# Selective Synthesis of 1-Aryl-2-ferrocenylethylene by Cross-Metathesis

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Novel synthesis of π-conjugated molecules by cross-metathesis reaction of vinylferrocene with a series of vinylarenes was 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 reactions occurred successfully and the cross-metathesis product, i.e., heterodimers, were readily obtained selectively, together with only small amounts of the corresponding self-dimers.

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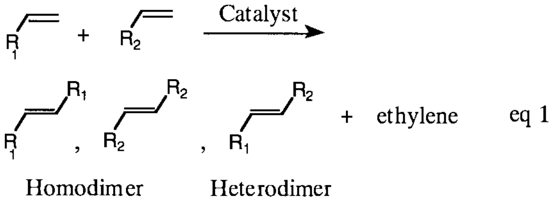
Numerous studies on metathesis of a broad range of alkenes have been reported for various kinds of heterogeneous and homogeneous catalysts.[1] The advent of well-defined transition metal catalysts, especially the ruthenium benzylidene complexes developed by Grubbs et al.[2] and the molybdenum imido alkylidene complexes developed by Schrock et al.[3] 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),[4] ring-closing metathesis,[5] ring-opening metathesis[6] and cross-metathesis[1,7] using various kinds of reactants.[8–15]

As for the cross-metathesis reactions, many studies between acyclic compounds have been reported, e.g., the synthesis of natural products, but only a few studies between aromatic compounds and acyclic compounds[1,16–19] have so far been reported. The simplified reaction scheme for the cross-metathesis of two α-olefins is depicted in Scheme 1.



**Scheme 1.**

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.[20–22] Crowe et al. reported interesting results on selective cross-metathesis to give heterodimer between styrene and α-olefins the presence of a Schrock catalyst (Figure 1).[18]

There are several studies related to self- and cross-metathesis of styrene. However, self-metathesis reactions of vinylarenes and vinyl derivatives of aromatic heterocycles, and their cross-metathesis reactions have not been adequately investigated.[23] The success of application of metathesis to the chemistry of vinylarenes and vinyl aromatic heterocycles will provide new approaches to the synthesis of valuable materials, which will unfold developments of new fields.

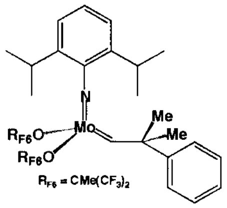


**Figure 1.** Schrock Catalyst

Here we report the cross-metathesis reaction between vinylferrocene and a series of vinylarenes to give π-conjugated molecules with a homogeneous well-defined metathesis Schrock catalyst. Ferrocene is a typical redox-active molecule and has been widely applied for functional molecules such as dendrimer,[24] C-T complex with TCNQ,[25] mixed-valence property of diferrocenes[26] and so on. Much attention should be given to such compounds due to their unique properties, e.g., magnetic, electric and nonlinear optical properties.

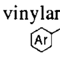
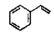
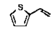
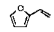
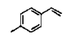
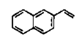
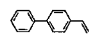
A Schrock catalyst, 2,6-diisopropylphenylimido-neophylidene-molybdenum(VI)-bis(hexafluoro-*t*-butoxide) was used without further purification.

Vinylferrocene, 2-vinylthiophene, 2-vinylfuran and 4-vinylbiphenyl were prepared in high yield by Wittig reaction in accordance with a procedure[27–29], that we adopted with modificaton.

All manipulations were performed using standard Schlenk techniques under an atmosphere of argon. Toluene dried and distilled from Na was used as a solvent. $^1$H NMR, FAB-MS, Gel Permeation Chromatography and elemental analysis were used for the analysis of metathesis products.

Vinylferrocene and vinylarenes undergo self-metathesis at reasonable rate, but surprisingly the cross-metathesis between vinylferrocene and vinylarenes occurred efficiently with high heterodimer selectivity as shown in Table 1.

**Table 1.** Results of cross-metathesis of vinylferrocene with various kinds of vinylarenes

| vinylarene  | Selectivity / % Homo-1[a] / Homo-2[b] / Hetero | Yield[c] / % | *Trans* / % |
|---|---|---|---|
|  | 4 / 9 / 87 | 62 | 100 |
|  | 0 / 9 / 91 | 51 | 100 |
|  | 7 / 14 / 79 | 65 | 100 |
|  | 6 / 13 / 81 | 55 | 100 |
|  | tr. / tr. / ~100 | 45 | 100 |
|  | 3 / 9 / 88 | 79 | 100 |

Condition ; vinylferrocene : vinylarene = 1 : 1, vinylferrocene / catalyst = 60 – 100, reaction temp = r. t., reaction time = 15 h, Ar atmosphere,
a ; 1,2-diferrocenylethylene, b ; 1,2-diarylethylene, c ; yield of heterodimer

The reaction products were the heterodimer and two homodimers. The heterodimer selectivity exceeded 80% and nearly 100% selectivity was achieved for the system of vinylferrocene and vinylnaphthalene. No side-reaction products and oligomers were detected. The homodimer of vinylarene (Homo-2) was formed in selectivity more than that of vinylferrocene (Homo-1). Although we could not get satisfactory heterodimer yields, higher yields will be achieved by investigating more suitable reaction conditions, e.g., reaction temperature, removal of ethylene formed, etc.

The geometry of the double bond of heterodimers was determined by $^1$H NMR and 100% trans isomer was found. An ORTEP diagram of 1-ferrocenyl-2-(2-naphthyl)ethylene is shown in Figure 2. The geometry of the double bond is trans isomer. Naphthalene ring and cyclopentadiene ring are on the same plane that suggests the delocalization of π electrons.

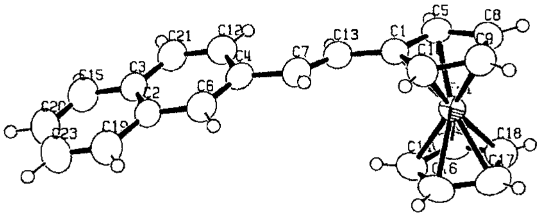


**Figure 2**. The structure of 1-ferrocenyl-2-(2-naphthyl) ethylene.

Several explanations for the selective dimer formation have been made.[16–18] Crowe et al. reported that the reaction of stable benzylidene carbene and terminal olefin with greater basicity is key to the reaction.[18] Since two olefins are aromatic compounds in our systems, similar amounts of both the corresponding carbenes will be formed. The yield curve of homodimer in self-metathesis of vinylarene as a function of reaction time was similar to that of heterodimer in vinylarene and vinylferrocene system. This suggested that both reactions occurred at similar reaction rates. Thus, selective heterodimer formation may be caused by: (i) selective reaction between ferrocenylidene carbene and vinylarene enhanced by the smaller size of the vinylarene, and (ii) selective reaction between arenilidene carbene and vinylferrocene, enhanced by the greater basicity of the vinylferrocene.

In conclusion, we succeeded for the first time to get a series of interesting π-conjugated molecules, 1-aryl-2-ferrocenylethylene selectively by cross-metathesis in the presence of a Schrock catalyst. A study of the mechanism of high heterodimer selectivity is currently in progress.

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## Reference and Notes

1 K. J. Ivin and J. C. Mol, “Olefin Metathesis and Metathesis Polymerization”, Academic Press, London 1997.
2 P. Schwab, R. H. Grubbs, and J. W. Ziller, *J. Am. Chem. Soc.*, **118**, 100(1996).
3 R. R. Schrock, J. S. Murdzek, G. C. Bazan, J. Robbins, M. Dimare, and M. O’Regan, *J. Am. Chem. Soc.*, **112**, 3875(1990).
4 J. T. Patton, J. M. Boncella, and K. B. Wagener, *Macromolecules*, **25**, 3862(1992).
5 J. T. Anhaus, V. C. Gibson, W. Clegg, and S. P. Collimgwood, *Organometallics*, **12**, 1780(1993).
6 G. C. Bazan, E. Khosravi, R. R. Schrock, W. J. Feast, V. C. Gibson, M. B. O'Regan, J. K. Thomas, and W. M. Davis, *J. Am. Chem. Soc.*, **112**, 8378(1990).
7 R. H. Grubbs and S. Chang, *Tetrahedron*, **54**, 4413(1998).
8 W. Ast and G. Rheinwald, *Rec. Trav. Chim. Pays-Bas*, **96**, M127(1977).
9 J-L. Couturier, K. Tanaka, M. Leconte, J-M. Basset, and J. Ollivier, *Angew. Chem., Int. Ed. Engl.*, **32**, 112(1993).
10 M. D. E. Forbes, J. T. Patton, T. L. Myers, H. D. Maynard, D. W. Smith, G. R. Schulz, and K. B. Wagener, *J. Am. Chem. Soc.* **114**, 10978(1992).
11 J. C. Marmo and K. B. Wagener, *Am. Chem. Soc., Polymer Prepr.*, **35**(1), 317(1994).
12 K. B. Wagener and J. T. Patton, *Macromolecules*, **26**, 249(1993).
13 T. Kawai, K. Shiga, T. Suzuki, and T. Iyoda, *J. Mol. Catl.*, **140**, 287(1999).
14 B. Marciniec and M. Lewandowski, *J. Inorg. Org. Polymers*, **5**, 115(1995).
15 R. Baker and M. J. Crimmin, *Tetrahedron Lett.*, 441(1977).
16 S. BouzBouz and Jonine Cossy, *Org. Lett.*, **3**(10), 1451(2001).
17 A. B. Smith, III, C. M. Adams, and S. A. Kozmin, *J. Am. Chem. Soc.*, **123**, 990(2001).
18 W. E. Crowe and Z. J. Zhang, *J. Am. Chem. Soc.*, **115**, 10998(1993). W. E. Crowe and D. R. Goldberg, *J. Am. Chem. Soc.*, **117**, 5162(1995).
19 S. Warwel and W. Winkelmuller, *J. Mol. Catal*, **28**, 247(1985).
20 R. Apronk and J. C. Mol, *Appl. Catal.*, **70**, 295(1991).
21 T. Kawai, N. Maruoka, M. Goke, and T. Ishikawa, *J. Mol. Catal.*, **49**, 261(1989).
22 T. Kawai, H. Goto, Y. Yamazaki, and T. Ishikawa, *J. Mol. Catal.*, **46**, 157(1988).
23 K. B. Wagener, J. M. Boncella, J. G. Nel, R. P. Duttweiler, and M. A. Hillmyer, *Makromol. Chem.*, **191**, 365(1990).
24 H. Tokuhisa, M. Zhao, L. A. Baker, V. T. Phan, D. L. Dermody, M. E. Garcia, R. F. Peez, R. M. Crooks, and T. M. Mayer, *J. Am. Chem. Soc.*, **120**, 4492(1980).
25 K-M. Chi, J. C. Calabrese, W. M. Reiff, and J. S. Miller, *Organometallics*, **10**, 688(1991).
26 R. T. Hembre, J. S. McQueen, and V. W. Day, *J. Am. Chem. Soc.*, **118**, 798(1996).
27 J. Arekion, M. Delmas, and A. Gaset, *Biomass*, **3**, 59(1983).
28 J. W. Van Reijiendam, G. H. Heeres, and M. J. Janssen, *Tetrahedron, Makromol. Chem*, **26**, 1291(1970).
29 C. G. Overberger, A. Wartman, and J. C. Salamone, *Org. Prep. Proced. Int.*, **1**(2), 117(1969).
30 The crystal data of 1-ferrocenyl-2-(2-naphthyl)ethylene are as follows; $C_{22}H_{18}Fe$, fw = 338.23 Monoclinic, Space Group $P2_1/c$(# 14), $a$ = 13.377(2), $b$ = 9.9889(10), $c$ = 12.111(1) Å, $\beta$ = 91.762°, $D_{\mathrm{calc}}$ = 1.39 g $\mathrm{cm}^{-3}$, $V$ = 1617.6(3) Å$^3$, $Z$ = 4, $R$ = 0.046, $R_w$ = 0.036 for 2514 reflection with I > 3σ(I).