



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

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## 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. © 2000 Elsevier Science Ltd. All rights reserved.

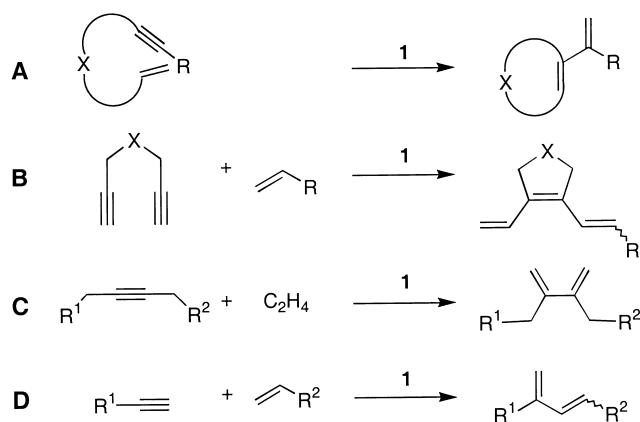
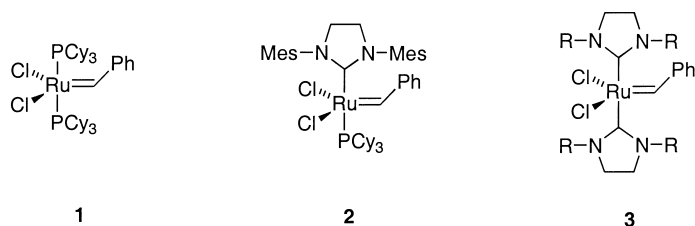
*Keywords:* carbene complex; cycloaddition; olefin metathesis; ruthenium.

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).<sup>1</sup> Comparably little is known on the use of triple bonds in such metathesis reactions. Besides well investigated polymerization reactions<sup>2</sup> yne–yne RCM reactions have been performed.<sup>3</sup> 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.<sup>4</sup> Moreover, alkynes can participate in RCM to enable the construction of five- to eight-membered rings (Scheme 1, A).<sup>5</sup>

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).<sup>6</sup> Also, the addition of ethylene to disubstituted alkynes to yield 1,3-dienes has been reported (Scheme 1, C).<sup>7</sup> We have developed a selective yne–ene cross metathesis reaction between a monosubstituted alkyne and a terminal alkene (Scheme 1, D).<sup>8</sup> This yne–ene cross metathesis has exclusively been performed with Grubbs catalyst **1**.<sup>9</sup> Utilization of Schrock's molybdenum complex leads to polymerization of the alkyne.<sup>10</sup>

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

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Scheme 1. Metathesis reactions of triple bonds utilizing Grubbs' catalyst **1**Figure 1. Ruthenium carbene complexes for olefin metathesis (Cy = cyclohexyl, Mes = C<sub>6</sub>H<sub>2</sub>-2,4,6-Me<sub>3</sub>)

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

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<sub>2</sub>Cl<sub>2</sub> 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*)-configured 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%.

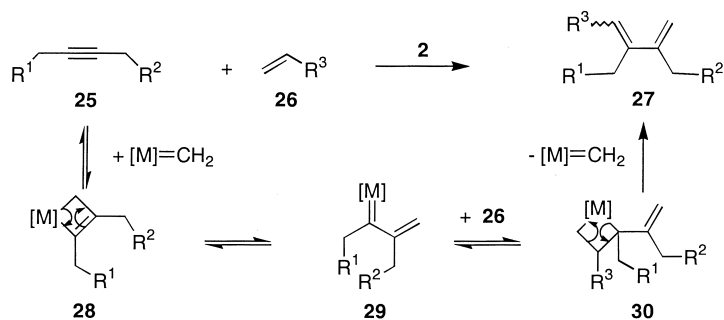
Remarkably, when using **2** it was possible for the first time to cross-react disubstituted acetylenes with terminal alkenes. Thus, 1,2,3-trisubstituted butadienes are accessible in moderate to good yields. The disubstituted dienes **20** and **24** are formed as side products. Attempts to transform 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<sub>2</sub>Cl<sub>2</sub>, rt, 18–24 h. (\* = 40°C, () = E/Z-ratio)

	10		<b>14</b> <b>1</b> : 86 % (1.4); <b>2</b> : 98 % (1.6)
	10		<b>15</b> <b>1</b> : 22 % (9); <b>2</b> : 77 % (6)
	10		<b>16</b> <b>1</b> : 0 %; <b>2</b> : 69 % (1.9)
	10 + 13		<b>17</b> <b>2</b> : 46 %
			<b>18</b> <b>2</b> : 21 %
			<b>19</b> <b>2</b> : R = SiMe <sub>3</sub> , 89 % (0.40)*
	10		11 %
	11	<b>21</b> <b>2</b> : R = OTBS, 80 % (0.38)*	20 %
	12	<b>22</b> <b>2</b> : R = CO <sub>2</sub> Bz, 61 % (0.50)*	30 %
			1: 0 %
			1: 0 %
			1: 0 %
	10		<b>23a</b> 47 % (0.40)*
			<b>23b</b> 39 % (0.36)*
			<b>24</b> 8 %
			1: 0 %
	<b>10</b>		
	<b>11</b>		
	<b>12</b>		
	<b>13</b>		

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.

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- All new compounds have been fully characterized. Selected spectral data of compound **19**: Z-isomer: (CDCl<sub>3</sub>, 400 MHz) <sup>1</sup>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). <sup>13</sup>C NMR δ 140.5 (C<sub>q</sub>), 131.4 (C<sub>q</sub>), 131.2 (CH), 116.4 (CH<sub>2</sub>), 68.4 (CH<sub>2</sub>), 65.7 (CH<sub>2</sub>), 20.9 (CH<sub>3</sub>), 20.8 (CH<sub>3</sub>), 19.9 (CH<sub>2</sub>), -1.8 (CH<sub>3</sub>).