Formation of Vinylidenes from Internal Alkynes at a Cyclotriphosphato Ruthenium Complex

Yousuke Ikeda, Takafumi Yamaguchi, Keiichiro Kanao, Kazuhiro Kimura, Sou Kamimura, Yuichiro Mutoh, Yoshiaki Tanabe, and Youichi Ishii


Downloaded from http://pubs.acs.org on March 9, 2009

More About This Article

Additional resources and features associated with this article are available within the HTML version:

• Supporting Information
• Access to high resolution figures
• Links to articles and content related to this article
• Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML
Formation of Vinylidenes from Internal Alkynes at a Cyclotriphosphato Ruthenium Complex

Yousuke Ikeda, Takafumi Yamaguchi, Keichiro Kanao, Kazuhiro Kimura, Sou Kamimura, Yuichiro Mutoh, Yoshiaki Tanabe, and Youichi Ishii*

Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University, Kasuga, Bunkyo-ku, Tokyo 112-8551, Japan

Received October 13, 2008; E-mail: yo-ishii@kc.chuo-u.ac.jp

Terminal alkynes are readily converted into the corresponding vinylidenes at transition metal complexes by a direct 1,2-hydrogen shift, C–H oxidative addition−1,3-hydrogen shift, sequential protonation−deprotonation, and other mechanisms.1 This tautomerization is now recognized as the key step in many metal-promoted or -catalyzed transformations of alkynes.2 Heteroatom-substituted alkynes such as silyl-,3 stannyl-,4 thio-,5 and iodoalkynes6 are also known to undergo similar rearrangement. In contrast, migration of carbon substituents of internal alkynes has been limited to very few rearrangements of acylalkynes,7 although the reverse process, i.e., the conversion of disubstituted vinylidenes to the nπ⁻-internal alkynes, has been described in the literature.8 In the course of our study on the transition metal cyclophosphato complexes which are structurally related to the hydroxyapatite-supported metal catalysts,9 we have revealed that this class of organometallic complexes exhibits unique structural and chemical properties based on the circular array of P–O groups as an effective σ-donor set.10 Now we have found that a ruthenium cyclotriphosphato (P₃O₉⁻) complex with a labile MeOH ligand can affect the vinylidene rearrangement of general internal alkynes via the 1,2-migration of alkyl, aryl, and acyl groups.

Coordination chemistry of ruthenium P₃O₉ complexes has not been explored extensively, but photochemical ligand substitution of the benzene complex (PPN)[Ru(P₃O₉)(C₆H₆)] (1; PPN = (Ph₃P)₂N⁺)11 was found to be a versatile entry to reactive ruthenium species. Thus, UV-irradiation of 1 in MeOH−CH₂Cl₂ in the presence of dppe (dppe = P₆PhCH₂CH₂P₆Ph; 1.2 equiv) led to isolation of the MeOH complex (PPN)[Ru(P₃O₉)(MeOH)(dppe)] (2) in 71% yield as orange crystals. An X-ray diffraction study of 2·3MeOH has confirmed its molecular structure with an octahedral geometry in which three facial coordination sites are occupied by the axial oxygen atoms of the P₃O₉ ligand (see Supporting Information). The MeOH ligand in 2 is highly labile and readily replaced by N₂ in CH₂Cl₂ to form (PPN)[Ru(P₃O₉)(N₂)(dppe)] (3), which exhibits a νₐs (νas) band at 2154 cm⁻¹ in the IR spectrum. On dissolution in MeOH under argon, 3 is quickly converted back to 2.

When 2 was allowed to react with 1-phenyl-1-propyne (4a, 2.6 equiv) in C₆H₅CH₂Cl at 70 °C for 3 days, the vinylidene complex (PPN)[Ru(P₃O₉)(C₆H₅CH₂)C≡C(Ph)Me(dppe)] (5a) was obtained in 85% yield as green crystals (Scheme 1; see Supporting Information for experimental details). Complex 5a exhibits ¹³C{¹H} NMR signals at δ 369.0 (t, JPC = 20 Hz) and 118.2 (s) characteristic of the α and β carbons of a vinylidene ligand, respectively. The molecular structure of 5a·2MeOH has been established unambiguously by an X-ray diffraction study to confirm that either Me or Ph migration took place to form the disubstituted vinylidene ligand (see Supporting Information). The metrical features including the Ru−Cα and Cα−Cβ bond distances of 1.842 (4) and 1.277(5) Å, respectively, and the Ru−Cα−Cβ bond angle of 178.4(3)° are comparable to common Ru(II)−vinylidene complexes.12 Similar reactions were also observed with other internal alkynes such as 4b−4g, providing the first example of alkyneto-vinylidene rearrangement of general internal alkynes. At present, the role of the P₃O₉ ligand is not fully understood, but we consider that its σ-donor character favors the formation of a π-acidic vinylidene ligand. It should be noted that the rate of the reaction is strongly dependent on the substituents; the reactions of 4a, 4b, and 4g are relatively slow and take a long time (3 days) to go to completion, while those of 4c, 4e, and 4f are completed within 3−6 h under the same conditions (70 °C). Intermediate complexes could not be isolated in any of these reactions.

Scheme 1

![Scheme 1](image)

<table>
<thead>
<tr>
<th>alkyn</th>
<th>R¹</th>
<th>R²</th>
<th>time</th>
<th>isolated yield(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>Ph</td>
<td>Me</td>
<td>3 days</td>
<td>85</td>
</tr>
<tr>
<td>4b</td>
<td>Et</td>
<td>Et</td>
<td>3 days</td>
<td>63</td>
</tr>
<tr>
<td>4c</td>
<td>CO₂Et</td>
<td>5 h</td>
<td>78</td>
<td></td>
</tr>
<tr>
<td>4d</td>
<td>Ph</td>
<td>Ph</td>
<td>1 day</td>
<td>44</td>
</tr>
<tr>
<td>4e</td>
<td>Ph</td>
<td>C₆H₄OMe-p</td>
<td>3 h</td>
<td>69</td>
</tr>
<tr>
<td>4f</td>
<td>Ph</td>
<td>C₆H₄Me-p</td>
<td>6 h</td>
<td>51</td>
</tr>
<tr>
<td>4g</td>
<td>Ph</td>
<td>C₆H₄CO₂Et</td>
<td>3 days</td>
<td>40</td>
</tr>
</tbody>
</table>

On the other hand, treatment of 2 with alkynes 4h−4k (4h: R¹ = R² = CO₂Me; 4i: R¹ = R² = CO₂Et; 4j: R¹ = Me, R² = CO₂Et; 4k: R¹ = Et, R² = CO₂Et) at 50 °C resulted in the formation of the nπ⁻-alkyn complexes (PPN)[Ru(P₃O₉)(R¹C≡CR²)(dppe)] (6) in 66−85% isolated yields, which were characterized by the ¹³C{¹H} NMR signals at δ 72−87 (coordinated C≡CR) and the IR absorption at 1920−1950 cm⁻¹ (νCO) as well as by a crystallographic study of 6j. These alkyn complexes were further transformed into the corresponding vinylidene complexes 5h−5k in 54−85% isolated yields either by heating in C₆H₅CH₂Cl (up to 5 days) or more effectively by UV-irradiation at room temperature.13ad
complex (using 13C-enriched alkynes PhC
product (Ru(II) center.14
1,2-hydrogen shift mechanism is most commonly operative with a vinylidene rearrangement involves the 1,2-alkyl/aryl shift of the complex seems unlikely. Therefore we presume that the present vinylidene rearrangement involves the 1,2-alkyl/aryl shift of the intermediary alkyl complex. Theoretical studies on the terminal alkyneto-vinylidene rearrangement have also suggested that the 1,2-hydrogen shift mechanism is most commonly operative with a Ru(II) center.14

To gain deeper insight into the reaction mechanism, the migratory aptitude of alkyl, aryl, and acyl groups has been investigated by using 13C-enriched alkenes PhC≡C13CR (4-13C, 25.9% 13C). Migration of the R group gives rise to the α-13C labeled vinylidene complex (5-α13C), while the Ph migration leads to the β-13C labeled product (5-β13C) (Scheme 2). When complex 1 was reacted with 4a-13C, the 13C(1H) NMR analysis of the reaction mixture indicated that the 13C content of the α-carbon in the product is 9.84 times as high as that of β-carbon, which implies that the ratio of Me and Ph migration is 94:6 (see Supporting Information). Detailed analysis of analogous reactions with a series of 4-13C disclosed that the migratory aptitude of alkyl substituents is in the order CO2Et, C6H4CO2Et-p > Me > Ph > C6H4Me-p > C6H4OMe-p.

Scheme 2 a

<table>
<thead>
<tr>
<th>Alkyne</th>
<th>R migration</th>
<th>Ph migration</th>
</tr>
</thead>
<tbody>
<tr>
<td>4α-13C</td>
<td>CO2Et &gt; 99:1</td>
<td>&gt; 99:1</td>
</tr>
<tr>
<td>4α-13C</td>
<td>C6H4Me-p &gt; 99:1</td>
<td></td>
</tr>
<tr>
<td>4β-13C</td>
<td>C6H4Me-p</td>
<td></td>
</tr>
<tr>
<td>4β-13C</td>
<td>C6H4OMe-p</td>
<td></td>
</tr>
</tbody>
</table>

"Reaction conditions: C2H4Cl2, 70 °C.

Observe, in these cases, the vinylidene rearrangement is much slower than the alkyne coordination.

A preliminary kinetic study on the conversion of 6k to 5k at 70 °C in the presence of excess 4k by means of 31P(1H) NMR clearly indicated that the reaction obeys first-order kinetics with an apparent rate constant (k) of 3.09 × 10⁻⁵ s⁻¹. This result demonstrated that the reaction proceeds via an intramolecular process, which is further supported by the fact that crossover of the alkyl substituents was not observed in the reactions with unsymmetric alkenes, especially 4f. On the other hand, judging from the normal νννννNMR Value of 3.13 the oxidative addition of an internal alkyne to the 16e 16f fragment to form the (alkyl/aryl)(alkynyl) complex seems unlikely. Therefore we presume that the present vinylidene rearrangement involves the 1,2-alkyl/aryl shift of the intermediary alkyl complex.

In conclusion, we have developed the first internal alkyne-to-vinylidene isomerization with high generality by using ruthenium P=O complexes 2 and determined the migratory aptitude of alkyl, aryl, and acyl groups. Detailed mechanisms and synthetic applications of this reaction are now under investigation.

Acknowledgment. This work was supported by Grants-in-Aid for Scientific Research (20037060) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Supporting Information Available: Experimental details and crystallographic data for 2-3MeOH, 5a-2MeOH, and 6j-2CH2Cl2 in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

References

17. (a) This point has recently been discussed contradictorily on the basis of a kinetic study of the vinylidene-to-alkyne rearrangement at an indenylrhodium complex. Bade, M.; Cadierno, V.; Gimeno, J.; Pasquini, C. Organometallics 2008, 27, 5009–5016.