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Formation of Carbocycles via a 1,4-Rh Shift Triggered by a Rhodium-Catalyzed Addition of Terminal Alkynes to 3,3-Diarylcyclopropenes

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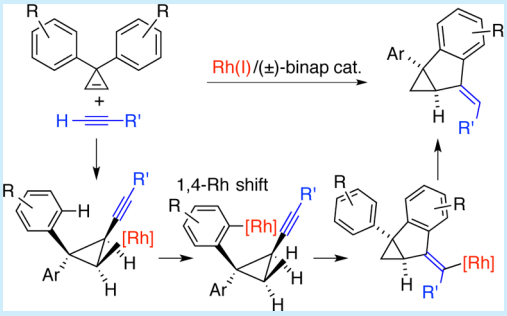
Supporting Information

ABSTRACT: The catalytic addition of terminal alkynes to 3,3-diarylcyclopropenes in the presence of a Rh(I)/binap complex proceeded to give the cycloaddition products in good yields, where a 1,4-Rh shift is involved as a key step.

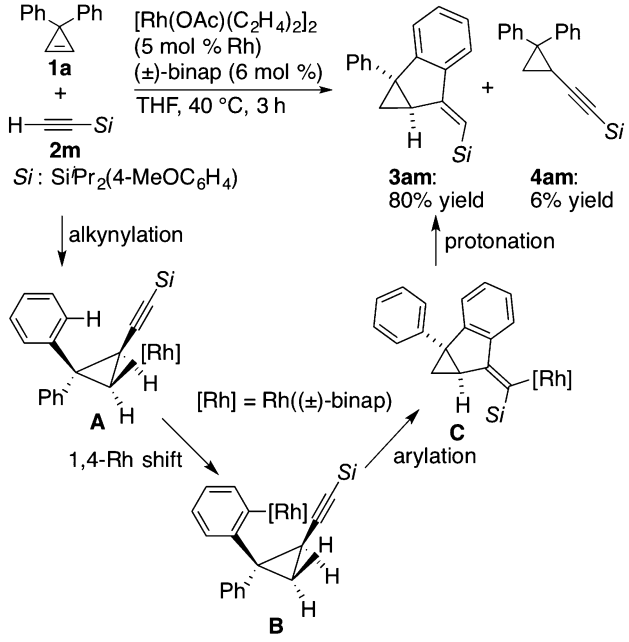


Transition-metal-catalyzed addition of terminal alkynes to carbon−carbon double bonds is a highly atom-economical and straightforward method to introduce an alkyne unit with the formation of a carbon−carbon bond.[1] Of a variety of transition-metal catalysts for the alkynylation reaction,[2−7] Rh catalysts have been recently developed to achieve the addition of terminal alkynes to α,β-unsaturated carbonyl compounds,[8] nitroalkenes,[9] allenes,[10] and strained bicyclic alkenes in high yields.[11]

Addition of nucleophiles to cyclopropenes, which have strained reactive double bonds, has provided an easy access to multisubstituted cyclopropanes, which are often included in bioactive molecules.[12] There have been several reports on the transition-metal-catalyzed addition of boron,[13] tin,[14] silane,[14a,d] and carbon nucleophiles to cyclopropenes.[15,16] The catalytic addition reaction of terminal alkynes to cyclopropenes was first reported by Chisholm and co-workers,[3b] where a variety of terminal alkynes are introduced into the cyclopropane rings in high yields by use of a Pd catalyst. Tenaglia reported that a highly diastereoselective alkynylation of unsymmetrically substituted cyclopropenes is achieved using a bulky Herrmann−Beller phosphapalladacycle catalyst.[3d] In this context, we found that the reaction of 3,3-diarylcyclopropenes with terminal alkynes proceeded in the presence of a Rh catalyst to give cycloaddition products, which are formed via a C−H activation of an aromatic ring. Here we report the rhodium-catalyzed cycloaddition reaction involving a 1,4-Rh shift as a key step.

Treatment of 3,3-diphenylcyclopropene (**1a**) with terminal alkyne **2m** (1.2 equiv) in the presence of $[Rh(OAc)(C_2H_4)_2]_2$ (5 mol % Rh) and (±)-binap (6 mol %) in tetrahydrofuran (THF) at 40 °C for 3 h gave cycloaddition product **3am** in 80% yield along with the formation of a small amount of addition product **4am** (6% yield) (Scheme 1). The formation of **3am** can be explained by the following proposed mechanism. The

Scheme 1. Rh-Catalyzed Addition of Alkyne 2m to 3,3-Diphenylcyclopropene (1a)



addition of in situ generated alkynylrhodium(I)[17] to 1,1-diphenylcyclopropene (**1a**) forms alkylrhodium **A**, which undergoes a 1,4-Rh shift to form arylrhodium **B**.[18] The intramolecular arylation of the alkyne gives alkenylrhodium **C**,[19] followed by the protonation giving **3am**. Since the pioneering studies of the 1,4-Rh shift by Miura and co-workers

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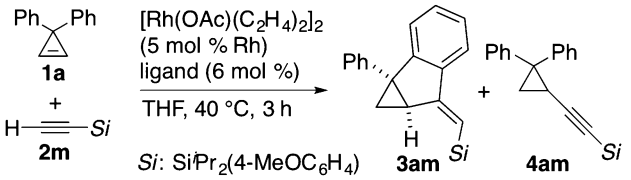
in 2000,[18a] the reaction involving the 1,4-Rh shift has been developed as a useful method for the construction of multiple carbon−carbon bonds successively.[18,19a,20,21] Very recently, Shintani and Nozaki reported a Rh-catalyzed polymerization of 3,3-diarylcyclopropenes, where a 1,4-rhodium migration of a cyclopropylrhodium(I) species cis to an aromatic ring takes place to form an arylrhodium(I) intermediate.[18m]

A proper choice of the ligand was found to be essential for the formation of the cycloaddition products in good yield (Table 1). In contrast to the reaction with (±)-binap giving an

Table 1. Ligand Effects[a]



entry	ligand	3am[b] (%)	4am[b] (%)
1	(±)-binap	81 (80)[c]	6
2	dppe	4	7
3	dppp	1	2
4	dppb	1	1
5	dppf	3	3
6	xantphos	0	0
7[d]	(±)-binap	88 (85)[c]	5

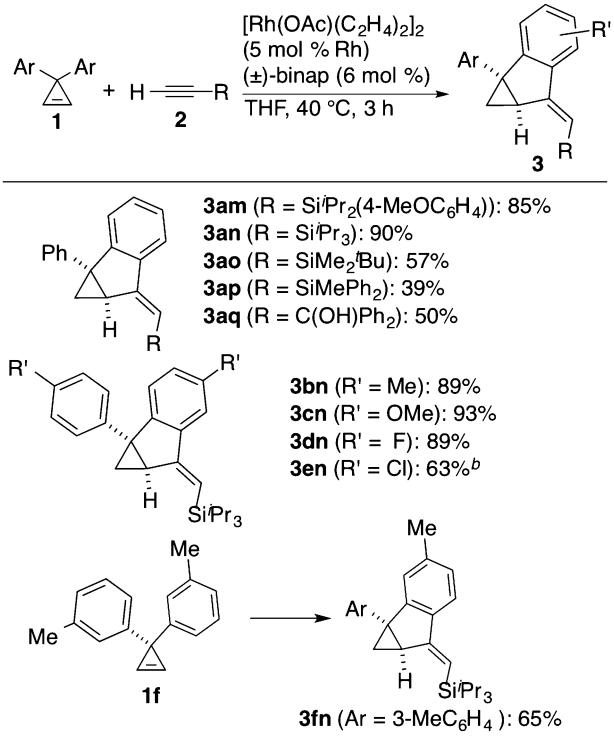
[a]Reaction conditions: **1a** (0.20 mmol), **2m** (0.24 mmol), [Rh(OAc)-$(C_2H_4)_2]_2$ (0.0050 mmol, 0.010 mmol of Rh), ligand (0.012 mmol), THF (1.0 mL) at 40 °C for 3 h. [b]Determined by ^{1}H NMR using nitromethane as an internal standard. [c]Isolated yields. [d]**1a** (0.24 mmol), **2m** (0.20 mmol).

80% yield of the cycloaddition product **3am** (entry 1), bisphosphine ligands, such as dppe, dppp, dppb, dppf, and xantphos, were ineffective in catalyzing the formation of both the cycloaddition product **3am** and the alkynylation product **4am** (entries 2−6).[22] The use of a slight excess of cyclopropene **1a** improved the yield of **3am** (85% yield, entry 7).[23]

The results obtained for the addition of terminal alkynes to 3,3-diarylcyclopropens are summarized in Scheme 2. The reactions with silylacetylenes, such as ((diisopropyl)(4-methoxyphenyl)silyl)acetylene (**2m**), (triisopropylsilyl)-acetylene (**2n**), (*tert*-butyldimethylsilyl)acetylene (**2o**), and (methyldiphenylsilyl)acetylene (**2p**), proceeded to give the corresponding cycloaddition products in 39−90% yields, where the use of alkynes substituted with a bulkier silyl group gave a higher yield of the product. A sterically hindered terminal alkyne **2q** other than silylacetylenes is also applicable to give the cycloaddition product **3aq** in 50% yield. On the other hand, in the reaction with 1-octyne, either the cycloaddition product or the addition product was not formed due to the alkyne oligomerization. The reactions of (triisopropylsilyl)acetylene (**2n**) with 3,3-diarylcyclopropenes having both the electron-withdrawing (Cl, F) and -donating groups (OMe, Me) at the para-position gave the corresponding products **3bn**−**en** in moderate to good yields (63−93% yields). In the reaction of cyclopropene **1f** possessing *m*-tolyl groups, the 1,4-Rh shift selectively took place at the less hindered C−H bond to give **3fn** in 65% yield. The observed selectivity of the 1,4-Rh shift is similar to those reported in the previous studies.[18a,j,21b,d,e]

The reaction of unsymmetrically substituted cyclopropenes **1g** and **1h** bearing a cyclohexyl and an isopropyl group at the 3-

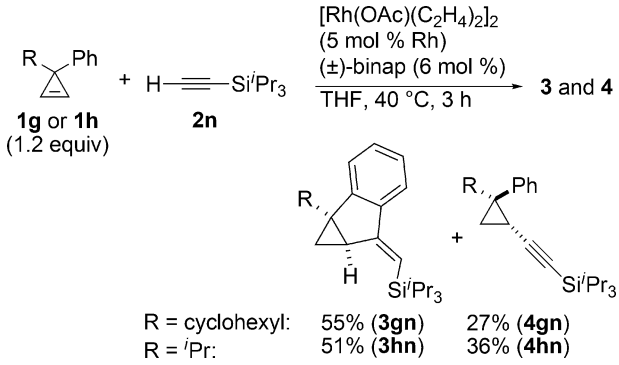
Scheme 2. Rh-Catalyzed Addition of Alkyne 2 to 3,3-Diarylcyclopropenes 1[a]



[a]Reaction conditions: **1** (0.24 mmol), **2** (0.20 mmol), [Rh(OAc)-$(C_2H_4)_2]_2$ (0.01 mmol of Rh), (±)-binap (0.012 mmol), THF (1.0 mL) at 40 °C for 3 h. Isolated yields are shown. [b]For 24 h.

position gave the corresponding cycloaddition products **3gn** and **3hn** in 55% and 51% yield, respectively, where an attack of the alkyne **2n** from the side of the alkyl group result in the formation of the addition product **4gn** and **4hn** in 27% and 36% yield, respectively (Scheme 3).

Scheme 3. Rh-Catalyzed Addition of Alkyne 2n to Unsymmetrically Substituted Cyclopropenes



The silyl group at the alkene moiety of **3am** can be removed by treatment of **3am** with tetrabutylammonium fluoride (TBAF) in dimethyl sulfoxide (DMSO) at 90 °C for 20 h. The reaction gave **5** in 73% yield (Scheme 4). The resulting cyclic compound **5** was further converted into 1,4-disubstituted naphthalene **6** in 85% yield in the presence of *p*-toluenesulfonic acid monohydrate (pTsOH·H_2O).

A deuterium-labeling experiment gave information about the protonation step in the catalytic cycle (Scheme 5). The reaction

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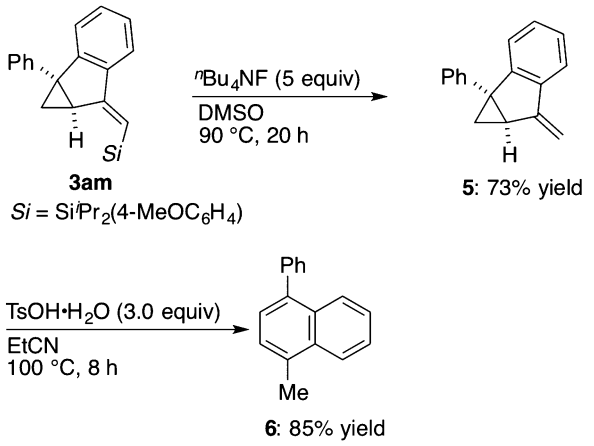
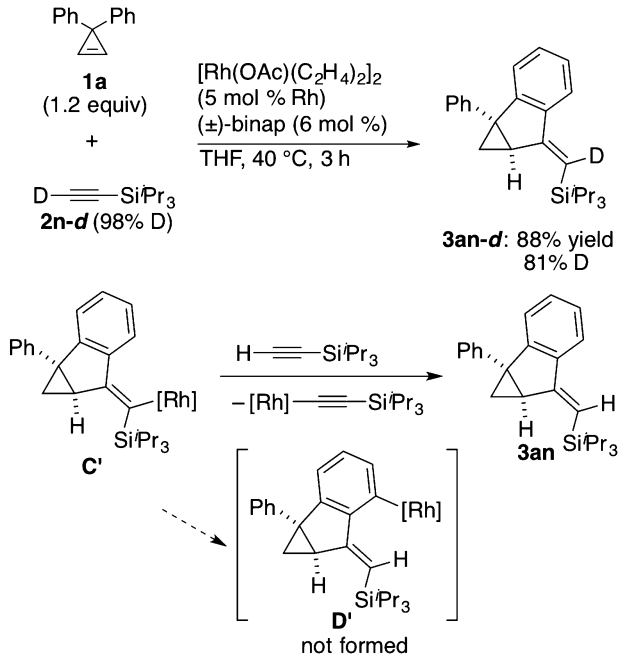
Scheme 4. Transformations of 3am



Scheme 5. Deuterium-Labeling Experiment



of **1a** with deuterated alkyne **2n-*d*** gave the cycloaddition product **3an-*d*** in 88% yield, where an 81% incorporation of deuterium at the alkene moiety was observed and any other position was not deuterated. This result indicates that alkenylrhodium(I) intermediate **C′** reacts with the terminal alkyne to give the corresponding cycloaddition product and to regenerate the alkynylrhodium(I) species in the catalytic cycle. In addition, alkenylrhodium **C′** does not undergo a further 1,4-Rh shift to the aromatic group forming **D′**, probably because the low flexibility of the alkenylrhodium **C′** inhibits the approach of the Rh center to the aromatic C−H bond.[21f]

In summary, we have developed a rhodium/binap complex-catalyzed reaction of 3,3-diarylcyclopropenes with terminal alkynes giving cycloaddition products, which involves a 1,4-Rh shift as a key step.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and spectroscopic and analytical data for the substrates and products. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b00984.

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Notes

The authors declare no competing financial interest.

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(22) Key: dppe, 1,2-bis(diphenylphosphino)ethane; dppp, 1,3-bis(diphenylphosphino)propane; dppb, 1,4-bis(diphenylphosphino) butane; dppf, 1,1′-bis(diphenylphosphino)ferrocene; xantphos, 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene.

(23) The use of (*R*)-binap gave **3am** in 60% ee.

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