Ruthenium-Catalyzed [1,*n*]-Metallotropic Shift (*n* = 3, 5) of Alkynyl Carbene Complex Intermediates

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The in situ generation of transient electrophilic carbenoids from organic compounds with various transition metal complexes is well-investigated to apply for various inter- or intramolecular carbene transfer reactions.[1,2] We have already demonstrated the in situ generation of vinylcarbene complexes from propargyl acetates with several transition metal compounds (Scheme 1).[3] Vinylcarbene complexes generated from secondary and tertiary propargyl carboxylates with ruthenium compounds have a rich chemistry that combines easy accessibility and high catalytic activity in cycloaddition reactions with olefins.

Recently, the [1,3] shifts of the carbene center to the remote alkynyl carbon in free alkynyl carbenes (Scheme 2a)[4] and alkynyl carbene complexes (Scheme 2b)[5–10] have been recognized as an intriguing dynamic organic process (Scheme 2). Since Padwa's pioneering work using in situ carbene generation from diazo compounds and the rhodium complex for the metallotropic [1,3]-carbene shift,[5] stoichiometric metallotropic [1,3]-shifts of alkynyl carbene species with transition metal compounds, such as Ti,[6] Cr,[7] Mo,[7] and W,[7] have been intensively studied.[8] The catalytic metallotropic [1,3]-carbene shift by ring-closing metathesis (RCM) of 1,3-diynes to afford π-conjugated enynes and oligoenynes has been independently developed by Lee et al. and van Otterlo et al.[9] We wish to report herein the generation and dynamic behavior of ruthenium–carbene complexes from oligoynes bearing the propargyl acetate moieties as a carbene trigger and their application to isomerization of oligoynes.

At first, we examined the generation of carbene complexes from the symmetrical diynes and a triyne. When the reaction of 2,7-diacetoxy-2,7-dimethylocta-3,5-diyne (**1a**) in dichloroethane (DCE) was carried out in the presence of $[RuCl_2(CO)_3]_2$ (5 mol %) at 50 °C for 72 h, 3,6-diacetoxy-2,7-dimethylocta-2,6-diene-4-yne (**2a**) was obtained in good yield (eq 1).[10] Furthermore, when the reaction of 2,9-diacetoxy-2,9-dimethyldeca-3,5,7-triyne (**3**) bearing the same propargyl acetate moieties was carried out, the same type of isomerization occurred to give 3,8-diacetoxy-2,9-dimethyldeca-2,8-diene-4,6-diyne (**4**) in 55% yield (eq 2).[11]
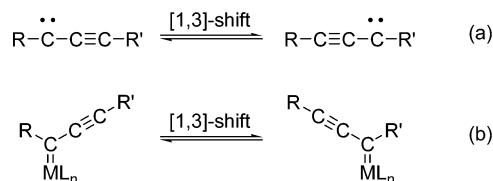
(1)

(2)

* In the presence of styrene (3 equiv)
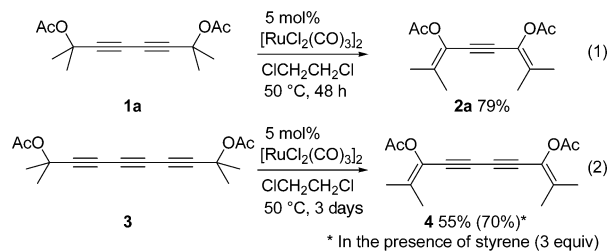
When we next examined the reaction of 1,6-diacetoxy-1,6-diphenylhexa-2,4-diyne (**1b**) bearing the secondary propargyl acetate moieties in the presence of ruthenium complex, we obtained
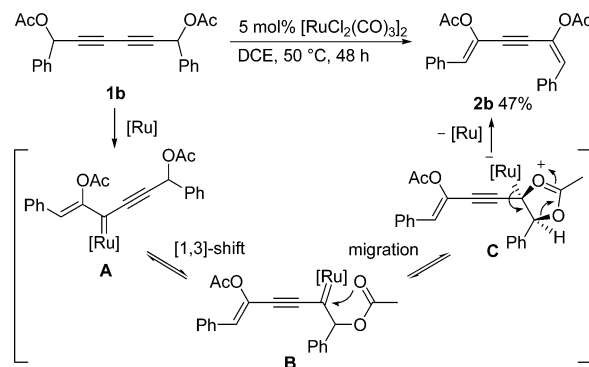
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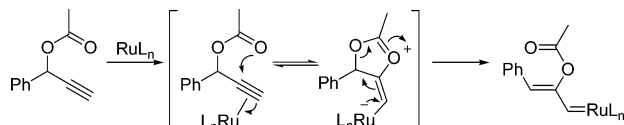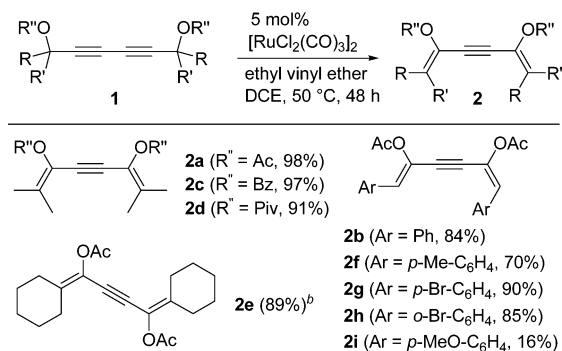
Scheme 1

Scheme 2

Scheme 3

(1*Z*,5*E*)-2,5-diacetoxy-1,6-diphenylhexa-1,5-diene-3-yne (**2b**) in 47% yield as an isomerized product exclusively (Scheme 3). On the basis of the stereochemistry of the isomerized product, we propose one of the most plausible reaction mechanisms for the isomerization of oligoynes. The formation of **2b** with *Z/E*-stereochemistry can be explained by assuming the generation and the collapse of the intermediates **A** and **B**, respectively, as shown in Scheme 3.[12] Since we know that the olefin moiety of a vinylcarbene complex generated from the secondary propargyl acetate is absolutely *Z* (Scheme 1),[3a,b] the *Z*-stereochemistry of **2b** strongly supports the generation of the vinylcarbene complex **A**. Subsequently, the intermediate **A** undergoes a [1,3] shift of the carbene center to the remote alkynyl carbon to form the intermediate **B**. Finally, the migratory insertion of an acetate moiety onto the carbene center of **B** via the transient structure **C** takes place to give the product **2b**.[13] Sterically favored trans configuration of phenyl and ruthenium moieties followed by migration in the five-membered structure **C** is considered to give the *E*-stereochemistry of **2b**.

Various diynes **1** having symmetrical tertiary and secondary propargyl carboxylates could participate in the catalytic isomerization via the [1,3]-carbene shift. Furthermore, the addition of an excess amount of an electron-rich alkene, such as ethyl vinyl ether,

Table 1. Ru-Catalyzed [1,3]-Carbene Shift Using Diynes **1**[a]

2a (R" = Ac, 98%)
2c (R" = Bz, 97%)
2d (R" = Piv, 91%)

2e (89%)[b]

2b (Ar = Ph, 84%)
2f (Ar = p-Me-C$_6$H$_4$, 70%)
2g (Ar = p-Br-C$_6$H$_4$, 90%)
2h (Ar = o-Br-C$_6$H$_4$, 85%)
2i (Ar = p-MeO-C$_6$H$_4$, 16%)

[a] Reaction conditions: substrate **1** (0.50 mmol), ethyl vinyl ether (3.0 equiv), [RuCl$_2$(CO)$_3$]$_2$ (5.0 mol %), DCE (2.5 mL), at 50 °C for 48 h. [b] For 72 h; 7% of starting material was recovered.

accelerates this isomerization and improves the yields.[14] Selected results are summarized in Table 1. The reactions of **1a**, dibenzoate **1c**, and dipivalate **1d** proceeded smoothly to afford the corresponding products **2a**, **2c**, and **2d** in good yields, respectively. Dicarboxylate **1e** was isomerized to afford the corresponding product **2e** in 89% yield with **1e** (7%) recovered. Under the optimized reaction conditions, the reaction of **1b** smoothly proceeded to afford **2b** in 84% yield. Electron-withdrawing substituents on the phenyl rings accelerated the reaction to afford the corresponding products in excellent yields, while diyne **1i** containing an electron-donating methoxy group gave **2i** in a low yield.

When the reaction of unsymmetrical diyne **1j** bearing both tertiary and secondary propargyl acetate moieties was carried out under the identical conditions, (*E*)-**2j** was obtained as a major product (eq 3).[15] Since both tertiary and secondary propargyl acetates can
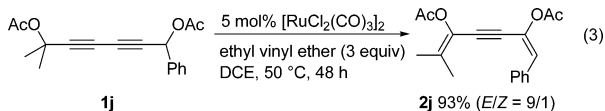
generate carbene complexes, this result shows that the tertiary propargyl acetate preferentially generates carbene complex, followed by carbene migration and migratory insertion at the secondary propargyl acetate moiety.

The isomerization of the diyne **1k** bearing primary propargyl acetate moieties did not occur at all (eq 4). This is consistent with no reaction of primary propargyl acetate with the ruthenium complex.[3b] On the other hand, the reaction of **1l** under the same conditions gave isomerization product **2l** (eq 5). The reaction of **1l**
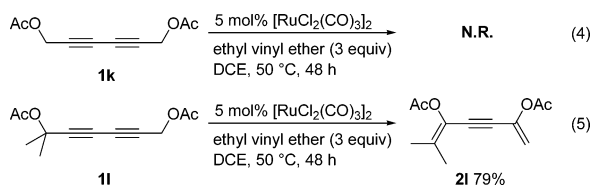
reveals that the generation of carbene complex took place at the tertiary propargyl acetate moiety with migration of the carbene center to give the isomerized product **2l** in good yield.

In conclusion, we have demonstrated the ruthenium-catalyzed isomerization of diynes and triynes by using in situ generation of transition metal carbene complexes from propargyl carboxylates, followed by a metallotropic [1,*n*]-carbene shift (*n* = 3, 5) (*carbene walk*) of initially generated alkynyl carbene complexes. Further studies to find the [1,*n*]-carbene shift (*n* > 5) as well as to construct more π-elongated materials by using this protocol are now in progress in our laboratory.

Supporting Information Available: General procedures and characterization of new compounds are provided as a PDF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) The reactions of **1a** with 5 mol % of PtCl$_2$ or AuCl(PPh$_3$)/AgSbF$_6$, which is well-known as one of the most excellent catalysts for catalytic carbene transfer reactions, also gave the corresponding product **2a** in 67 and 47% yields, respectively.

(11) At present, it is not clear why the yield is increased by the addition of styrene.

(12) The unsymmetrical structure of **2b** could exclude a dicarbene complex **D** generated from the 1:2 complexation of **1b** and ruthenium complexes.
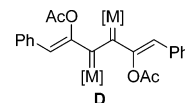
(13) The similar intramolecular cyclization of ene-carbonyl-carbene complexes to give furan ring has been reported. See: (a) Ghorai, B. K.; Herndon, J. W. *Organometallics* **2003**, *22*, 3951. (b) Zhang, Y.; Herndon, J. W. *J. Org. Chem.* **2002**, *67*, 4177.

(14) No cyclopropanated product of vinyl ether was observed in each case.

(15) The stereochemistry of product **2j** was deduced by nOe experiments. See Supporting Information.

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