ChemPubSoc Europe
DOI: 10.1002/chem.201504937
CHEMISTRY
A European Journal
Communication

Arenes

Ruthenium-Catalyzed Cycloisomerization of 2,2′-Diethynylbiphenyls Involving Cleavage of a Carbon–Carbon Triple Bond

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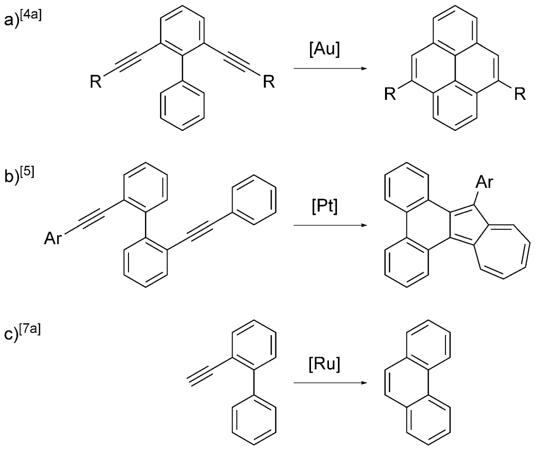
Abstract: A ruthenium complex catalyzes a new cycloisomerization reaction of 2,2′-diethynylbiphenyls to form 9-ethynylphenanthrenes, thereby cleaving the carbon–carbon triple bond of the original ethynyl group. A metal–vinylidene complex is generated from one of the two ethynyl groups, and its carbon–carbon double bond undergoes a [2+2] cycloaddition with the other ethynyl group to form a cyclobutene. The phenanthrene skeleton is constructed by the subsequent electrocyclic ring opening of the cyclobutene moiety.

A reaction of terminal alkynes with complexes of transition metals, such as ruthenium, rhodium, and tungsten, generates the corresponding metal–vinylidene (M=C=C) complexes.[1] A number of catalytic reactions involving those transition-metal-vinylidene complexes as the key intermediate have been developed in the past two decades.[2] In most of the catalytic processes, reactions of the intermediate metal–vinylidene complexes are associated with their metal–carbon double bond. On the other hand, the carbon–carbon double bonds of the metal–vinylidene complexes are also reactive to participate in various pericyclic reactions.[2d,e,h] However, there have been no examples of catalytic reactions in which the carbon–carbon double bond of the metal vinylidenes undergoes a [2+2] cycloaddition with a carbon–carbon unsaturated bond.[3] Herein, we report a skeletal rearrangement reaction of 2,2′-diethynylbiphenyls in which a carbon–carbon double bond of an intermediate ruthenium–vinylidene complex generated from an ethynyl group undergoes an intramolecular [2+2] cycloaddition with another ethynyl group. Finally, the original carbon–carbon triple bond is cleaved to furnish 9-ethynylphenanthrenes.

We previously reported an intramolecular hydroarylation reaction of 2,6-dialkynylbiphenyls (Scheme 1 a).[4] The two alkynyl groups, which were located on the opposite sides of one of the two phenyl rings, were both activated by π acidic gold complexes to undergo the intramolecular hydroarylation reaction. Two vinylene bridges were formed between the two phenyl groups in parallel to construct a pyrene skeleton. We attempted an analogous twofold intramolecular hydroarylation reaction with 2,2′-dialkynylbiphenyls using various π acidic catalysts. In contrast to our expectation, a new skeletal rearrangement reaction was identified with 2,2′-bis(arylethynyl)biphenyls that was transformed to azulenophenanthrenes (Scheme 1 b).[5] It is likely that this unique reaction worked with 2,2′-dialkynylbiphenyls, because the two alkynyl substituents on the two phenyl rings can get in proximity to each other through axis rotation.[6]



Scheme 1. Intramolecular hydroarylation reactions

Another method has also been reported in order to formally carry out the intramolecular hydroarylation reaction.[7] in which a phenanthrene skeleton is constructed from the 2-ethynylbiphenyl by using a ruthenium catalyst. The 6π electrocyclization occurs with an intermediate ruthenium–vinylidene complex to form a vinylene bridge between the two phenyl rings (Scheme 1 c). This electrocyclic pathway led us to study a reaction of 2,2′-diethynylbiphenyl (**1 a**) with ruthenium catalysts. Thus, **1 a** was treated with a ruthenium catalyst generated in situ from [$RuCl_2(PPh_3)$(*p*-cymene)] (10 mol %) and NH_4PF_6

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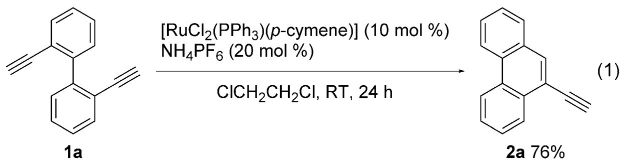
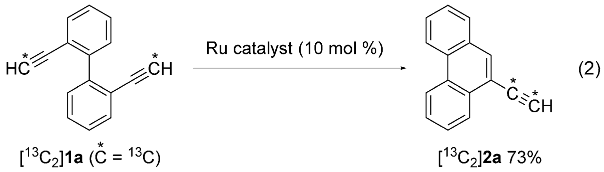
Supporting information for this article and ORCID for one of the authors are available on the WWW under http://dx.doi.org/10.1002/chem.201504937.

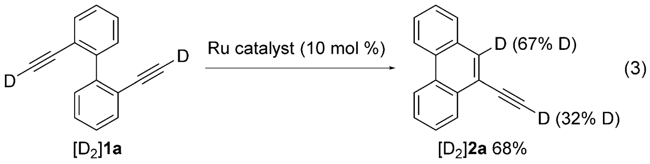
(20 mol%) in 1,2-dichloroethane at room temperature. After 24 h, **1 a** was consumed to give a different hydrocarbon product of a same molecular weight. To our surprise, neither pyrene or 4-ethynylphenanthrene, but 9-ethynylphenanthrene (**2 a**) was exclusively produced and isolated in 76% yield [Eq. (1)].[8,9]



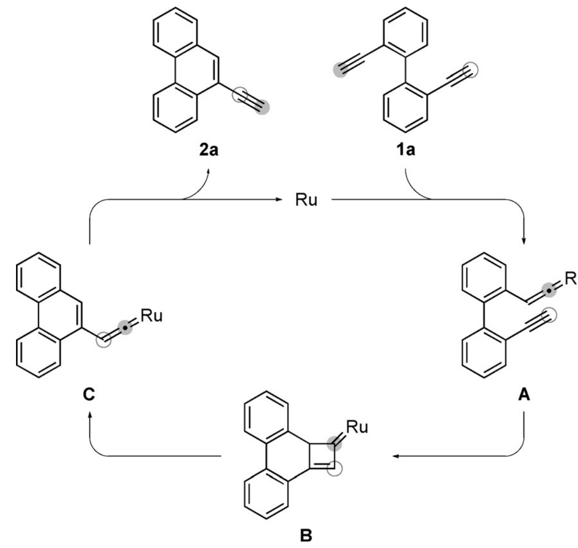
A significant skeletal change occurred with the unexpected product **2 a** that incited us to carry out labeling experiments for a mechanistic information. Thus, two kinds of labeled biphenyls [$^{13}C_2$]**1 a** and [D_2]**1 a** were prepared. The two terminal ethynyl carbons of the biphenyl [$^{13}C_2$]**1 a** were labeled with ^{13}C nuclides, and another labeled substrate [D_2]**1 a** had the two ethynyl termini labeled with deuterium atoms. When the biphenyl [$^{13}C_2$]**1 a** was subjected to the cycloisomerization reaction, the two ^{13}C nuclides were found to constitute the ethynyl group at the 9-position of the resulting phenanthrene [$^{13}C_2$]**2 a** [Eq. (2)].



On the other hand, when the biphenyl [D_2]**1 a** was used, one of the deuterium atoms was located at the 10-position of the resulting phenanthrene skeleton, and the other deuterium atom was found at the terminal position of the 9-ethynyl substituent [Eq. (3)].



On the basis of the results of the labeling experiments, we assume the mechanism depicted in Scheme 2 for the ruthenium-catalyzed cycloisomerization. First, one of the ethynyl groups of **1 a** reacts with the ruthenium(II) to generate vinylidene ruthenium complex **A**. The other ethynyl group undergoes a [2+2] cycloaddition with the cumulated carbon–carbon double bond of **A**, forming cyclobutenylidene ruthenium **B**. Then, the four-membered ring opens through a 4π electrocyclic process, generating new vinylidene ruthenium species **C**. An ethynyl group is liberated from **C** to produce **2 a** together with the regeneration of the ruthenium(II) catalyst. Neither 4-ethynylphenanthrene nor pyrene was found in the reaction mixture, indicating that the [2+2] cycloaddition proceeded to 6π electrocyclization with the intermediate **A**.



Scheme 2. Proposed mechanism.

Identical reaction conditions were applied to the octa-1,7-diyne, the structure of which was significantly more flexible than **1 a**. However, an analogous cycloisomerization reaction failed to occur, suggesting that the reaction mode observed with 2,2′-diethynylbiphenyl (**1 a**) could be attributed to the structural rigidity of the biphenyl backbone.

Other substituted 2,2′-diethynylbiphenyls were also subjected to the cycloisomerization reaction. Substrates **1 b** and **1 c**, with methyl and methoxy substituents at the 4 and 4′ positions, respectively, were suitable substrates, whereas the reaction of **1 d** bearing electron-withdrawing CF_3 groups was sluggish (Figure 1 a). Methyl and fluoro substituents were also tolerated at the 5 (5′) positions (Figure 1 b). However, the attempted cycloisomerization reaction of 3,3′,5,5′-tetramethyl derivative **1 g**, 2,2′-diethynyl-1,1′-binaphthyl (**1 h**), and diyne **1 i** carrying an internal alkyne moiety were unsuccessful; the starting materials remained unchanged (Figure 1 c).[10]

In summary, we have described the new ruthenium-catalyzed cycloisomerization reaction of 2,2′-diethynylbiphenyls affording 9-ethynylphenanthrenes. The carbon–carbon triple bond of the ethynyl substituent was cleaved and its terminal sp carbon was coupled with another terminal sp carbon of the other ethynyl substituent to form a new ethynyl group at the 9-position of the phenanthrene.

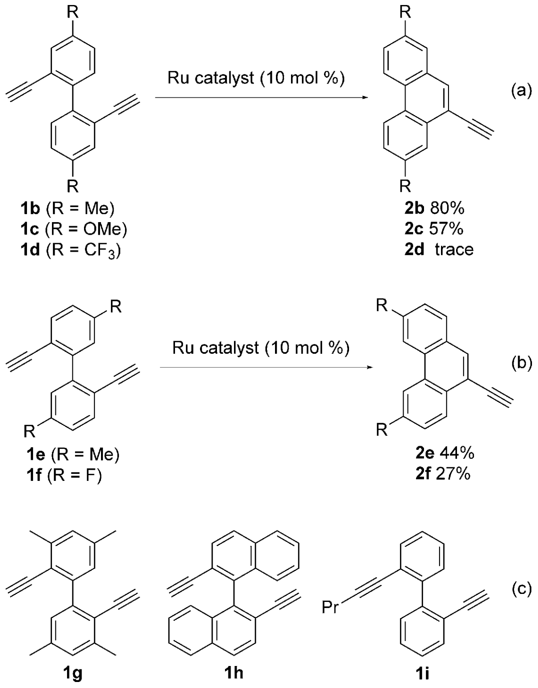


Figure 1. a) and b) Successful substrates, c) unsuccessful substrates.

Experimental Section

General procedure for the ruthenium-catalyzed cycloisomerization of 1

A Schlenk tube was charged with 2,2′-diethynylbiphenyl **1** (0.200 mmol), [RuCl$_2$(PPh$_3$)(*p*-cymene)] (0.020 mmol, 10 mol%), and NH$_4$PF$_6$ (0.040 mmol, 20 mol%), and then the tube was evacuated and backfilled with nitrogen. 1,2-Dichloroethane (4.0 mL) was added by syringe through the septum, and the mixture was stirred at room temperature. The disappearance of the starting material was checked by GC analysis. The reaction mixture was concentrated under reduced pressure. The residue was subjected to preparative thin-layer chromatography on silica gel (hexane/AcOEt) to afford 9-ethynylphenanthrenes **2**.

Acknowledgements

This work was supported by JSPS, Japan (Grant-in-Aid for Scientific Research (C) No. 25410054) and the Sumitomo Foundation. We thank S. Shiose for help with some experiments.

Keywords: alkynes · cycloisomerization · phenanthrenes · ruthenium · vinylidene ligands

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Received: December 8, 2015