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Ruthenium-Catalyzed Cross-Metathesis between Diallylsilanes and Electron-Deficient Olefins

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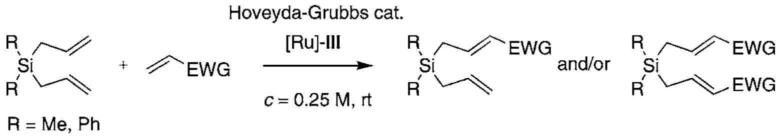
ABSTRACT

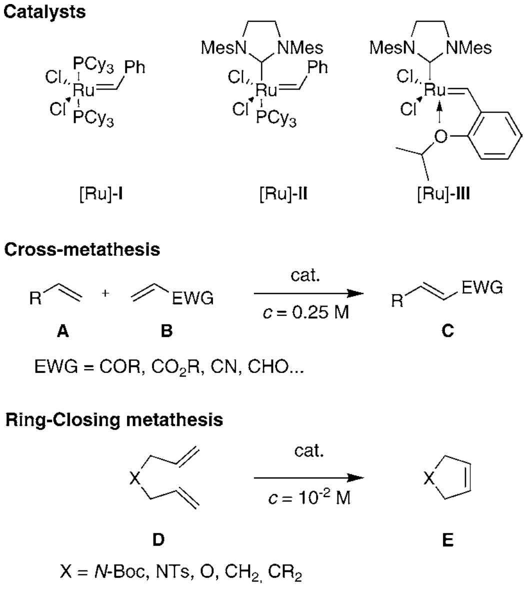


Diallylsilanes can be selectively coupled with electron-deficient olefins under cross-metathesis (CM) conditions using the Hoveyda–Grubbs catalyst to produce mono- and/or bis-CM compounds in good yield. The formation of the mono- and the bis-CM compounds depends on the nature of the electron-deficient olefin.

During the past decade, olefin metathesis has emerged as a powerful synthetic tool for the construction of carbon−carbon double bonds.[1] Recently, it has been demonstrated that highly selective cross-coupling can occur between terminal olefins in the presence of well-defined catalysts such as [Ru]-**I**,[2] [Ru]-**II**,[3] and [Ru]-**III**[4] (Scheme 1).

While these catalysts are used to perform selective cross-coupling reactions (CM) between terminal olefins of type **A** and **B** in order to produce olefins of type **C**,[5] they can also be used to achieve a ring-closing metathesis (RCM) of ω-dienes of type **D** to generate cyclic olefins of type **E**. Generally, ring-closing metathesis (RCM) is performed under

Scheme 1. Reaction Conditions and Catalysts for Ring-Closing Metathesis and Cross-Metathesis



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(1) For recent reviews, see: (a) Schuster, M.; Blechert, S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2067. (b) Grubbs, R. H.; Chang, S. *Tetrahedron* **1998**, *54*, 4413. (c) Armstrong, S. K. *J. Chem. Soc., Perkin Trans. 1* **1998**, 371. (d) Phillips, A. J.; Abell, A. D. *Aldrichim. Acta* **1999**, *32*, 75. (e) Blechert, S. *Pure Appl. Chem.* **1999**, *71*, 1393. (f) Fürstner, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3013. (g) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18.(h) Grubbs, R. H. *Handbook of Metathesis*; Wiley-VCH: Weinheim, 2003.

(2) (a) Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039. (b) Schwab, P.; Grubbs, R. R.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100.

(3) (a) Huang, J.; Stevens, E. D.; Nolan, S. P.; Petersen, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 2674. (b) Scholl, M.; Trnka, T. M.; Morgan, J. P.; Grubbs, R. H. *Tetrahedron Lett.* **1999**, *40*, 2247.

(4) (a) Kingsbury, J. S.; Harrity, J. P. A.; Bonitatebus, P. J., Jr.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1999**, *121*, 791. (b) Garber, S. B.; Kingsbury, J. S.; Gray, B. L.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2000**, *122*, 8168.

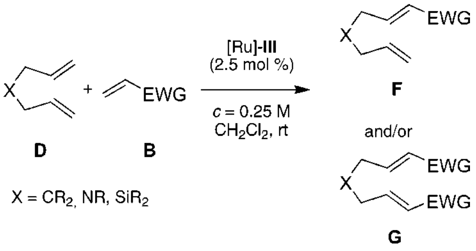
(5) For, a recent review on olefin cross-metathesis, see: Connon, S. J.; Blechert, S. *Angew. Chem, Int. Ed.* **2003**, *42*, 1900.

10.1021/ol0712632 CCC: $37.00

high dilution conditions, typically around 10^{-2} M, to favor the intramolecular coupling of the dienes. In contrast, CM is performed at higher concentration, 0.25 M, to favor the intermolecular coupling of the two olefins **A** and **B** (Scheme 1).

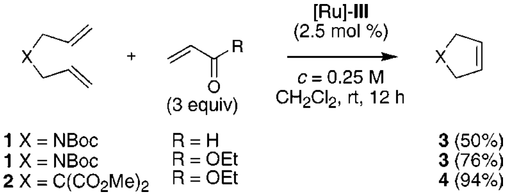
As olefins **F** and **G** can be useful synthetic intermediates, particularly when X = SiR_2,[6] their synthesis was envisaged by achieving a CM reaction between *ω*-dienes of type **D** and electron-deficient olefins of type **B** at a concentration of 0.25 M in order to favor the CM reaction (Scheme 2).

Scheme 2. Cross-Metathesis between Diallylic Compounds and Electron-Deficient Olefins: Two Possible Outcomes



Preliminary studies were performed on *ω*-dienes **1** and **2** (0.25 M solution in CH_2Cl_2) with electron-deficient olefins such as acrolein and ethyl acrylate (3 equiv) in the presence of catalyst [Ru]-**III** (2.5 mol %), for 12 h. Under these conditions, and despite the high concentration used, **1** and **2** were transformed to cyclic olefins **3** and **4** in good to excellent yields (50−94%) and no trace of the expected CM products was observed (Scheme 3).

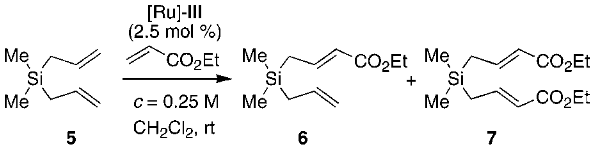
Scheme 3. Reaction of **1** and **2** under CM Conditions



These results suggested that these *ω*-dienes are not sufficiently reactive to undergo CM and have the predisposition toward cyclization by RCM. To circumvent the RCM, we decided to examine a class of substrates with a longer C−X bond length that should thermodynamically render the cyclization process more difficult and hence favor CM over RCM.[7]

As it has been demonstrated that allylsilanes are good coupling partners toward electron-deficient olefins under CM conditions,[7] and since a Si−C bond is longer than a C−C bond (~1.89 Å vs 1.54 Å), we reasoned that dimethylallylsilane **5** would represent a suitable substrate in the CM. Dimethyldiallylsilane **5** was first examined and treated with ethyl acrylate in the presence of the catalyst [Ru]-**III** at a concentration of 0.25 M in order to preferentially form CM products. In contrast to the reaction with *ω*-dienes **1** and **2**, the reaction with diallylsilane **5** afforded the corresponding product **6** as the major product (53%) together with bis-CM product **7** (12%) as a mixture of *E*,*E*/*Z*,*Z* isomers in a ratio of 5/1. No trace of the cyclized product was observed and the starting substrate was completely consumed. In order to optimize the product ratio between **6** and **7** and to improve the yields of the CM products, the effect the number of equivalents of ethyl acrylate has on the CM was examined. Compound **5** was treated with 1.5 equiv, 3.0 equiv, and 6.0 equiv of ethyl acrylate in the presence of 2.5 mol % of [Ru]-**III** catalyst, in CH_2Cl_2, at rt for 12 h (Table 1).

Table 1. Optimization of the CM in between **5** and Ethyl Acrylate by Varying the Number of Equivalents of Ethyl Acrylate



entry	CO_2Et equiv	yield% **6**	yield% **7** (*E,E/E,Z*)
1	1.5	60	12 (5/1)
2	3.0	53	16 (5/1)
3	6.0	40	53 (7/1)

When **5** was treated with 1.5 equiv of ethyl acrylate, mono-CM product (*E*)-**6** was obtained in 60% yield, accompanied by bis-CM product **7** (12% yield) as a mixture of *E*,*E*/*E*,*Z*-isomers in a ratio of 5/1 (Table 1, entry 1). In the presence of 3 equiv of ethyl acrylate, **5** was transformed to the mono-CM compounds (*E*)-**6** in 53% yield and the bis-CM compound was isolated in 16% yield as a mixture of *E*,*E*/*E*,*Z* products in a ratio of 5/1 (Table 1, entry 2). Although an increase in the number of equivalents of ethyl acrylate (6 equiv) leads to overall improvement in conversion to cross-metathesis products, the ratio of the mono-CM products to the bis-CM products appears to favor the bis-CM product (Table 1).

Dimethyldiallylsilane **5** turned out to be an excellent cross-coupling partner, and a good selectivity in the mono-CM product was obtained when the reaction was performed either with 1.5 or 3 equiv of ethyl acrylate. Having established

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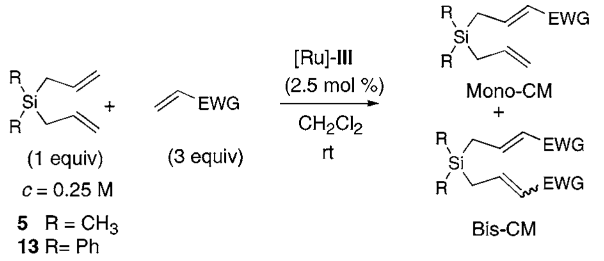
(6) See, for example: (a) Denmark, S.E.; Coe, D. M.; Pratt, N. E.; Grieder, B. D. *J. Org. Chem.* **1994**, *59*, 6161. (b) Lowe, J. T.; Panek, J. S. *Org. Lett.* **2005**, *7*, 1529 and 3231. (c) Hackman, B. M.; Lambardi, P. J.; Leighton, J. L. *Org. Lett.* **2004**, *6*, 4375. (d) Miles, S. M.; Mardsen, S. P.; Latherbarrow, R.; Coates, W. J. *J. Org. Chem.* **2004**, *69*, 6874.

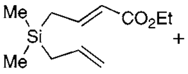
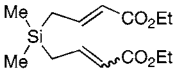
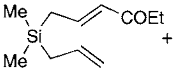
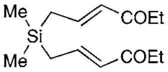
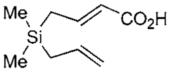
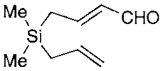
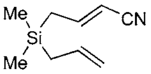
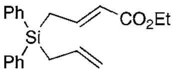
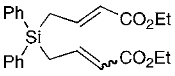
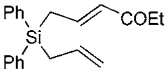
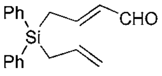
(7) Kaiser, E. T.; Panar, M.; Westheimer, F. H. *J. Am. Chem. Soc.* **1963**, *85*, 602. (b) Perozzi, E. F.; Michalak, R. S.; Figuly, G. D.; Stevenson, W. H., III; Dess, D. B.; Ross, M. R.; Marin, J. C. *J. Org. Chem.* **1981**, *46*, 1049.

(8) (a) Thibaudeau, S.; Gouverneur, V. *Org. Lett.* **2003**, *5*, 4891. (b) BouzBouz, S.; De Lemos, E.; Cossy, J. *Adv. Synth. Catal.* **2002**, *344*, 637. (c) Crowe, W. E. Goldberg, D. R. *J. Am. Chem. Soc.* **1995**, *117*, 5162.

optimal reaction conditions, we proceeded to explore other electron-deficient olefin partners of type **B** (3 equiv) with ω-diene **5**, in the presence of catalyst [Ru]-**III** (2.5 mol %) (rt, CH_2Cl_2). In all cases, the isolated major products were the mono-CM products (Table 2, entries 1−5). Ethyl vinyl ketone was found to react with **5** to produce mono-CM product **8** as the major compound (57%), accompanied by the bis-CM product **9** (14% yield) (Table 2, entry 2). When ω-diene **5** was treated with acrylic acid and acrolein, only the corresponding mono-CM compounds **10** and **11** were isolated in 44% and 48% yield, respectively (Table 2, entries 3 and 4). It is worth noting that when **5** was reacted with acrylonitrile, only a trace of the mono-CM product **12** was detected by ^{1}H NMR (Table 2, entry 5). Due to the volatility of mono-CM products **6**, **8**, and **11**, their isolation was problematic, and to overcome this difficulty, diphenyldiallylsilane **13** was used as an alternative substrate for the CM with electron-deficient olefins.

Table 2. CM between Diallylsilanes and Various Electron-Deficient Olefins



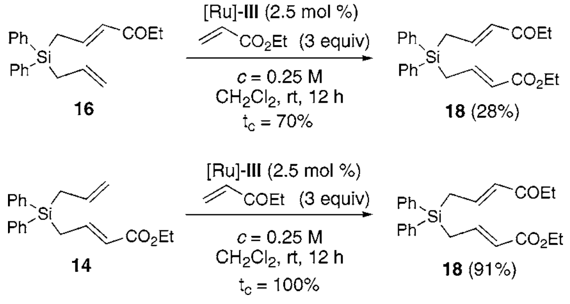
entry	5 or 13	electron-deficient olefin EWG	Mono-CM (yield)	+	Bis-CM (yield; *E*,*E*/*E*,*Z*)
1	**5**	CO_2Et	 **6** (53%)	+	 **7** (16%; 5/1)
2	**5**	COEt	 **8** (57%)	+	 **9** (14%)
3	**5**	CO_2H	 **10** (44%)		–
4	**5**	CHO	 **11** (48%)		–
5	**5**	CN	 **12** (traces)		–
6	**13**	CO_2Et	 **14** (5%)	+	 **15** (87%; 40/1)
7	**13**	COEt	 **16** (61%)		–
8	**13**	CHO	 **17** (68%)		–

Diphenyldiallylsilane **13** was treated with ethyl acrylate, ethyl vinyl ketone, and acrolein as the coupling partners in the presence of catalyst [Ru]-**III** (2.5 mol %). When **13** was reacted with ethyl acrylate, mono-CM product **14** was isolated in 5% yield and bis-CM product **15** was produced in 87% yield with a (*E*,*E*)/(*E*,*Z*) ratio of 40/1 (Table 2, entry 6). By using ethyl vinyl ketone and acrolein, the mono-CM products **16** and **17** were the only isolated products in 61% and 68% yield, respectively (Table 2, entries 7 and 8).

The cross-coupling metathesis between dimethyl-/diphenyldiallylsilanes was selective when ethyl vinyl ketone, acrylic acid, and acrolein were used, as the mono-CM compounds were the only isolated compounds. On the contrary, when ethyl acrylate was employed, the reaction was not as selective as when the other electron-deficient olefins were used, and the mono- and/or the bis-CM products were formed (Table 2, entries 1 and 6).

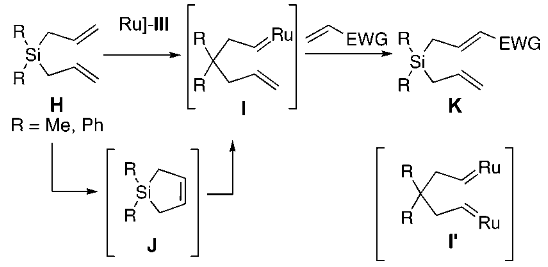
The methodology can be elaborated to synthesize nonsymmetric bis-CM products from mono-CM compounds. This was demonstrated when compound **16** was treated with 3 equiv of ethyl acrylate. After 12 h, compound **18** was isolated in 28% yield and 30% of starting material **16** was recovered. A better result was obtained when **14** was treated with ethyl vinyl ketone as the starting material was completely consumed and the nonsymmetric bis-CM product **18** was isolated in 91% yield, suggesting that compound **14** is more reactive than compound **16** in the CM process (Scheme 4).

Scheme 4. Reaction of the Mono-CM Products with Electron-Deficient Olefins



One of the main consideration for the formation of the mono-/bis-CM products from ω-dienes is the predisposition of the starting material to cyclize (Scheme 5).

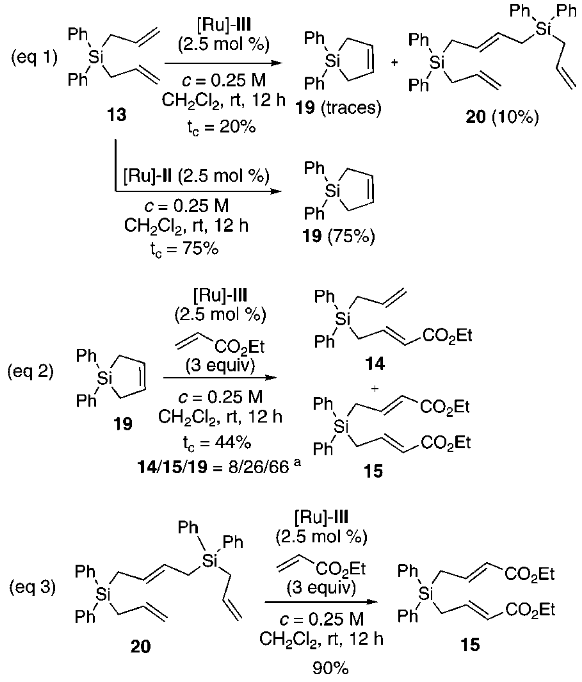
Scheme 5. Possible Reaction Pathways for the Formation of the Mono-CM Product



The mono-CM products can be the result of a direct cross-metathesis reaction between the diallylsilanes of type **H** and an electron-deficient olefin via intermediate **I**, but we cannot rule out that a fast RCM reaction may take place to produce an unsaturated cyclic silane intermediate of type **J** which can then undergo a ring-opening metathesis (ROM) to generate the same intermediate **I** as five-membered cyclic silane can be opened easily[7] (Scheme 5). In order to verify if **I** could be produced from cyclic intermediate **J**, **19** has to be synthesized and treated with [Ru]-**III** catalyst in the presence of ethyl acrylate (Scheme 6).

When compound **13** was treated with catalyst [Ru]-**III** (2.5 mol %) in CH_2Cl_2 at rt for 12 h, **19** was not formed, and dimer **20** was obtained in 10% yield (Scheme 6, eq 1). This result suggests that the mono- and bis-CM products are not generated through the cyclic intermediate **J**. Furthermore, when cyclic olefin **19** [prepared from **13** in the presence of [Ru]-**II** (2.5 mol %) in CH_2Cl_2 for 12 h, 75% yield] was subjected to the ring-opening metathesis (ROM) with ethyl acrylate in the presence of [Ru]-**III** (2.5 mol %) in CH_2Cl_2 at rt for 12 h, the GC/MS analysis of the crude mixture showed three compounds: mono-CM product **14**, bis-CM compound **15,** and starting material **19** in a ratio of 8/26/66 (Scheme 6, eq 2). This result indicates that **19** is not participating or only has a minor contribution to the formation of the mono- and the bis-CM compounds (Table 2, entry 6), thus ruling out a RCM-ROM process in the synthesis of dienes **K**. However, we cannot exclude that bis-CM product **15** comes from dimer **20** as the treatment of the dimer with ethyl acrylate (3 equiv) and [Ru]-**III** (2.5 mol %) (CH_2Cl_2, rt, 12 h) produced **15** in 90% yield (Scheme 6, eq 3).

Scheme 6. CM of **13**, **19**, and **20** with Ethyl Acrylate



[a] The ratio of products was determined by GC/MS.

We have shown that under the cross-metathesis conditions ([Ru]-**III**, CH_2Cl_2, rt, 12 h, $c = 0.25$ M), diallylsilanes can be selectively coupled with electron-deficient olefins to produce mono-CM products and/or bis-CM compounds in good yields and the ratio of the mono-CM and bis-CM products depends on the nature of the electron-deficient olefin partners. The mono-CM products of type **F** and the bis-CM products of type **G** are readily accessible from diallylsilanes and can be useful synthetic intermediates.

In conclusion, and according to these results, it appears that the cross-metathesis reaction of diallylsilanes with electron-deficient olefins in the presence of Ru-[III], can produce an intermediate of type **I**; however, the formation of intermediate **I'** (Scheme 5) cannot be excluded in the formation of the mono- and bis-CM products.

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Supporting Information Available: Experimental procedures and characterization data for compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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