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Cationic Rhodium(I) Complex-Catalyzed [3 + 2] and [2 + 1] Cycloadditions of Propargyl Esters with Electron-Deficient Alkynes and Alkenes

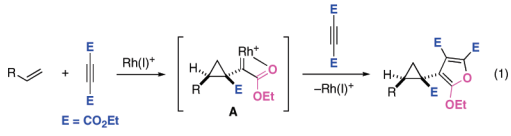
Yu Shibata,[†] Keiichi Noguchi,[‡] and Ken Tanaka*,[†]

Department of Applied Chemistry, Graduate School of Engineering, and Instrumentation Analysis Center, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan

Received March 23, 2010; E-mail: tanaka-k@cc.tuat.ac.jp

Catalytic cycloadditions via metal carbene intermediates have been extensively studied, and a number of efficient methods are available.[1] However, the majority of reports involve cycloadditions with electron-rich unsaturated compounds because of the electrophilic nature of metal carbene intermediates.[1] Recently, several notable examples employing electron-deficient unsaturated compounds were reported.[2−5] For cyclopropanations of electron-deficient alkenes with diazo compounds, Ru(II)/salen[2] or Co(II)/porphyrin[3] complex-catalyzed reactions were reported. For cycloadditions of electron-deficient alkenes,[4] alkynes,[5a,b] and allenes[5c] with Fischer carbene complexes, Ni(0)-catalyzed cyclopropanations[4] and Rh(I)-catalyzed [3 + 2] cycloadditions[5] were reported. As an alternative method for the generation of metal carbene intermediates that is convenient as well as atom-economical, the 1,2-acyloxy rearrangement of terminal propargyl esters leading to alkenylcarbene intermediates catalyzed by Pd(II),[6] Ru(II),[7] and Au(I)[8] complexes was developed, while cycloaddition partners are limited to electron-rich unsaturated compounds.[9] Here we describe cationic rhodium(I) complex-catalyzed [3 + 2][10] and [2 + 1] cycloadditions of propargyl esters with *electron-deficient alkynes and alkenes*.

Our research group recently reported the cationic Rh(I)/(*R*)-Segphos [5,5′-bis(diphenylphosphino)-4,4′-di-1,3-benzodioxole]-catalyzed enantio- and diastereoselective cotrimerization of electron-rich alkenes and diethyl acetylenedicarboxylate, leading to furylcyclopropanes presumably through carbonyl-stabilized cationic Rh(I) carbene intermediate **A** (eq 1):[11]

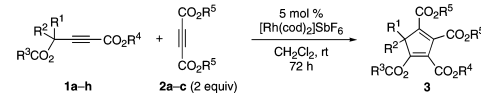


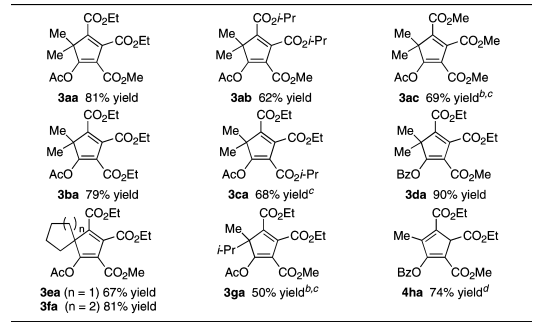
(1)

This result indicates the nucleophilic nature of Rh(I) carbene **A**.

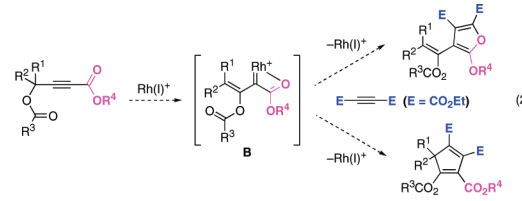
On the other hand, it is well-known that the electrophilic cationic Rh(I) complex is able to activate alkynes through the formation of a complex with the π electrons of the alkyne triple bond.[12] Thus, we anticipated that the cationic Rh(I) complex would react with an alkoxycarbonyl-substituted propargyl ester to generate the carbonyl-stabilized cationic Rh(I) carbene intermediate **B** via the 1,2-acyloxy rearrangement; **B** would then react with diethyl acetylenedicarboxylate to yield the corresponding furan or cyclopentadiene through the [3 + 2] cycloaddition of the carbonyl or alkene moiety of **B** (eq 2):

Table 1. Rhodium-Catalyzed [3 + 2] Cycloaddition[a]





[a] $[Rh(cod)_2]SbF_6$ (0.025 mmol), **1a**−**h** (0.50 mmol), **2a**−**c** (1.00 mmol), and CH_2Cl_2 (1.0 mL) were used. Cited yields are of isolated products. [b] Catalyst: 10 mol %. [c] At 40 °C. [d] Determined by ^1H NMR spectroscopy because of the instability of the product toward silica gel chromatography.



(2)

It was also expected that the alkoxycarbonyl group would facilitate the regioselective 1,2-migration of the acyloxy group because of the electronic polarization of the alkyne triple bond.[13]

We first examined the reaction of methoxycarbonyl-substituted propargyl ester **1a** and diethyl acetylenedicarboxylate (**2a**) at room temperature using cationic Rh(I)/bisphosphine complexes, which are effective for the reaction shown in eq 1, but no cycloaddition product was generated. After screening catalysts and reaction conditions,[14] we were pleased to find that $[Rh(cod)_2]SbF_6$ effectively catalyzed the [3 + 2] cycloaddition when excess **2a** and high concentration were employed, affording cyclopentadiene **3aa** in 81% yield (Table 1). Not only diethyl but also diisopropyl and dimethyl acetylenedicarboxylates reacted with **1a**, giving cyclopentadienes **3ab** and **3ac**, respectively, in good yields. With respect to propargyl esters, a variety of tertiary propargyl esters reacted with **2a** to yield cyclopentadienes **3ba**−**ga** in good yields.[15] Furthermore, a secondary propargyl ester was able to react with **2a** to yield the isomerized cyclopentadiene **4ha**. Not only electron-deficient alkynes **2** but also electron-deficient alkenes, acrylamides **5**,[16] were suitable cycloaddition partners (Table 2). *N*,*N*-dimethyl-,

[†] Department of Applied Chemistry.
[‡] Instrumentation Analysis Center.

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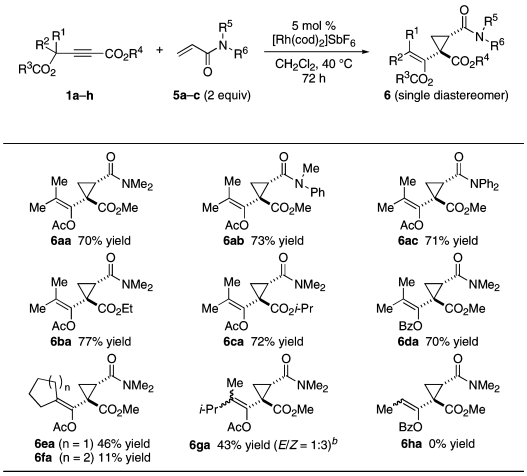
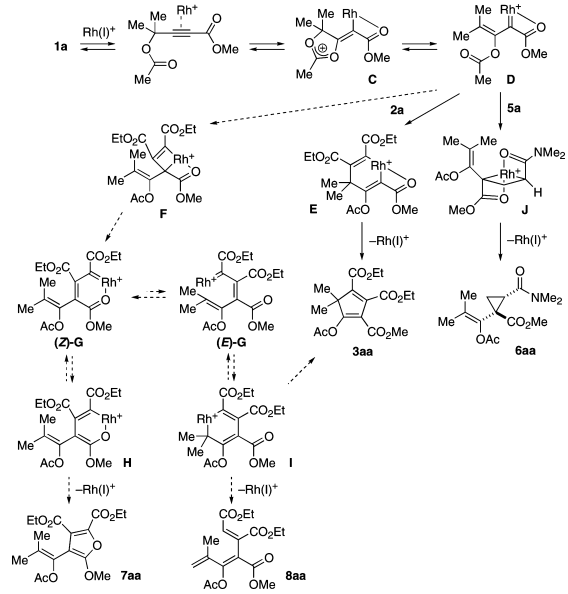
Table 2. Rhodium-Catalyzed [2 + 1] Cycloaddition[a]



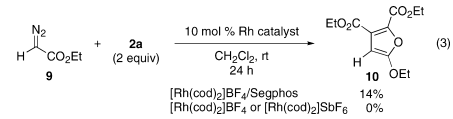
[a] $[Rh(cod)_2]SbF_6$ (0.025 mmol), **1a**−**h** (0.50 mmol), **5a**−**c** (1.00 mmol), and CH_2Cl_2 (1.0 mL) were used. Cited yields are of isolated products. [b] Catalyst: 10 mol %.

Scheme 1



N-methyl-*N*-phenyl-, and *N*,*N*-diphenylacrylamides reacted with **1a** at 40 °C to give cyclopropanes **6aa**−**ac** in good yields with perfect diastereoselectivity. The cyclopropanation of acrylamide **5a** with a variety of tertiary propargyl esters proceeded to afford cyclopropanes **6ba**−**ea** and **6ga** in good yields as single diastereomers, while *exo*-alkylidenecyclohexane **6fa** was generated in low yield and a secondary propargyl ester failed to react with **5a**.

A plausible mechanism for the formation of **3aa** and **6aa** is shown in Scheme 1. A metalla-Diels−Alder reaction[5,17] of alkenylcarbene **D** with **2a** furnishes rhodacycle **E**, and subsequent reductive elimination yields **3aa**. According to the proposed mechanism of the [3 + 2] cycloaddition of diazoacetates with alkynes to give furans,[18] the formation of furan **7aa** through intermediates **F**, (*Z*)-**G**, and **H** would also be possible. The metalla-Diels−Alder reaction rather than the [2 + 2] cycloaddition of $Rh(I)^+$/cod alkenylcarbene **D** with **2a** proceeds preferentially under the present reaction conditions, which might account for the observed chemoselective formation of **3aa** rather than **7aa**. Indeed, the $Rh(I)^+$/cod complexes failed to catalyze the cycloaddition of ethyl diazoacetate (**9**) with **2a**, while the $Rh(I)^+$/bisphosphine complex did catalyze the cycloaddition (eq 3):



The formation of **3aa** through intermediates **F**, (*E*)-**G**, and **I** might also be excluded as a result of the stable Rh−O chelation in (*Z*)-**G** and the absence of possible β-hydride elimination product **8aa**. On the other hand, the [2 + 2] cycloaddition of intermediate **D** with **5a** furnishes rhodacyclobutane **J**. Subsequent reductive elimination yields **6aa**. Trans chelation of the ester and amide carbonyl groups to the cationic rhodium in intermediate **J** might account for the observed perfect diastereoselectivity.[19,20] Chelation of the alkenylacetate carbonyl group might be excluded because of the equilibration between intermediates **C** and **D**.[13a,b]

Future work will focus on further investigations into mechanistic insights and applications in organic synthesis.

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Supporting Information Available: Experimental procedures, compound characterization data, optimization of reaction conditions, and X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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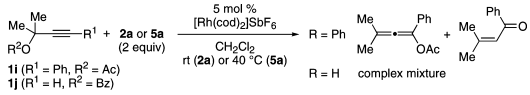
(14) Ru(II), Pd(II), Pt(II), and Au(I) complexes failed to catalyze the reaction.

(15) When phenyl-substituted propargyl ester **1i** was employed, the corresponding cycloaddition products were not obtained at all. The corresponding allene, generated through the 1,3-acyloxy rearrangement, and its hydrolyzed ketone were obtained as major products. The reactions of terminal propargyl ester **1j** led to a complex mixture of products:



(16) We have previously found that acrylamides are suitable coupling partners for the cationic rhodium(I)-catalyzed hydroacylation and cycloaddition. See: (a) Shibata, Y.; Tanaka, K. *J. Am. Chem. Soc.* **2009**, *131*, 12552. (b) Tanaka, K.; Hagiwara, Y.; Noguchi, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 7260.

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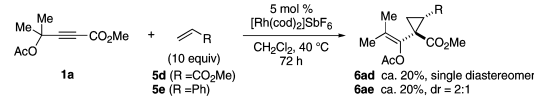
(19) Indeed, the reaction of **1a** with methyl acrylate (**5d**) furnished cyclopropane **6ad** as a single diastereomer, but that with styrene (**5e**) bearing no carbonyl group furnished cyclopropane **6ae** as a mixture of diastereomers, although these products could not be isolated in a pure form:



(20) The same diastereoselectivity was observed in the Ru(II)- (ref 2) and Co(II)-catalyzed (ref 3a) cyclopropanations of acrylates with **9**.

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