Pergamon

Tetrahedron Letters 41 (2000) 5465–5468

TETRAHEDRON
LETTERS

Improved yne–ene-cross metathesis utilizing a dihydroimidazole carbene ruthenium complex

Roland Stragies, Ulrike Voigtmann and Siegfried Blechert*

Institut für Organische Chemie, Technische Universität Berlin, Straße des 17. Juni 135, D-10623 Berlin, Germany

Received 28 April 2000; accepted 24 May 2000

Abstract

Improved yne–ene cross metathesis with a 4,5-dihydroimidazolin-2-ylidene ruthenium benzylidene complex is described. The *N*-heterocyclic carbene ligands complex **2** shows significantly increased activity in the case of sterically hindered olefins when compared to **1**. Even disubstituted triple bonds are transformed into 1,2,3-trisubstituted-1,3-dienes.

Keywords: carbene complex; cycloaddition; olefin metathesis; ruthenium.

Olefin metathesis between two double bonds has become very useful as a ring closing reaction (RCM) during recent years, but it is also increasingly gaining importance as a selective cross coupling reaction (CM).[1] Comparably little is known on the use of triple bonds in such metathesis reactions. Besides well investigated polymerization reactions[2] yne–yne RCM reactions have been performed.[3] Cross coupling reactions between double and triple bonds by olefin metathesis are also possible. In contrast to ene–ene (and yne–yne) metatheses these reactions show atom economy.[4] Moreover, alkynes can participate in RCM to enable the construction of five- to eight-membered rings (Scheme 1, A).[5]

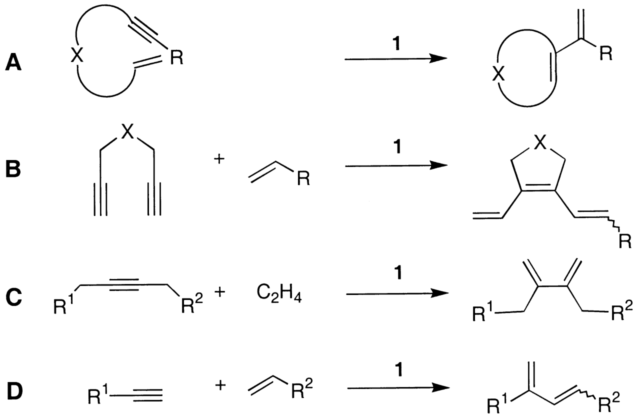
1,6-Heptadiynes can be transformed into carbo- and heterocycles by a ruthenium-catalyzed combination of RCM and CM with an alkene (Scheme 1, B).[6] Also, the addition of ethylene to disubstituted alkynes to yield 1,3-dienes has been reported (Scheme 1, C).[7] We have developed a selective yne–ene cross metathesis reaction between a monosubstituted alkyne and a terminal alkene (Scheme 1, D).[8] This yne–ene cross metathesis has exclusively been performed with Grubbs catalyst **1**.[9] Utilization of Schrocks molybdenum complex leads to polymerization of the alkyne.[10]

Herein, we report on an improved yne–ene cross metathesis using a new 4,5-dihydroimidazolin-2-ylidene ruthenium benzylidene complex **2** (Fig. 1).[11] These types of catalysts (**2**, **3**) with *N*-heterocyclic

---

* Corresponding author. Fax: 49 30 030 3142 3619; e-mail: Blechert@chem.tu-berlin.de

0040-4039/00/$ - see front matter
PII: S0040-4039(00)00858-3



Scheme 1. Metathesis reactions of triple bonds utilizing Grubbs' catalyst **1**

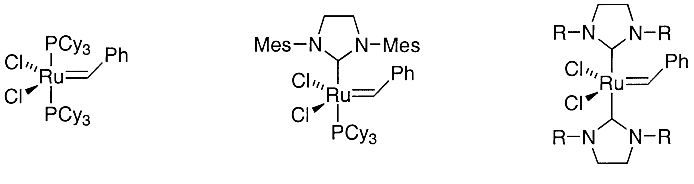


Figure 1. Ruthenium carbene complexes for olefin metathesis (Cy = cyclohexyl, Mes = C_6H_2-2,4,6-Me_3)

carbene (NHC) ligands shows considerably increased metathesis activity.[12] Even the construction of tetrasubstituted double bonds by RCM became possible.[13]

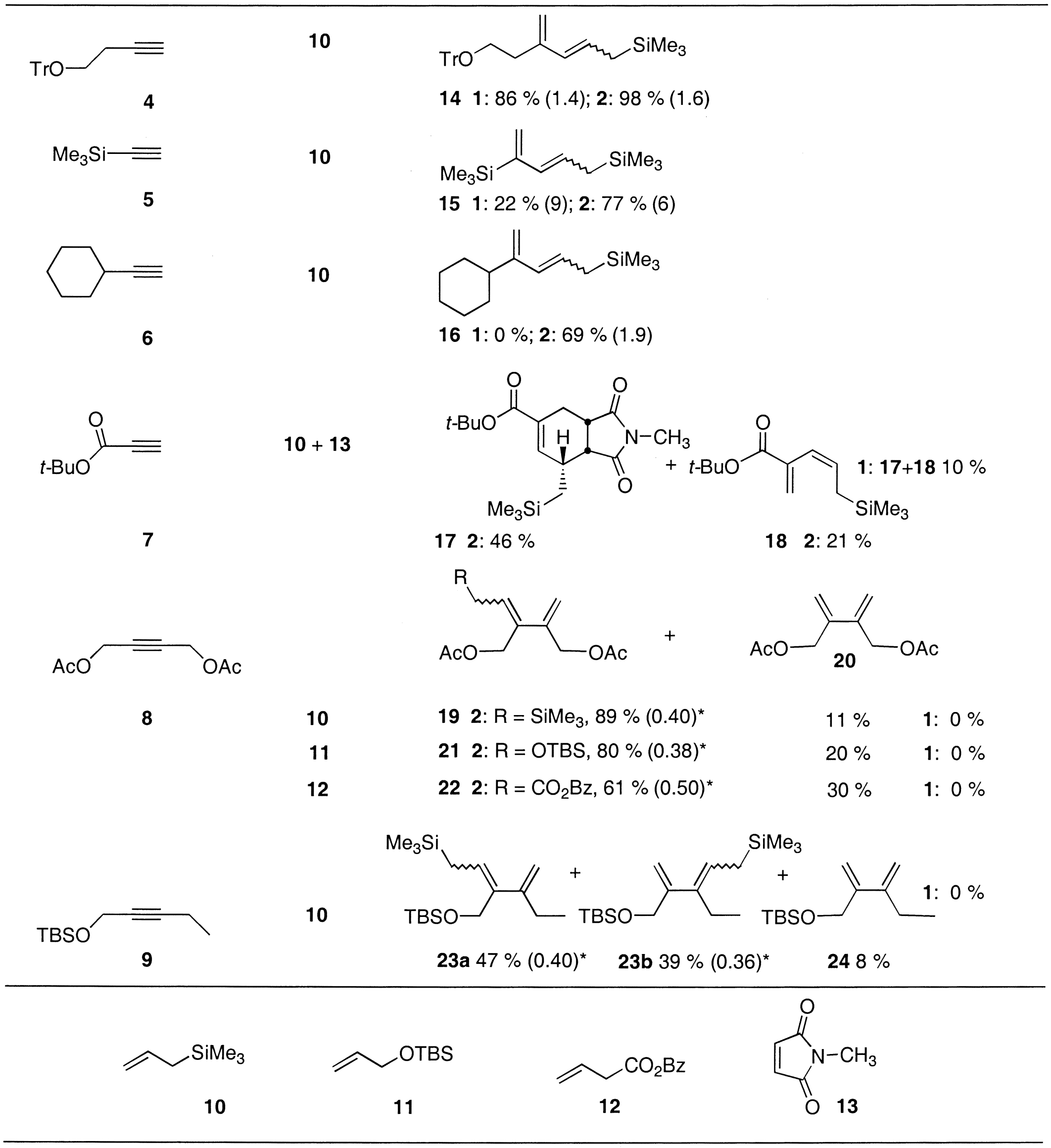
The aim of this study was to compare **1** and **2** in their ability to catalyze the yne–ene cross metathesis of different alkenes and alkynes (Table 1). All reactions have been performed with 5 mol% of **1** or **2** in CH_2Cl_2 using 3 equiv. of the alkene.

The use of **2** results in significantly improved yields in reactions of monosubstituted alkynes with trimethylallyl silane (**10**). This effect is especially pronounced in the case of sterically hindered alkynes. Notably, cross-coupling of **6** is catalyzed by **2**, exclusively. An increased yield is also observed in the conversion of the acceptor substituted acetylene **7**. The (*E*)-configurated 1,3-disubstituted butadiene resulting from the cross-coupling with **10** is not stable under the reaction conditions and easily dimerizes via a Diels–Alder reaction (not shown). However, this dimerization is prevented by the addition of a stoichiometric amount of dienophile **13** (relative to **7**) to the CM reaction. The resulting stereocontrolled synthesis of **17** represents an interesting three-component domino process. The (*Z*)-isomer **18** not participating in this Diels–Alder reaction was formed in 21% yield. The analogous reaction catalyzed by **1** afforded **17** and **18** with a combined yield of only 10%.

Remarkably, when using **2** it was possible for the first time to cross-react disubstituted acetylenes with terminal alkenes. Thus, 1,2,3-trisubstituted butadienes are accessible in moderate to good yields. The disubstituted dienes **20** and **24** are formed as side products. Attempts to transform isolated **20** into trisubstituted **19** via cross metathesis with **10** failed. These side products result from the reaction of the intermediate **29** with the corresponding olefin or ethylene. It was found

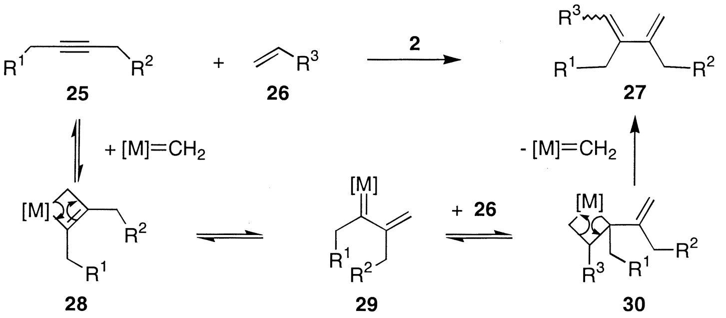
Table 1

Yne–ene metathesis. Conditions: 5 mol% **1** or **2**, CH_2Cl_2, rt, 18–24 h. (* = 40°C, ( ) = *E*/*Z*-ratio)



that the amount of side-products can be reduced by increasing the reaction temperature from 25°C to 40°C.

As to be expected, cross-coupling of the unsymmetrically substituted acetylene **9** affords regioisomeric products **23a** and **23b**. Based on our work on yne–ene metatheses, we suggest the mechanism depicted in Scheme 2. After initial attack of the catalytically active ruthenium methylidene complex at the triple bond and a subsequent [2+2]-cycloaddition–cycloreversion sequence an ene–ene cross metathesis of the resulting intermediate **29** with the olefin **26** leads to



Scheme 2. Proposed reaction path of the yne–ene cross metathesis

butadiene **27**. The formation of the 1,3-diene unit makes the overall process irreversible. Currently, we are investigating concepts to improve the regioselectivity of this process.

Acknowledgements

This work was supported by the Volkswagen Stiftung. Further, we thank S. Gessler for the preparation of catalyst **2**.

References

1. For examples and literature for CM, 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**, *112*, 58.
2. Schrock, R. R. *Pure Appl. Chem.* **1994**, *66*, 1447.
3. (a) Fürstner, A.; Seidel, G. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1734; (b) Peters, J.-U.; Blechert, S. *Chem. Commun.* **1997**, 1983.
4. Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 259.
5. (a) Kinoshita, A.; Mori, M. *Synlett* **1994**, 1020; (b) Kinoshita, A.; Mori, M. *J. Org. Chem.* **1996**, *61*, 8356. (c) Mori, M.; Kitamura, T.; Sakakibara, N.; Sato, Y. *Org. Lett.* **2000**, *2*, 543.
6. Stragies, R.; Schuster, M.; Blechert, S. *Chem. Commun.* **1999**, 273.
7. (a) Kinoshita, A.; Sakakibara, N.; Mori, M. *J. Am. Chem. Soc.* **1997**, *119*, 12388; (b) Kinoshita, A.; Sakakibara, N.; Mori, M. *Tetrahedron* **1999**, *55*, 8155.
8. (a) Stragies, R.; Schuster, M.; Blechert, S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2518; (b) Schürer, S. C.; Blechert, S. *Chem. Commun.* **1999**, 1203; (c) Schürer, S. C.; Blechert, S. *Tetrahedron Lett.* **1999**, *40*, 1877.
9. Schwab, P.; France, M. B.; Ziller, J. W., Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039.
10. Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875.
11. Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *6*, 953.
12. (a) Weskamp, T.; Schattenmann, W. C.; Spiegler, M.; Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2490; (b) Weskamp, T.; Kohl, F. J.; Hieringer, W.; Gleich, D.; Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2416; (c) Huang, J.; Stevens, E. D.; Nolan, S. P.; Petersen, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 2674.
13. Ackermann, L.; Fürstner, A.; Weskamp, T.; Kohl, F. J.; Herrmann, W. A. *Tetrahedron Lett.* **1999**, *40*, 4787.
14. All new compounds have been fully characterized. Selected spectral data of compound **19**: *Z*-isomer: ($CDCl_3$, 400 MHz) ^{1}H NMR: δ 5.65 (t, J = 9 Hz, 1H), 5.28 (s, 1H), 4.97 (s, 1H), 4.56 (s, 2H), 4.53 (s, 2H), 2.06 (s, 3H), 2.01 (s, 3H), 1.55 (d, J = 9 Hz, 2H), –0.2 (s, 9H). ^{13}C NMR δ 140.5 (C_q), 131.4 (C_q), 131.2 (CH), 116.4 (CH_2), 68.4 (CH_2), 65.7 (CH_2), 20.9 (CH_3), 20.8 (CH_3), 19.9 (CH_2), –1.8 (CH_3).