

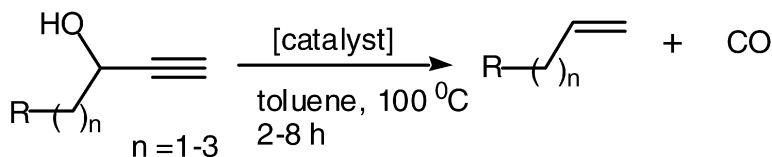
Communication

**A New Ruthenium-Catalyzed Cleavage of a Carbon–Carbon Triple Bond:
 Efficient Transformation of Ethynyl Alcohol into Alkene and Carbon Monoxide**

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[catalyst] = TpRu(PPh₃)(CH₃CN)₂PF₆ (10 mol%)
 LiCF₃SO₃ (20 mol%)

R = alkyl, aryl, heteroaryl

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A New Ruthenium-Catalyzed Cleavage of a Carbon–Carbon Triple Bond: Efficient Transformation of Ethynyl Alcohol into Alkene and Carbon Monoxide

Swarup Datta, Chia-Lung Chang, Kuo-Liang Yeh, and Rai-Shung Liu*

Department of Chemistry, National Tsing-Hua University, Hsinchu, Taiwan, 30043, Republic of China

Received May 21, 2003; E-mail: rslu@mx.nthu.edu.tw

Metal-catalyzed cleavage of carbon–carbon bonds is an interesting topic in organic reactions.¹ Cleavage of the carbon–carbon triple bond of alkynes is very difficult because this functionality normally gives products containing an unstrained C=C or C–C bond during catalytic transformation.^{1,2} Most studies on alkyne cleavage have focused on stoichiometric organometallic reactions,^{3,4} including oxidative cleavage of alkyne to carboxylic acid,³ alkyne cleavage across metal–metal multiple bonds,⁴ water-assisted splitting of alkyne into alkane and coordinated CO,⁵ as well as alkyne–ligand scission on metal complexes.⁶ There have been very few reported examples for the catalytic cleavage of organic alkyne via a nonmetathesis pathway.⁷ Jun et al. reported catalytic cleavage of alkynes through rhodium-catalyzed hydroiminoacylation.⁸ Very recently, Yamamoto reported the cleavage of diynes⁸ via ruthenium-catalyzed hydroamination.⁸ These reactions require additional promoters 2-aminopyridine or 2-aminophenol to facilitate cleavage of the alkyne.⁸ Because of the importance of carbon–carbon bond cleavage, we sought to identify a new pathway for the cleavage of alkyne in the absence of organic promoters. In this report, we describe a new ruthenium-catalyzed reaction in which ethynyl alcohol is split into alkene and carbon monoxide. The mechanism of this new process was elucidated on the basis of the results of an isotope-labeling experiment.

We sought to achieve cleavage of alkynes via generation of a metal vinylidene intermediate in a catalytic reaction.⁵ We examined various ruthenium and rhodium catalysts (Scheme 1), because they readily form metal vinylidene species in the presence of alkynes.⁵ TpRu(PPh₃)(CH₃CN)₂PF₆⁹ (10 mol %, Tp = tris(1-pyrazolyl)borate) is the most active for the transformation of ethynyl alcohol (**1a**) (100 °C, toluene, 16 h) into alkene in an isolated yield of 33%. GC-analysis of gaseous mixtures confirmed the formation of carbon monoxide (35%), indicative of the catalytic reaction depicted in Scheme 1. Under the same conditions, C₅H₅Ru(PPh₃)(CH₃CN)₂PF₆ and other catalysts (entries 2–6) including TpRu(PPh₃)₂Cl, TpRu(PPh₃)(CH₃CN)Cl, RuCl₂(PPh₃)₃, and ClRh(PPh₃)₃ failed to give significant amounts of alkene **1b** but rather gave uncharacterized black tar. The efficiency of this process can be further improved with Lewis-acid catalysts (entries 7–10) with LiOTf (20 mol %) being the most effective: the reaction time is reduced (toluene 100 °C, 3 h), and alkene **1b** is obtained in an isolated yield of 75%. Carbon monoxide is found in ca. 72% yield according to GC-analysis.

We further examined the scope of organic substrates, and the results are summarized in Table 1. A mixture of TpRu(PPh₃)(CH₃CN)₂PF₆ (10 mol %) and LiOTf (20 mol %) catalysts was employed. This method also works for tertiary ethynyl alcohol **2a** to give 1,1-disubstituted **2b** in 52% yield. It can be extended to phenyl groups containing electron-rich 1,2-(methylenedioxy) and diphenylamino substituents **3a–5a** (entries 2–4) and electron-withdrawing cyano and methoxycarbonyl groups **6a–7a** (entries 5, 6), and the corresponding alkenes **3b–7b** were obtained in yields

Scheme 1^a



entries	catalysts ^a	Lewis acids ^b	yields ^c
1	TpRu(PPh ₃)(CH ₃ CN) ₂ PF ₆	—	31% ^d
2	TpRu(PPh ₃)(CH ₃ CN)Cl	—	2%
3	C ₅ H ₅ Ru(PPh ₃)(CH ₃ CN) ₂ PF ₆	—	2%
4	TpRu(PPh ₃) ₂ Cl	—	2%
5	RuCl ₂ (PPh ₃) ₃	—	—
6	RhCl(PPh ₃) ₃	—	—
7	TpRu(PPh ₃)(CH ₃ CN) ₂ PF ₆	LiOTf	75% ^d
8	TpRu(PPh ₃)(CH ₃ CN) ₂ PF ₆	Zn(OTf) ₂	48%
9	TpRu(PPh ₃)(CH ₃ CN) ₂ PF ₆	Sn(OTf) ₂	41%
10	TpRu(PPh ₃)(CH ₃ CN) ₂ PF ₆	Sc(OTf) ₃	37%

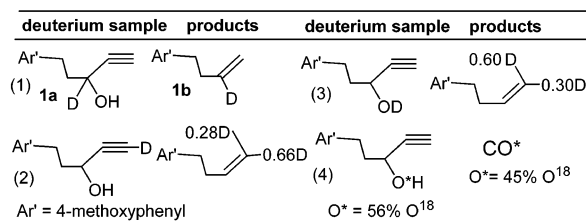
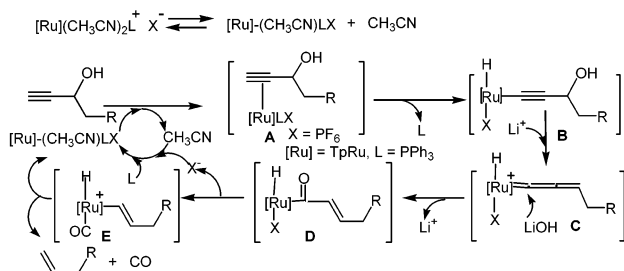
^a (a) 10 mol % catalysts, 100 °C in toluene 16 h for entries 1–6, and 3 h for entries 7–10. (b) 20 mol % Lewis acid was used. (c) Isolated yields from the silica column. (d) CO was determined from GC with 35% and 72% yields in entries 1 and 7, respectively.

Table 1. Ruthenium-Catalyzed Cleavage of Ethynyl Alcohols

Substrates	Products ^a (yields) ^b	Substrates	Products(yields)

^a 10 mol % TpRu(PPh₃)(CH₃CN)₂PF₆, 20 mol % LiOTf, toluene (0.15 M substrate), 110 °C, 5 h. ^b Yields were reported after separation from the silica column.

of 74–91%. This new reaction is also compatible with substrates bearing 2-naphthyl and oxygen, nitrogen, and sulfur heteroaryl functionalities (entries 7–10), and alkene products **8b–11b** were

Scheme 2. Deuterium Labeling for Cleavage of Alkyne**Scheme 3**

obtained in reasonable yields (64–88%). We also prepared substrates **12a–15a** to examine the tolerance with regard to functional groups and found that this new approach is compatible not only with acidic fluorenyl protons but also with allyl, alcohol, and dioxolane groups (entries 11–14). The *cis*-olefin functionality of alkene **16b** is completely retained in the catalytic cleavage of ethynyl alcohol **16a** (entry 15). This new method can also be applied to the synthesis of unfunctionalized 1-decene **17b**, and a chelating effect is not required for this catalytic reaction (entry 16).

Scheme 2 shows the results of isotope-labeling experiments to elucidate the reaction mechanism. The deuterium migration of ethynyl alcohol **1a** to alkene **1b** proceeded rather regiospecifically. The C₂-hydrogen of alkene **1b** arose primarily from the C₃-hydrogen of ethynyl alcohol **1a**. Most of the alkyne proton of **1a** was migrated to the *trans*-C₁-proton of alkene **1b**, whereas the alcohol proton underwent migration to the *cis*-C₁-proton of alkene **1b**. We also prepared O¹⁸-labeled (58%-content O¹⁸) alcohol **1a**, which led to enriched-CO¹⁸ with a content of 48%.

In toluene, TpRuPPh₃(CH₃CN)₂PF₆ likely becomes TpRu–PPh₃(CH₃CN)PF₆ via dissociation of an acetonitrile. On the basis of the results of the deuterium experiments, we propose a plausible mechanism (Scheme 3) that involves the formation of ruthenium- η^1 -alkynyl hydride species **B** via proton migration of ruthenium- π -alkyne complex **A**.¹⁰ In the presence of LiOTf, species **B** will undergo ionization to form ruthenium-allenylidene species **C**,¹¹ and the counterattack of LiOH at the C _{α} carbon of species **B** yielded ruthenium-acyl species **D**.⁵ Subsequent decarbonylation of species **D** yielded vinylruthenium hydride species **E**⁵ which upon reductive elimination regenerated active ruthenium catalyst in addition to alkene and carbon monoxide. This proposed mechanism is consistent with the results of the isotope-labeling experiment except for the minor deuterium contents on the *cis*- and *trans*-vinyl protons in entries 2 and 3, respectively. This may be attributed to proton exchange between ruthenium hydride **B** with residual water in

catalytic system. It is also likely to arise from the formation of *Z/E* (1/2) isomers of species **D** and **E**.

In summary, we have reported a new and efficient catalytic cleavage of organic alkynes in which ethynyl alcohol is split into alkene and CO by ruthenium complex.¹² This reaction is synthetically useful because it can tolerate various functional groups. The mechanism of this catalytic reaction was elucidated with an isotope-labeling experiment. The development of new catalytic processes based on this principle is under investigation.

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Supporting Information Available: Experimental procedures and spectral data of compounds **1a–17a** and **1b–17b** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (12) Related to this process is the water-assisted splitting of alkyne into alkane (or alky) and coordinated CO, which requires a stoichiometric amount of metal complexes. The latter reaction has not been effected catalytically despite its popularity and long history.⁵

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