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Cross metathesis reactions using γ,δ-unsaturated chromium carbene complexes

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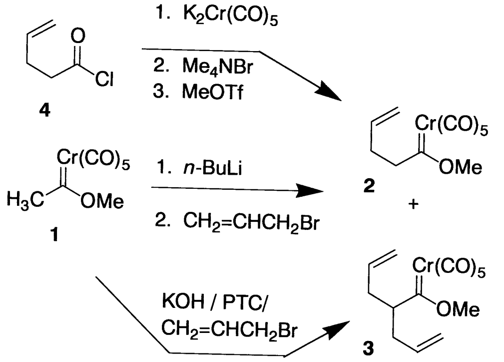
Abstract—Cross metathesis reactions of γ,δ-unsaturated carbene complexes have been explored. Successful cross metathesis was observed in cases involving electron neutral alkenes and allylic ether/ester derivatives. Attempted metathesis reactions using ethyl acrylate were not competitive with cyclopropanation reactions. © 2002 Elsevier Science Ltd. All rights reserved.

Recently, numerous uses for γ,δ-unsaturated Fischer carbene complexes have been reported. Coupling with simple alkynes leads to the formation of bicyclo[4.1.0]heptane derivatives via alkyne insertion followed by intramolecular cyclopropanation.[1] Photolysis leads to the formation of bicyclo[2.1.1]hexanones via the corresponding ketene derivatives.[2] Coupling of γ,δ-unsaturated carbene complexes with enyne–aldehydes results in construction of the hydronaphthalene ring system through isobenzofuran[3] or pyrone intermediates.[4] Thermolysis[5] or photolysis[2] of vinylcyclopropylcarbene complexes leads to cyclopentenone derivatives. Mild thermolysis of these complexes can lead to stable chelated alkene–metal carbene complexes.[6] Primary synthetic routes to these complexes (Scheme 1) involve conversion of γ,δ-unsaturated acid chlorides to carbene complexes,[2] or more conveniently through the reaction of carbene complex-stabilized carbanions with allylic halides.[1,7] The latter reaction is often complicated by overallylation, leading to formation bis allylated derivatives (e.g. **3**). Optimal conditions for the formation of **3** involve the use of phase transfer catalysts, but conditions to form **2** in the absence of **3** through allylation have not been realized. Compounds **2** and **3** are virtually inseparable due to their highly non-polar nature. Cross metathesis reactions of readily available γ,δ-unsaturated carbene complex **2** have been examined as a general synthetic route into more structurally elaborate γ,δ-unsaturated carbene complexes, and these studies are the subject of this manuscript. Only metathesis dimerization[6c,8] and ring closing metathesis[6c,9] had previously been reported for alkene-containing Fischer carbene complexes.



Scheme 1.

Initially the metathesis dimerization of simple γ,δ-unsaturated carbene complex **2** was examined (Scheme 2). A mixture of carbene complexes **2** and **3**, prepared through allylation of methylcarbene complex **1**, was treated with Grubbs' catalyst I at 40°C. This reaction provided a mixture of the RCM product **7**, a trace of dimerization product **8**, and recovered complex **2**; carbene complex **3** was completely consumed under these conditions. Subjection of the pure diallylated complex **3**[7] to catalyst **5** led to efficient formation of the RCM product **7** in 81% yield. The pure butenylcarbene complex **2**, afforded only a low yield (21%) of the dimerization product (1:1 *cis*:*trans*) using Grubbs' catalyst **5**. Reaction with the second generation Grubbs' catalyst (**6**) led to efficient formation of the metathesis dimerization product in 77% yield in a 7:1 *trans*:*cis* ratio.

Keywords: carbene complexes; metathesis; cyclopropanation.

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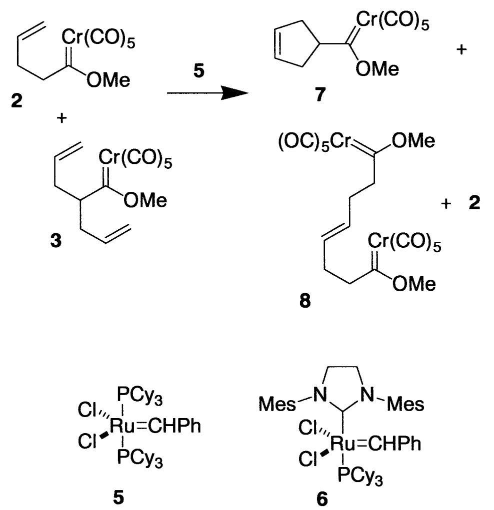
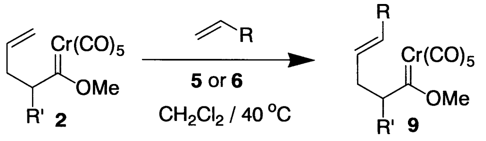


Scheme 2.

Cross metathesis reactions were examined for complex **2** and a series of monosubstituted alkenes (Table 1). In all cases using catalyst **5**, formation of cross metathesis products **9** was minimal (entries A and C).[10] Efficient formation of cross metathesis products was noted in several cases using catalyst **6** (entries B, D, and E). In general, metathesis in the presence of a 2–4 fold excess of alkene led to efficient formation of cross metathesis products with minimal formation of metathesis dimerization product **8**. The *E*:*Z* ratios were typically >9:1 using catalyst **6**. Styrene and various heteroatom-substituted alkenes (ethyl vinyl ether, *N*-vinylpyrrolidinone, and *N*-vinylphthalimide) were not useful partners in the cross metathesis reaction. Separation of γ,δ-unsaturated carbene complexes **2** and **3** is virtually impossible since both are non-polar. However, the mixture of **2** and **3** can be treated with excess allyl phenyl ether and catalyst **6** to afford mixtures of RCM product **7** and cross metathesis product **9***E* (R = OPh), which are easily separable. The cross metathesis reaction was less efficient in the more hindered system in entry G.

Table 1. Cross metathesis reactions using complex **2**

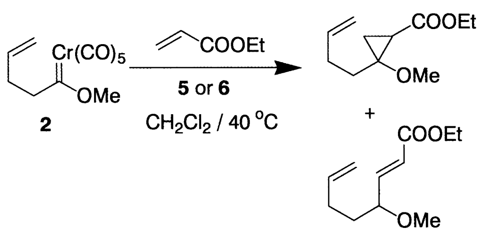


Entry	R, R′	Cat.[a]	Yield **9** (**8**)	*E*:*Z*[b]
A	CH_2OAc, H	**5**	16% (4%)	[c]
B	CH_2OAc, H	**6**	67% (6%)	9:1
C	$CH_2OCOOMe$, H	**5**	12% (3%)	[c]
D	$CH_2OCOOMe$, H	**6**	73% (12%)	10:1
E	CH_2OPh, H	**6**	90%	9:1
F	-$(CH_2)_4OH$, H	**6**	41% (1%)	9:1
G	CH_2OPh, Pr	**6**	55% (1%)	[c]

[a] In all cases, 5 mol% catalyst was used and the reaction was conducted for 7 h.

[b] The ratio could only be determined through integration of the olefinic signals in the carbon-13 spectrum.

[c] The *E*:*Z* ratio could not be determined.



Scheme 3.

No cross metathesis products were formed in the reaction involving ethyl acrylate and carbene complex **2** (Scheme 3). The exclusive products of this reaction were the cyclopropanation product **10** and its ring opening product **11**. Although this process is known to proceed at higher temperatures,[11] there is apparently no activation of this process by the metathesis catalyst since the yields of products are similar regardless of the presence or absence of the ruthenium catalyst. The cyclopropanation reaction is likely more facile in this case due to the presence of the γ,δ-unsaturation; formation of an activated complex through replacement of a CO ligand by a chelating alkene has been reported for γ,δ-unsaturated carbene complexes,[6b] and facile alkene exchange would then led to the cyclopropane derivative.

In summary, efficient cross metathesis reactions have been demonstrated for electroneutral alkenes and simple γ,δ-unsaturated carbene complex **2**. Continued examination of this process and potential uses of the highly functionalized γ,δ-unsaturated carbene complexes for phenanthrene formation is currently underway.

Acknowledgements

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References

1. Hoye, T. R.; Vyvyan, J. R. *J. Org. Chem.* **1995**, *60*, 4184–4195.
2. Moser, W. H.; Hegedus, L. S. *J. Am. Chem. Soc.* **1996**, *118*, 7873–7880.
3. Ghorai, B. K.; Herndon, J. W.; Lam, Y. F. *Org. Lett.* **2001**, *3*, 3535–3538.
4. Zhang, Y.; Herndon, J. W. *Tetrahedron Lett.* **2001**, *42*, 777–779.
5. For the most recent citation, see: Hill, D. K.; Herndon, J. W. *Tetrahedron Lett.* **1996**, *37*, 1359–1362.
6. (a) Toledano, C. A.; Levisalles, J.; Rudler, M.; Rudler, H.; Daran, J. C.; Jeanin, Y. *J. Organomet. Chem.* **1982**,

228, C7–C11; (b) Alvarez-Toledano, C.; Parlier, A.; Rudler, H.; Rudler, M.; Daran, J. C.; Knobler, C.; Jeanin, Y. *J. Organomet. Chem.* **1987**, *328*, 357–373; (c) Alvarez, C.; Pacreau, A.; Parlier, A.; Rudler, H.; Daran, J. C. *Organometallics* **1987**, *6*, 1057–1064.

7. Amin, S. R.; Sarkar, A. *Organometallics* **1995**, *14*, 547–550.
8. Licandro, E.; Maiorama, S.; Vandoni, B.; Perdicchia, D.; Paravidino, P.; Baldoli, C. *Synlett* **2001**, 757–760.
9. Sultemeyer, J.; Dötz, K. H.; Hupfer, H.; Nieger, M. *J. Organomet. Chem.* **2000**, *606*, 26–36.
10. Allylic alcohol derivatives are among the best substrates for cross metathesis reactions. See: Blackwell, H. E.; O'Leary, D. J.; Chatterjee, A. K.; Washenfelder, R. A.; Bussmann, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 58–71.
11. Wienand, A.; Reissig, H. U. *Organometallics* **1990**, *9*, 3133–3142.