moderate rate and did not reach equilibrium within 100 min. In the self-metathesis, the yields of stilbene and 1,2-diferrocenylethylene reached 40% and 16%, respectively. This shows that the reactivity of styrene is about 2.5 times greater than that of vinylferrocene. On the other hand, in the cross-metathesis, both homodimers were formed with less than 5% yields. The heterodimer, 1-ferrocenyl-2-phenylethylene, was formed as a main product at a rate similar to stilbene formation in the self-metathesis, and heterodimer selectivity reached up to 89%.

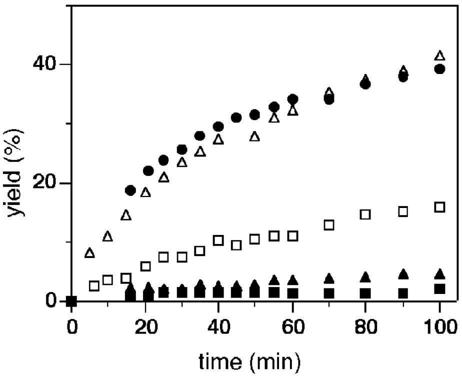


Figure 2. Products yields in self- and cross-metathesis of vinylferrocene and styrene as a function of reaction time. Reaction conditions; vinylferrocene/styrene molar ratio = 1, reactant concentration = 0.14 M, 20 °C. (vinylferrocene + vinylarene)/catalyst molar ratio = 100. Reaction products by self-metathesis (□; 1,2-diferrocenylethylene, △; stilbene). Reaction products by cross-metathesis (●; 1-ferrocenyl-2-phenylethylene, ■; 1,2-diferrocenylethylene, ▲; stilbene).

The self-metathesis and cross-metathesis of vinylferrocene and a series of vinylarenes were further carried out in a Schlenk reactor and/or in an NMR tube to investigate the reaction behavior, and the results are summarized in Table 1.

In each cross-metathesis reaction, the corresponding heterodimers were formed efficiently with selectivities greater than 71% at a reaction temperature of 20 °C, and nearly 100% selectivity was achieved for the system of vinylferrocene and vinylnaphthalene, as shown in Table 1. No side reaction products or oligomers were detected. The reaction products were the heterodimer and the two homodimers, and the homodimer of vinylarene was formed to a greater extent than that of vinylferrocene. As all reactions were carried out in a

Table 1. Results of self- and cross-metathesis of vinylferrocene and various kinds of vinylarene.[a]

Entry	Substrate	Solvent	Temp. [C]	Yield [%]	Selectivity [%]			Geometry
					homo-1[b]	homo-2[c]	hetero[d]	
self-metathesis								
1	vinylferrocene	benzene-d_6	20	16[e]		100		*trans*
2	styrene	benzene-d_6	20	40[e]	100			*trans*
3	2-vinylnaphthalene	benzene-d_6	20	-[f]				
4	4-chlorostyrene	benzene-d_6	20	25[e]	100			*trans*
5	4-*t*-butylstyrene	benzene-d_6	20	27[e]	100			*trans*
cross-metathesis								
6	styrene	CH_2Cl_2	20	55[g]	19	8	73	*trans*
7	styrene	$CHCl_3$	20	35[g]	8	3	89	*trans*
8	styrene	*n*-hexane	20	41[g]	20	16	64	*trans*
9	styrene	toluene	20	39[g]	19	3	78	*trans*
10	styrene	toluene	-15	42[g]	8	0	92	*trans*
11	styrene	toluene	50	59[g]	32	11	57	*trans*
12	2-vinylfuran	toluene	20	53[g]	7	14	79	*trans*
13	2-vinylthiophene	toluene	20	39[g]	0	9	91	*trans*
14	4-vinylbiphenyl	toluene	20	42[g]	3	9	88	*trans*
15	4-methylstyrene	toluene	20	59[g]	6	13	81	*trans*
16	styrene	benzene-d_6	20	38[e]	9	2	89	*trans*
17	2-vinylnaphthalene	benzene-d_6	20	32[e]	trace	trace	100	*trans*
18	3-methylstyrene	benzene-d_6	20	39[e]	11	3	86	*trans*
19	4-chlorostyrene	benzene-d_6	20	40[e]	29	0	71	*trans*
20	4-*t*-butylstyrene	benzene-d_6	20	28[e]	11	2	87	*trans*

[a] Reaction conditions; in self-meathesis (reactant concentration = 0.28 M, reactant/catalyst molar ratio = 100); cross-meathesis (vinylferrocene/vinylarene molar ratio = 1, each reactant concentration = 0.14 M, vinylferrocene + vinylarene)/catalyst molar ratio = 100).

[b] 1,2-Diarenylethylene.

[c] 1,2-Diferrocenylethylene.

[d] 1-Arenyl-2-ferrocenylethylene.

[e] Data at reaction time 100 min.

[f] Yield could not be determined, due to incomplete solubility of reaction products.

[g] Data at reaction time 17 h.

sealed NMR tube or a Schlenk reactor in a closed system, higher yields can be expected by removing the ethylene gas evolved.

The effect of reaction temperature on product selectivity was investigated, and the results are shown in Table 1, entries 9–11. It was found that the product selectivity depends greatly on reaction temperature and that the heterodimer selectivity increases with decreasing temperature.

The type of solvent also greatly affected product selectivity, as shown in Table 1, entries 6–9, 16. Although the effects of solvent were considered on the basis of dielectric constant and polarity, it was difficult to explain the correlation between heterodimer selectivity and these physical properties. It was found that chloroform and benzene were the most favorable solvents to obtain the heterodimer selectively.

The geometry of the vinyl moiety of the heterodimers was determined by ^1H NMR and was found to be 100% *trans* isomer. 1-Ferrocenyl-2-phenylethylene is a novel compound and the ORTEP diagram is shown in Figure 3.

It was found that the geometry of the vinyl moiety is *trans.* The benzene ring and the cyclopentadiene ring are in the same plane, suggesting the delocalization of π electrons. 1-Ferrocenyl-2-(2-naphthyl)ethylene[26] and 1-ferrocenyl-2-(3-tolyl)ethylene also have structural geometries similar to that of 1-ferrocenyl-2-phenylethylene, and the crystal data of the tolyl analogue are shown in the Experimental Section.

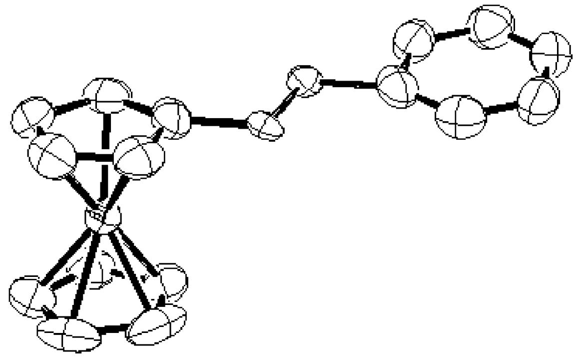


Figure 3. ORTERP diagram of *trans*-1-ferrocenyl-2-phenylethylene.

Reactivities of Reactants

The reactivities of the reactants were investigated at a molar ratio (vinylarene/vinylferrocene) of 1:1 *in situ* in an NMR tube, and the results of the heterodimer yield are shown in Figure 4.

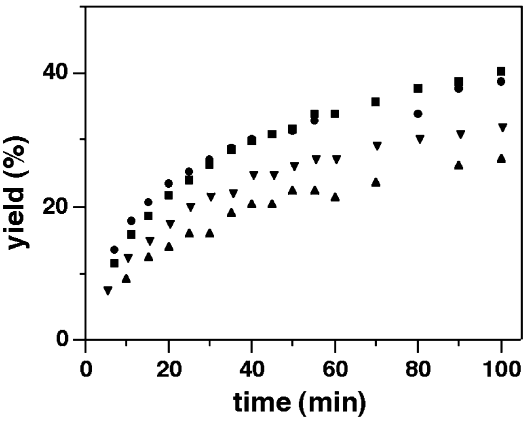


Figure 4. Heterodimer yields in the cross-metathesis of vinylferrocene and vinylarene as a function of reaction time. Reaction conditions are shown in Table 1. ●: 1-ferrocenyl-2-(3-toluyl)ethylene, ▲: 1-(4-*t*-butylphenyl)-2-ferrocenylethylene, ▼: 1-ferrocenyl-2-(2-naphthyl)ethylene, ■: 1-(4-chlorophenyl)-2-ferrocenylethylene.

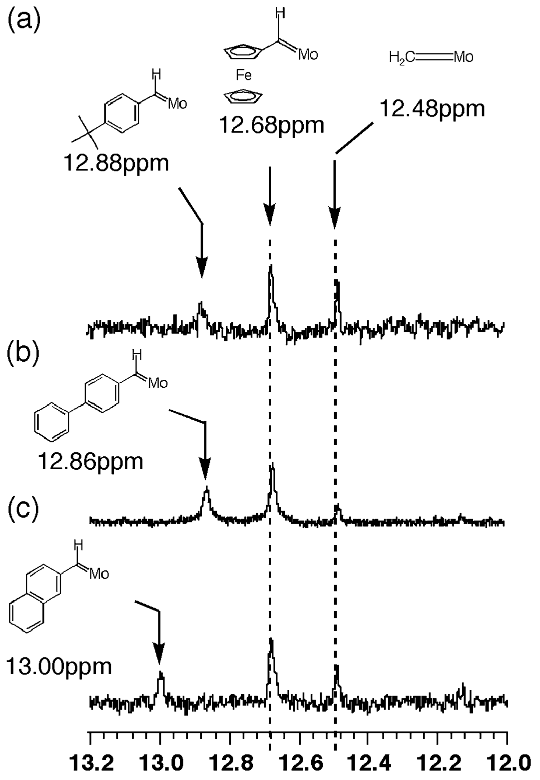


Figure 5. Observation of carbene intermediates by ^{1}H NMR in the cross-metathesis of the system; (a) vinylferrocene and 4-*t*-butylstyrene, (b) vinylferrocene and 2-vinylbiphenyl, and (c) vinylferrocene and 2-vinylnaphthalene. Reaction conditions; vinylferrocene/vinylarene molar ratio = 1, each reactant concentration = 2.5×10^{-3} M, (vinylferrocene + vinylarene)/catalyst molar ratio = 3.

The reactivities of reactants decreased as follows; styrene, *m*-methylstyrene, *p*-chlorostyrene > 2-vinylnaphthalene > *p-tert*-butylstyrene. The order of the reactivities could not be explained simply on any of the following bases; steric hindrance or basicity of the vinyl moiety.

Reaction Mechanism

In the cross-metathesis reaction of styrene and aromatic heterocycles such as vinylthiophene or vinylfuran with 1-octene, heterodimers have been obtained with selectivities greater than 90%. A plausible proposed mechanism is: (i) the aromatic carbene is easily formed, and this is attributed to the stability of the arylcarbene due to the polarizable, electron-rich metal-carbon bond;[23] and (ii) the carbene reacts much faster with 1-octene, which has a basicity stronger than that of the vinylaromatics and which has also higher steric hindrance.[21,22]

It is of interest to clarify the reasons why the cross-metathesis product, i.e., the heterodimer, is readily obtained selectively, together with only small amounts of the respective homodimers in the cross-metathesis of vinylarene with vinylferrocene, where both reactants are vinylarenes.

The observations of carbenes in the reaction solution by *in situ* ^{1}H NMR spectroscopy were carried out at room temperature. The spectra obtained for the vinylferrocene/vinylarenes system, with a molar ratio of 1:1 are shown in Fig. 5.

Three peaks derived from carbene protons were observed for each cross-metathesis. Ferrocenylidene, arenylidene, and methylidene carbene protons were assigned by the observation of carbene protons formed in each self-metathesis reaction. The methylidene carbene proton was found at 12.48 ppm in each self-metathesis species, in agreement with literature data.[21,30] It was found from the amounts of carbenes that the ratio of ferrocenylidene and arenylidene carbenes was about 2:3. The relation between the amount of carbenes and the distribution of the three dimers might also be explained through the carbene mechanisms. A plausible reaction mechanism is shown in Figure 6.

The methylidene carbene (**C**) formed after producing a dimer reacts competitively with vinylarene and vinylferrocene, and the corresponding carbenes (**A**) and (**B**) are formed. Interconversion between the two carbenes (**A**) and (**B**) *via* the α,α'-disubstituted metallacycle is much faster than other reactions [(**1**) – (**4**)] to form the α,β-disubstituted metallacycles due to smaller steric hindrance. It was found from the observation of the vinylfeocene carbenes by ^{1}H NMR that the methylidene carbene (**C**) reacted with vinylarene and vinylferrocene with an equal rate, leading to almost the same carbene concentration, as shown in Figure 5. In the self-metathesis of styrene and vinylferrocene, fair amounts of stilbene and 1,2-diferrocenylethylene were produced, as

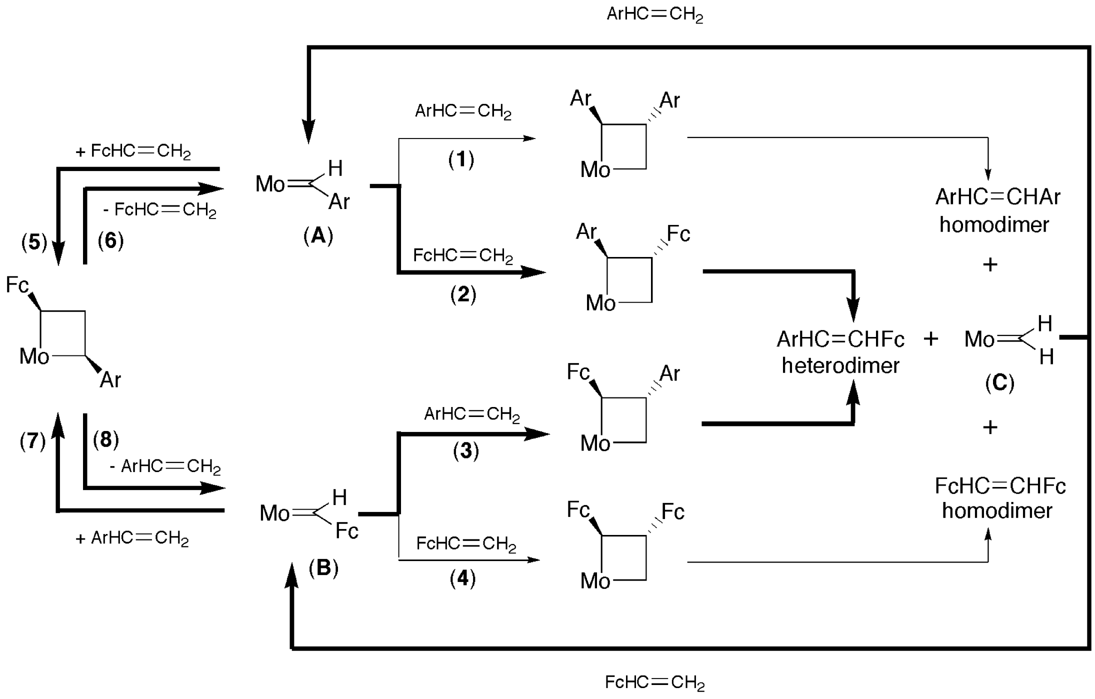


Figure 6. Plausible reaction mechanism.

shown in Figure 2 and Table 1, entries 1 and 2, and their relative reaction rates were about 2.5:1. However in the cross-metathesis, the formation of homodimers was scant, suggesting that reactions (**1**) and (**4**) are slow and that reactions (**2**) and/or (**3**) are very fast. The reaction (**3**) between the ferrocenylidene carbene (**B**) and vinylarene might be similar to that of (**2**) between arenylidene carbene (**A**) and vinylferrocene, because similar structures of metallacyclobutane intermediates are formed by their combinations. However, by considering the basicity and steric hindrance of the incoming olefins, the rate of reaction (**2**) must be much faster than reaction (**3**). Reaction (**4**) is slow due to the steric effect the even though the incoming vinylferrocene has higher basicity, compared to the reaction (**1**), where the smaller size of the incoming vinylarene is more effective in promoting the reaction than is the weaker basicity. The main pathways to produce the heterodimer are indicated by bold arrows in Figure 6. It has been clarified that the heterodimer is produced with high selectivity in a mechanism analogous to that of the system of styrene and vinylaromatic heterocycles with 1-octene.[21]

The key step controlling selective heterodimer formation is conclusively the reaction between the stable carbene and incoming olefin with higher basicity in the vinyl moiety, where steric effects have to be taken into consideration. In other words, the most favorable combination of two olefins to synthesize the heterodimer selectively is a vinylarene that produces a stable carbene easily with a Schrock catalyst and an olefin with high basicity in the vinyl moiety and small steric hindrance.

Cross-Metathesis of Divinylferrocene and Divinylbenzene

We succeeded in synthesizing a series of interesting π-conjugated molecules of the type 1-arenyl-2-ferrocenylethylene selectively by a simple one-step cross-metathesis of monovinylarene, and monovinylferrocene as described above. In order to expand this result, the cross-metathesis of divinylferrocene and divinylbenzene was attempted, and the result is shown in Figure 7.

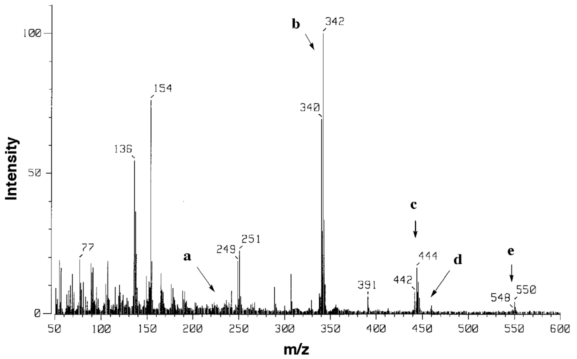
The heterodimer and alternative heterotrimer were synthesized exclusively, and the homodimer and homotrimer were not formed.

Further studies on this system will provide exciting and novel methods to synthesize more complicated and interesting π-conjugated molecules by an efficient one-step formation *via* cross-metathesis.

Conclusions

The cross-metathesis of vinylferrocene and various kinds of vinylarenes was studied in the presence of a molybdenum-based Schrock catalyst. We succeeded in selectively synthesizing a series of interesting π-conjugated molecules of the type 1-arenyl-2-ferrocenylethylene. The results can be summarized as follows.

1. The cross-metathesis product, the heterodimer with *trans* geometry, was readily obtained with high selectivity, and only small amounts of the respective homodimers were formed.



Products[a]	Formula weight		Result
homo-type products			
R^1-Ph-C=C-Ph-R^2	232.3, 234.3, 236.4	**a**	not found
C=C-Fc-C=C-Fc-C=C	448.1	**d**	not found
hetero-type products			
C=C-Fc-C=C-Ph-R^1	340.3, 342.3	**b**	found
R^1-Ph-C=C-Fc-C=C-Ph-R^2	442.4, 444.4, 446.2	**c**	found
C=C-Fc-C=C-Ph-C=C-Fc-C=C	550.3	**e**	found

[a] R^1 and/or R^2 are ethyl and/or vinyl group.

Figure 7. Cross-metathesis of 1,1′-divinylferrocene and divinylbenzene. Commercial divinylbenzene used is composed of *m*-and *p*-isomers, *ca.* 55% in ethylvinylbenzene and diethylbenzene. Reaction conditions; divinylbenzene/1,1′-divinylferrocene molar ratio = 1, 1,1′-divinylferrocene/catalyst molar ratio = 19. Reaction temperature = 0 °C, solvent = toluene. Reaction time = 40 hours.

2. The origin of the high selectivity of heterodimer formation was elucidated through the metallacyclobutane intermediate mechanism, the observation of ^{1}H NMR, and the reaction products. The key step in synthesizing the heterodimer selectively is the reaction between the stable carbene formed from vinylarene and olefin with higher basicity in the vinyl moiety.
3. Alternative π-conjugated molecules were selectively synthesized for the first time by the cross-metathesis of divinylbenzene and divinylferrocene.
4. Heterodimer selectivity was affected greatly by reaction temperature and solvent. Carrying out the reaction at low temperatures and the use of benzene or chloroform as solvents are favorable.

Experimental Section

Catalysts and Reagents

The Schrock catalyst, 2,6-diisopropylphenylimidoneophylidene-molybdenum(VI) bis(hexafluoro-*t*-butoxide) was purchased from Strem Chemicals, Inc. and used without further purification. 2-Vinylthiophene, 2-vinylfuran, and 4-vinylbiphenyl were prepared in a high yield by the Wittig reaction, according to a modified literature procedure.[31–33] 1,1′-Divinylferrocene was prepared according to literature procedures.[34] Styrene and all other chemicals including solvents were purchased from Tokyo Chemical Industry Co., Ltd. All chemicals and solvents were purified by distillation from Na under nitrogen and dried over activated 4 Å molecular sieves. 2-Vinylnaphthalene, vinylferrrocene, and 1,1′-divinylferrocne were purified by vacuum sublimation prior to use.

Procedures

All manipulations were performed using standard Schlenk techniques, and the reactions were carried out at an atmospheric pressure of nitrogen gas in a closed system. The catalysts were transferred to the Schlenk tube in a nitrogen atmosphere dry box. All glassware was carefully dried, and much attention was paid to ensure the dryness and to avoid contamination. The typical reaction conditions were as follows: reactant/catalyst molar ratio, 100/1, solvent toluene (*ca.* 1 mL), temperature = 20 °C and reaction time = 17 h unless otherwise stated. The yields and selectivities of metathesis products were calculated from the NMR spectra. The reaction behavior in a sealed NMR tube was monitored by ^{1}H NMR during the reaction time. The reactions to observe the carbenes were performed in benzene-d_6 (*ca.* 0.8 mL) using a catalyst potion of *ca.* 20 mg and a reactant/catalyst molar ratio of 3:1 at room temperature. ^{1}H NMR spectra were recorded on a JEOL JNM -EX270 (270 MHz) spectrometer. Benzene-d_6 and $CDCl_3$ were used as solvents and tetramethylsilane as the internal standard. FAB/MS (JEOL JML-LX1000), FT-IR (BIORAD FTS3000) and X-ray (Bruker Smart Apex) were used to identify the reaction products and their structures. Gel permeation chromatography (SHODEX) was used to isolate the metathesis products for spectral analysis and to check the formation of oligomer and polymer products.

***trans*-1-Ferrocenyl-2-phenylethylene:** ^{1}H NMR ($CDCl_3$): δ = 7.36 (d, *J* = 7.3 Hz, 2H), 7.25 (t, *J* = 7.3 Hz, 2H), 7.14 (t, *J* = 7.3 Hz, 1H), 6.71 (dd, *J* = 48.6 Hz, *J* = 16.2 Hz, 2H), 4.39 (t, *J* = 1.9 Hz, 2H), 4.21 (t, *J* = 1.9 Hz, 2H), 4.06 (s, 5H); FAB-MS: calcd. for $(C_{18}H_{16}Fe)^+$: 288,2; found: 288. The crystal data are as follows: $C_{18}H_{16}Fe$, Fw = 288.17, monoclinic, space group *P*2(1)/c, $D_{calc} = 4.337$ g cm^{-3}, *a* = 6.0861, *b* = 32.8338, *c* = 20.8314 Å, β = 93.619°, *V* = 4154.43 Å^3, *Z* = 12, R = 0.0878, Rw = 0.1632 for 7032, reflection with $I > 2σ$ (I).

***trans*-1-Ferrocenyl-2-thienylethylene:** ^{1}H NMR ($CDCl_3$): δ = 7.12 (d, *J* = 1.4 Hz, 1H), 6.95 (d, *J* = 3.5 Hz, 1H), 6.93 (dd, *J* = 3.5 Hz, *J* = 1.4 Hz, 1H), 6.73 (dd, *J* = 41.0 Hz, *J* = 15.9 Hz, 2H), 4.41 (t, *J* = 1.6 Hz, 2H), 4.26 (t, *J* = 1.6 Hz, 2H), 4.11 (s, 5H); FAB-MS: calcd. for $(C_{16}H_{14}SFe)^+$: 294.2; found: 294.

***trans*-1-Ferrocenyl-2-(2-furanyl)ethylene:** ^{1}H NMR ($CDCl_3$): δ = 7.36 (H, d, *J* = 7.3 Hz, 1H), 6.63 (dd, *J* = 75.9 Hz, *J* = 15.9 Hz, 2H), 6.38 (dd, *J* = 3.2 Hz, *J* = 1.9 Hz, 1H), 6.20 (d, *J* = 3.2 Hz, 1H), 4.41 (t, *J* = 1.9 Hz, 2H), 4.26 (t, *J* = 1.9 Hz, 2H), 4.11 (s, 5H); FAB-MS: calcd. for $(C_{16}H_{14}OFe)^+$: 278.1; found: 278.

***trans*-1-Ferrocenyl-2-(3-tolyl)ethylene:** ^{1}H NMR ($CDCl_3$): δ = 7.36 (d, *J* = 7.3 Hz, 2H), 7.25 (t, *J* =7.3 Hz, 2H) 7.14 (t, *J* = 7.3 Hz, 1H), 6.71 (dd, *J* = 0.18 Hz, *J* = 16.2 Hz, 2H), 4.39 (t, *J* = 18.9 Hz, 2H), 4.21 (t, *J* = 18.9 Hz, 2H), 4.06 (s, 5H); FAB-MS: calcd. for $(C_{19}H_{18}Fe)^+$: 302.2; found: 302. The crystal date are as follows: monoclinic, space group *P*21/c (No. 14), *a* = 13.377(2), *b* = 9.9889(10), *c* = 12.111(1) Å, β = 91.762°, $D_{calc} = 1.39$ g cm^{-3},

$V = 1617.6(3)$ Å^3, $Z = 4$, $R = 0.046$, $Rw = 0.036$ for 2514 reflection with $I > 3\sigma(I)$.

***trans*-1-Ferrocenyl-2-(4-biphenyl)ethylene:** ^{1}H NMR ($CDCl_3$): $\delta = 7.59$ (t, $J = 8.1$ Hz, 2H), 7.44 (H, m, 6H), 7.33 (t, $J = 7.0$ Hz, 1H), 6.75 (dd, $J = 73.7$ Hz, $J = 15.4$ Hz, 2H), 4.64 (s, 2H), 4.44 (s, 2H), 4.25 (s, 5H); FAB-MS: calcd. for $(C_{24}H_{20}Fe)^+$: 364.3; found: 364.

***trans*-1-Ferrocenyl-2-(3-tolyl)ethylene:** ^{1}H NMR ($CDCl_3$): $\delta = 7.33$ (d, $J = 8.1$ Hz, 2H), 7.13 (d, $J = 8.1$ Hz, 2H), 6.74 (dd, $J = 40.0$ Hz, $J = 16.2$ Hz, 1H), 4.44 (t, $J = 1.9$ Hz, 2H), 4.26 (t, $J = 1.9$ Hz, 2H), 4.12 (s, 5H), 2.33 (s, 3H); FAB-MS: calcd. for $(C_{19}H_{18}Fe)^+$: 302.2; found: 302.

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References and Notes

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[30] Due to the olefins with a bulky moiety, the reactivity in this system is fairly low, as shown in Figure 2. This suggests that the main reaction must be the following degenerative reaction, which does not contribute to the formation of carbenes (**A**) and (**B**), and the following productive metathesis reaction (**2**) and (**3**) in Figure 6.

$$\mathrm{Mo{=}^{*}CH_2} \xrightarrow{\mathrm{H_2C{=}CHR}} \mathrm{Mo{=}CH_2} + \mathrm{H_2{}^{*}C{=}CHR}$$

This must be the reason why the higher methylidene carbene was observed compared with the cross-metathesis between styrene and 1-octene, where only a small amounts of methylidene carbene were formed.[21]

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