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# A novel non-metathetic behavior of Grubbs catalyst: Ruthenium-mediated intramolecular [3 + 2] cycloaddition of bis-1,3-dienes

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### 1. Introduction

The stable and highly active ruthenium–carbene complexes developed by Grubbs and others as catalysts for olefin metathesis are a series of innovative reagents for carbon–carbon bond formation reactions in organic synthesis (Fig. 1) [1]. Nowadays, ruthenium-catalyzed olefin metathesis has become an important tool in many fields of chemistry, including organic synthesis [2,3], biochemistry [4], and green chemistry [5]. Furthermore, ruthenium–carbene complexes have been reported to catalyze non-metathetic reactions [6].

Several tandem processes involving olefin metathesis have been developed by taking advantage of both the potential reactivity of olefins and the tolerance of ruthenium–carbene complexes to various functional groups. Many successful tandem processes involve combinations of olefin metathesis reactions with ruthenium-catalyzed non-metathetic reactions that proceed under the same conditions [7].

The  $6\pi$ -electrocyclization is also a suitable reaction for the development of tandem process [8]. We hypothesized that a combination of an RCM between terminal bis-1,3-diene to generate a 1,3,5-hexatriene with the subsequent  $6\pi$ -electrocyclization would provide a useful tandem process for building polycyclic molecules in a one-pot process (Scheme 1).

### ABSTRACT

A ruthenium-mediated intramolecular [3+2] cycloaddition of bis-1,3-dienes to give bicyclic products, which is a novel non-metathetic behavior of Grubbs catalyst, is reported. The formation of a ruthenium–olefin complex is proposed to be a key step for the success of the reaction.

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On the basis of this hypothesis, we examined the reaction of diene 1a with ruthenium-carbene complex I (Scheme 2, entry 1). In this reaction, a stoichiometric amount of complex I was required to ensure complete consumption of diene 1a. Although the compounds **3** and **4**, which are the products of an RCM or a tandem RCM/ $6\pi$ -electrocyclization process of diene **1a**, respectively, were not obtained, an unexpected bicyclic compound 2a was obtained in 29% yield, together with styrene (ca. 35% yield) and benzaldehyde (ca. 10% yield) (Fig. 2) [9,10]. When diene 1a was treated with complex II or III, which are more reactive olefin metathesis catalysts than complex I, a stoichiometric amount of complex was not required to ensure complete consumption of diene 1a (Scheme 2, entries 2 and 3). However, no improvement on the chemical vield of 2a was observed. In this article, we wish to report the detail of the novel non-metathetic behavior of Grubbs catalyst in the reaction of diene 1.

### 2. Results and discussion

A plausible reaction pathway for the reaction of diene **1a** with complex **I** is outlined in Scheme 3. The reaction pathway can be rationalized by a ruthenium-mediated intramolecular [3 + 2] cycloaddition. Thus, cross metathesis reaction of diene **1a** with complex **I** produce ruthenium-alkenyl carbene complex **5**, followed by an intramolecular [3 + 2] cycloaddition to afford bicyclic compound **2a**. The reaction pathway accords with the formation of styrene and the requirement for a stoichiometric amount of complex **I**. Benzaldehyde may be formed in the reaction of complex





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Fig. 1. Ruthenium-carbene complexes I-III.



Scheme 1. Hypothesized tandem process of bis-dienes.



<sup>a</sup> Isolated yield.

Scheme 2. Reaction of diene 1a with complexes I–III.



Fig. 2. RCM product 3 and RCM/ $6\pi$ -electrocyclization product 4.

I with adventitious traces of  $H_2O$  in the solvent and/or atmosphere [11]. There was no improvement in the chemical yield of **2a** when we used complex II or III. This may be as a result that complex II or III more catalyze oligomerization of diene **1a** by cross metathesis than complex I. Therefore, we considered complex I to be a suitable reagent for the ruthenium-mediated intramolecular [3 + 2] cycloaddition. Complex I was used for the further investigations to explore the scope of the cycloaddition.

Next, we examined the effects of the substituents on the diene moieties to the novel non-metathetic reaction (Table 1). The chemical yields of compounds **2** formed in the reactions of the C3'-demethylated diene **1b** and the C2-methylated diene **1c** were superior to that of **2a**. The reaction of diene **1c** proceeded with a satisfactory yield. This improvement in reaction yield may be due to inhibition of cross metathesis oligomerization of diene **1c** as a result of the introduction of the methyl groups at the C2- and the C3'-position.

The formation of other bicyclic systems (5-5 and 5-7 ring systems) by the ruthenium-mediated intramolecular [3 + 2] cycloaddition of dienes **1d** and **1e** were examined (Table 2). The bicyclic product **2d** was formed by treating diene **1d** with complex I in refluxing CH<sub>2</sub>Cl<sub>2</sub> for 3 h [10]. In the case of diene **1e**, the ruthenium-mediated intramolecular [3 + 2] cycloaddition of the initially generated ruthenium–alkenyl carbene complex **5** did not proceed. Instead, the ruthenium–alkenyl carbene complex **5** reacted with styrene to give the cross metathesis product **6**.

The ruthenium-mediated intramolecular [3 + 2] cycloaddition of dienes **1f-h**, which are geometric isomers of dienes **1c,d** at the C3–C4 or the C3'–C4' double bonds, was also examined (Table 3). The reaction of diene **1f** with complex **I** did not afford a [3 + 2]cycloaddition product but the cross metathesis product **7**. When dienes **1g** and **1h** were treated with complex **I**, a high reaction temperature was required to ensure consumption of the dienes. In the reactions, the trace amounts of corresponding [3 + 2] cycloaddition products **2g** and **2h** were obtained, respectively (Table 3, entries 2 and 3). These experimental results suggest that the substituents and geometry of the diene moieties and the ring sizes



Scheme 3. Plausible reaction pathway for the reaction of diene 1a with complex I to bicyclic compound 2a.

Reaction of dienes <b>1b,c</b> with complex <b>I</b> .			
Entry	Diene	Conditions	Product <sup>a</sup>
1	$1 \xrightarrow{2} CO_2Me$ $3 \xrightarrow{4} CO_2Me$ $1 \xrightarrow{2'} 4'$ $1 \xrightarrow{2'} 3'$ $1 \xrightarrow{2'} 1 \xrightarrow{4'}$	Complex I (0.7 equiv.), 4 h	СО <sub>2</sub> Ме <u>H</u> СО <sub>2</sub> Ме <b>2b</b> : 43%
2	CO <sub>2</sub> Me CO <sub>2</sub> Me	Complex I (1.6 equiv.), 12 h	$\overline{H}$ CO <sub>2</sub> Me $\overline{CO_2}$ Me <b>2c</b> : 72%

<sup>a</sup> Isolated yield.

Table 1

### Table 2 Reaction of dienes 1d.e with complex I.



<sup>a</sup> Isolated yield.

<sup>b</sup> Compound **6** could not be completely purified due to instability.

### Table 3

Reaction of dienes **1f-h** with complex **I**.



<sup>a</sup> Isolated yield.

<sup>b</sup> Compound **7** could not be completely purified due to instability.

of the products are important factors for the formation of the ruthenium-mediated intramolecular [3 + 2] cycloadducts.

In the ruthenium-mediated intramolecular [3 + 2] cycloaddition, new C–C bonds are formed between the C3–C4 double bond and the C2'–C4' moiety. At the same time, the C1–C2 double bond does not formally participate in the C–C bond formation. To elucidate the role of the C1–C2 double bond, we examined the reaction of complex **I** with diene **1i**, in which the C1–C4 diene moiety was replaced by one double bond (Scheme 4). In this case, the ruthenium-mediated intramolecular [3 + 2] cycloaddition did not proceed and the cross metathesis product **8** was obtained. The



Scheme 4. Reaction of diene 1i with complex I.

result suggests that the coordination of the C1–C2 double bond to Ru metal in ruthenium–alkenyl carbene complex **5** is essential for the success of the intramolecular [3 + 2] cycloaddition as is the case in olefin metathesis [12]. When dienes **1a,b** were treated with complex **I**, other bicyclic product, which was formed by the ruthenium-mediated intramolecular [3 + 2] cycloaddition between the C2–C4 moiety and the C3'–C4' double bond, was not observed. The fact may indicate that the coordination of the C1'–C2' double bond to Ru metal in ruthenium–alkenyl carbene complex, which is generated by cross metathesis between the C1–C2 double bond and complex **I**, is relatively unstable and the ruthenium–alkenyl carbene complex lead to oligomerization.

A proposed mechanism for the ruthenium-mediated intramolecular [3 + 2] cycloaddition is outlined in Scheme 5. This mechanism, which is based on that of a metal-mediated [3 + 2]cycloaddition of Fischer alkenyl carbene complexes [13], involves the formation of ruthenacycle **A** by an intramolecular metalla-Diels-Alder reaction of ruthenium–alkenyl carbene complex **5**. This is followed by the reductive elimination to generate the [3 + 2]



Scheme 5. Proposed mechanism for the ruthenium-mediated intramolecular [3 + 2] cycloaddition and relative energies for the model system.

cycloaddition product **2a**. The computations on the model reaction, using the density functional theory (BP86), support the reaction mechanism [14]. Thus, the Gibbs energy of activation ( $\Delta G^{\ddagger}$ ) at 298 K was computed to be 28.7 kcal mol<sup>-1</sup>, which is relative to complex **5** (Scheme 5) [15].

### 3. Conclusion

In conclusion, a ruthenium-mediated intramolecular [3 + 2] cycloaddition of bis-1,3-dienes to give bicyclic products, which is a novel non-metathetic behavior of Grubbs catalyst, is discovered. It is suggested that the coordination of the C1–C2 double bond to Ru metal in ruthenium–alkenyl carbene complex **5** is a key step for the success of the intramolecular [3 + 2] cycloaddition. Although the ruthenium-mediated intramolecular [3 + 2] cycloaddition is very narrow scope at present stage, the mechanistically and synthetically fascinated reaction would stimulate further investigation on the novel type of ruthenium-mediated non-metathetic reactions.

### 4. Experimental section

## 4.1. General procedure for the reaction of diene **1** with ruthenium–carbene complexes **I–III**

Diene **1** and ruthenium—carbene complex **I** were dissolved in  $CH_2Cl_2$  (10 mM). The mixture was refluxed until diene was disappeared. The solvent was evaporated. The residue was purified by preparative TLC on silica gel (hexane/AcOEt).

4.2. 5,5-Dimethoxycatbonyl-3,7a-dimethyl-1-vinyl-3a,4,5,6,7,7a-hexahydro-1H-indene (**2a**)

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) δ 5.76 (ddd, J = 18.2, 10.4, 7.8 Hz, 1H), 5.29 (bs, 1H), 5.07 (d, J = 7.8 Hz, 1H), 5.04 (s, 1H), 3.39 (s, 3H), 3.30 (s, 3H), 2.74–2.71 (m, 1H), 2.70 (dt, J = 12.7, 1.8 Hz, 1H), 2.57 (d, J = 13.7 Hz, 1H), 2.23 (d, J = 13.7 Hz, 1H), 2.13 (dd, J = 13.7, 12.5 Hz, 1H), 1.99 (td, J = 13.7, 4.6 Hz, 1H), 1.81 (td, J = 13.7, 4.2 Hz, 1H), 1.61–1.54 (m, 1H), 1.55 (bs, 3H), 0.77 (s, 3H); <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>) δ 172.8, 171.8, 142.0, 137.5, 126.7, 115.8, 59.6, 56.4, 52.8, 52.2 (×2), 49.2, 33.7, 28.0, 27.7, 14.3, 13.4; HR-EIMS m/z [M<sup>+</sup>] calcd. for C<sub>17</sub>H<sub>24</sub>O<sub>4</sub> 292.1675, found 292.1680.

4.3. 5,5-Dimethoxycarbonyl-7a-methyl-1-vinyl-3a,4,5,6,7,7a-hexahydro-1H-indene (**2b**)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  5.84–5.77 (m, 1H), 5.76–5.74 (m, 1H), 5.71 (ddd, *J* = 5.8, 3.2, 1.5 Hz, 1H), 5.10–5.09 (m, 1H), 5.07 (ddd, *J* = 4.6, 2.1, 1.1 Hz, 1H), 3.76 (s, 3H), 3.71 (s, 3H), 2.77–2.75 (m, 1H), 2.49 (dt, *J* = 13.1, 2.0 Hz, 1H), 2.35 (dddd, *J* = 14.2, 5.9, 2.7, 1.8 Hz, 1H), 2.11 (dddd, *J* = 14.0, 6.3, 3.4, 2.0 Hz, 1H), 2.04 (dd, *J* = 14.0, 13.1 Hz, 1H), 1.87 (ddd, *J* = 14.2, 12.2, 5.9 Hz, 1H), 1.69–1.58 (m, 2H), 0.75 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  172.8, 171.9, 136.6, 133.5, 133.3,

116.0, 59.9, 56.0, 52.7, 52.6, 50.7, 49.0, 33.0, 28.7, 27.4, 12.9; HR-EIMS m/z [M<sup>+</sup>] calcd. for C<sub>16</sub>H<sub>22</sub>O<sub>4</sub> 278.1518, found 278.1508.

4.4. 5,5-Dimethoxycarbonyl-3,7a-dimethyl-1-(prop-1-en-2-yl)-3a,4,5,6,7,7a-hexahydro-1H-indene (**2c**)

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  5.39 (dq, *J* = 4.7, 1.6 Hz, 1H), 4.92 (dq, *J* = 2.1, 1.5 Hz, 1H), 4.87 (dq, *J* = 2.1, 1.0 Hz, 1H), 3.40 (s, 3H), 3.31 (s, 3H), 2.72–2.68 (m, 1H), 2.71 (dt, *J* = 13.1, 2.5 Hz, 1H), 2.58 (ddt, *J* = 13.3, 3.8, 2.5 Hz, 1H), 2.28 (ddq, *J* = 14.1, 2.5, 1.6 Hz, 1H), 2.15 (dd, *J* = 14.1, 13.1 Hz, 1H), 2.02 (td, *J* = 13.3, 4.6 Hz, 1H), 1.94 (td, *J* = 13.3, 3.8 Hz, 1H), 1.70 (ddd, *J* = 13.3, 4.6, 2.5 Hz, 1H), 1.62 (s, 3H), 1.57 (dt, *J* = 2.7, 1.6 Hz, 3H), 0.75 (s, 3H); <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  172.7, 171.7, 144.5, 141.2, 127.2, 111.7, 62.0, 56.2, 53.4, 52.2 (×2), 48.7, 35.1, 28.1, 28.0, 24.0, 14.4, 13.2; HR-EIMS *m*/*z* [M<sup>+</sup>] calcd. for C<sub>18</sub>H<sub>26</sub>O<sub>4</sub> 306.1831, found 306.1844.

4.5. 2,2-Dimethoxycarbonyl-3a,6-dimethyl-4-(prop-1-en-2-yl)-1,2,3,3a,4,6a-hexahydropentalene (**2d**)

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  5.52 (s, 1H), 4.88 (s, 1H), 4.87 (s, 1H), 3.37 (s, 3H), 3.33 (s, 3H), 2.95–2.87 (m, 1H), 2.68 (d, *J* = 12.3 Hz, 1H), 2.67 (bs, 1H), 2.59 (dd, *J* = 12.1, 6.0 Hz, 1H), 2.38 (d, *J* = 12.3 Hz, 1H), 2.24 (dd, *J* = 13.9, 12.2 Hz, 1H), 1.57 (bs, 3H), 1.54 (s, 3H), 0.82 (s, 3H); <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  173.2, 172.5, 144.2, 139.9, 130.8, 110.9, 65.2, 62.4, 58.4, 57.5, 52.4 (×2), 43.4, 31.7, 23.0, 15.5, 15.0; HR-EIMS *m*/*z* [M<sup>+</sup>] calcd. for C<sub>17</sub>H<sub>24</sub>O<sub>4</sub> 292.1675, found 292.1679.

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### Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2012.09.004.

### References

- For some recent reviews: (a) A. Fürstner, Angew. Chem. Int. Ed. 39 (2000) 3012;
   (b) T.M. Trnka, R.H. Grubbs, Acc. Chem. Res. 34 (2001) 18;
  - (c) R.R. Schrock, Chem. Rev. 102 (2002) 145;
  - (d) R.R. Schrock, A.H. Hoveyda, Angew. Chem. Int. Ed. 42 (2003) 4592;
  - (e) A.H. Hoveyda, A.R. Zhugralin, Nature 450 (2007) 243;
  - (f) C. Samojłowicz, M. Bieniek, K. Grela, Chem. Rev. 109 (2009) 3708;
- (g) G.C. Vougioukalakis, R.H. Grubbs, Chem. Rev. 110 (2010) 1746.
  [2] For some recent reviews related to organic synthesis: (a) D.V. Jarikote, P.V. Murphy, Eur. J. Org. Chem. (2010) 4959;
  - (b) H.M.A. Hassan, Chem. Commun. 46 (2010) 9100;
  - (c) J.C. López, J. Plumet, Eur. J. Org. Chem. (2011) 1803;
  - (d) J. Prunet, Eur. J. Org. Chem. (2011) 3634;

(e) T.J. Donohoe, J.F. Bower, L.K.M. Chan, Org. Biomol. Chem. 10 (2012) 1322; (f) S. Kotha, M.K. Dipak, Tetrahedron 68 (2012) 397.

- For some reviews related to ring-opening metathesis polymerization: (a) M.R. Buchmeiser, Chem. Rev. 100 (2000) 1565;
- (b) C.W. Bielawski, R.H. Grubbs, Prog. Polym. Sci. 32 (2007) 1.
  [4] (a) J.B. Binder, R.T. Raines, Curr. Opin. Chem. Biol. 12 (2008) 767;
  (b) J.B. Matson, R.H. Grubbs, J. Am. Chem. Soc. 130 (2008) 6731;
  (c) Y.A. Lin, J.M. Chalker, B.G. Davis, J. Am. Chem. Soc. 132 (2010) 16805.
- (c) Y.A. Lin, J.M. Chalker, B.G. Davis, J. Am. Chem. Soc. 132 (2010) 16805.5] Y. Schrodi, T. Ung, A. Vargas, G. Mkrtumyan, C.W. Lee, T.M. Champagne,
- R.L. Pederson, S.H. Hong, Clean Soil Air Water 36 (2008) 669. [6] For Reviews: (a) B. Schmidt, Angew. Chem. Int. Ed. 42 (2003) 4996;
  - (b) B. Alcaide, P. Almendros, Chem. Eur. J. 9 (2003) 1258;
  - (c) B. Schmidt, Eur. J. Org. Chem. (2004) 1865;
  - (d) V. Dragutan, I. Dragutan, J. Organomet. Chem. 691 (2006) 5129;
  - (e) B. Schmidt, Pure Appl. Chem. 78 (2006) 469;
  - (f) V. Dragutan, I. Dragutan, L. Delaude, A. Demonceau, Coord. Chem. Rev. 251 (2007) 765;
  - (g) B. Alcaide, P. Almendros, A. Luna, Chem. Rev. 109 (2009) 3817 (For some recent reports);
  - (h) M. Mori, N. Saito, D. Tanaka, M. Takimoto, Y. Sato, J. Am. Chem. Soc. 125 (2003) 5606;
  - (i) F. López, Á. Delgado, J.R. Rodríguez, L. Castedo, J.L. Mascareñas, J. Am. Chem. Soc. 126 (2004) 10262;
  - (j) B.P. Peppers, S.T. Diver, J. Am. Chem. Soc. 126 (2004) 9524;
  - (k) B. Alcaide, P. Almendros, J.M. Alonso, Chem. Eur. J. 12 (2006) 2874;
  - (1) C. Han, D. Uemura, Tetrahedron Lett. 49 (2008) 6988;
  - (m) Q.-H. Chen, T. Ganesh, Y. Jiang, A. Banerjee, S. Sharma, S. Bane, J.P. Snyder, D.G.J. Kingston, Chem. Commun. 46 (2010) 2019:
  - (n) J. Gavenonis, R.V. Arroyo, M.L. Snapper, Chem. Commun. 46 (2010) 5692; (o) A.A. Poeylaut-Palena, S.A. Testero, E.G. Mata, Chem. Commun. 47 (2011)
  - (p) C. Han, Y. Yamano, F. Kakiuchi, K. Nakamura, D. Uemura, Tetrahedron 67
  - (2011) 9622.
- [7] For some recent representative reports: (a) B. Schmidt, S. Krehl, Chem. Commun. 47 (2011) 5879;
  - (b) D.F. Finnegan, M.L. Snapper, J. Org. Chem. 76 (2011) 3644;
- (c) E. Ascic, J.F. Jensen, T.E. Nielsen, Angew. Chem. Int. Ed. 50 (2011) 5188.
  [8] For some recent reports: (a) R. Hayashi, J.B. Feltenberger, R.P. Hsung, Org. Lett. 12 (2010) 1152;
  - (b) G.S. Creech, O. Kwon, J. Am. Chem. Soc. 132 (2010) 8876;
  - (c) I. Nakamura, D. Zhang, M. Terada, J. Am. Chem. Soc. 132 (2010) 7884;
  - (d) F. Maria, L. Valeria, P. Rocc, S. Piero, Synlett (2010) 77;
  - (e) M. Alajarin, M. Marin-Luna, M.-M. Ortin, P. Sanchez-Andrada, A. Vidal,
  - Tetrahedron 67 (2011) 5590;
  - (f) W. Peng, T. Hirabaru, H. Kawafuchi, T. Inokuchi, Eur. J. Org. Chem. (2011) 5469;

(g) M. Alajarin, B. Bonillo, M.-M. Ortin, P. Sanchez-Andrada, A. Vidal, Eur. J. Org. Chem. (2011) 1896.

- [9] Oligomers of diene 1a by cross metathesis were also observed by GC-MS analysis of the reaction mixture.
- [10] The relative stereochemistry of 2a, d was determined by 1H NMR dif-NOE experiments (see Supplementary material). The relative stereochemistry of 2b,c was determined by analogy with that of 2a.
- [11] (a) M. Kim, M.-S. Eum, M.Y. Jin, K.-W. Jun, C.W. Lee, K.A. Kuen, C.H. Kim, C.S. Chin, J. Organomet. Chem. 689 (2004) 3535;
  - (b) M. Toumi, F. Couty, G. Evano, J. Org. Chem. 73 (2008) 1270.
- [12] (a) J.A. Tallarico, P.J. Bonitatebus Jr., M.L. Snapper, J. Am. Chem. Soc. 119 (1997) 7157;
  - (b) T.M. Trnka, M.W. Day, R.H. Grubbs, Organometallics 20 (2001) 3845;(c) D.R. Anderson, D.D. Hickstein, D.J. O'Leary, R.H. Grubbs, J. Am. Chem. Soc. 128 (2006) 8386;
  - (d) D.R. Anderson, D.J. O'Leary, R.H. Grubbs, Chem. Eur. J. 14 (2008) 7536;
  - (e) I.C. Stewart, D. Benitez, D.J. O'Leary, E. Tkatchouk, M.W. Day, W.A. Goddard III, R.H. Grubbs, J. Am. Chem. Soc. 131 (2009) 1931;
- (f) K.-P. Wang, S.Y. Yun, D. Lee, D.J. Wink, J. Am. Chem. Soc. 131 (2009) 15114.
  [13] (a) J. Barluenga, M. Tomás, A. Ballesteros, J. Santamaría, C. Brillet, S. García-Granda, A. Piñera-Nicolás, J.T. Vázquez, J. Am. Chem. Soc. 121 (1999) 4516;
  (b) H. Kagoshima, T. Akiyama, J. Am. Chem. Soc. 122 (2000) 1741;
  (c) H. Kagoshima, T. Okamura, T. Akiyama, J. Am. Chem. Soc. 123 (2001) 7182;
  (d) J. Barluenga, A. Ballesteros, J. Santamaría, M. Tomás, J. Organomet. Chem. 643-64 (2002) 363;
  (e) J. Barluenga, R. Vicente, P. Barrio, L.A. López, M. Tomás, J. Am. Chem. Soc. 126 (2004) 5974;
  (g) J. Barluenga, R. Vicente, L.A. López, E. Rubio, M. Tomás, C. Álvarez-Rúa, J. Am. Chem. Soc. 126 (2004) 470;
  - (h) J. Barluenga, R. Vicente, L.A. López, M. Tomás, J. Am. Chem. Soc. 128 (2006) 7050.
- [14] The model complex 5 was optimized from the Ru-olefin coordinated structure. A stepwise metalla-Diels-Alder reaction via a Ru-π-allyl intermediate from complex 5 may be also possible. However, the reaction pathway could not be optimized on our computational studies.
- [15] The final ruthenium species, which is formed in the ruthenium-mediated intramolecular [3 + 2] cycloaddition, is not clear at present stage. On the other hand, a catalytic ruthenium-mediated intramolecular [3 + 2] cycloaddition was also attempted. Diene 1c was treated with propyl 1-ethynylcy-clohexyl ether (1.2 eq) in the presence of [RuCl(n<sup>6</sup>-aree)(PCy<sub>3</sub>)]CF<sub>3</sub>SO<sub>3</sub> (0.1 eq). However, the reaction did not proceed: (a) A. Fürstner, M. Liebl, C.W. Lehmann, M. Picquet, R. Kunz, C. Bruneau, D. Touchard, P.H. Dixneuf, Chem. Eur. J. 6 (2000) 1847;
  - (b) R. Castarlenas, M. Eckert, P.H. Dixneuf, Angew. Chem. Int. Ed. 44 (2005) 2576.