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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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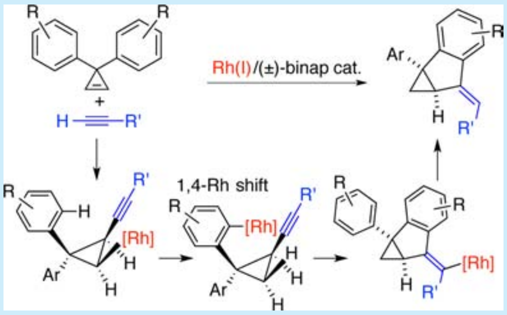
Supporting Information

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.

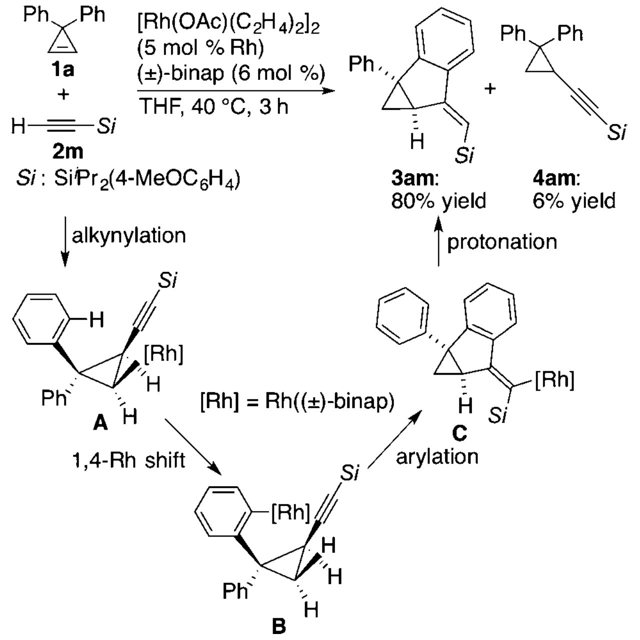


Transition-metal-catalyzed addition of terminal alkynes to carbon−carbon double bonds is a highly atom-economical and straightforward method to introduce an alkyne unit with the formation of a carbon−carbon bond.[1] Of a variety of transition-metal catalysts for the alkynylation reaction,[2−7] Rh catalysts 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 Hermann−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 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

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



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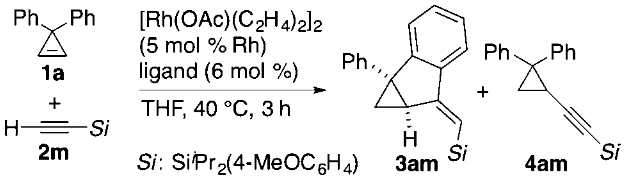
in 2000,[18a] the reaction involving the 1,4-Rh shift has been developed as a useful method for the construction of multiple carbon−carbon bonds successively.[18,19a,20,21] Very recently, Shintani and Nozaki reported a Rh-catalyzed polymerization of 3,3-diarylcyclopropenes, where a 1,4-rhodium migration 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 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]

Table 1. Ligand Effects[a]

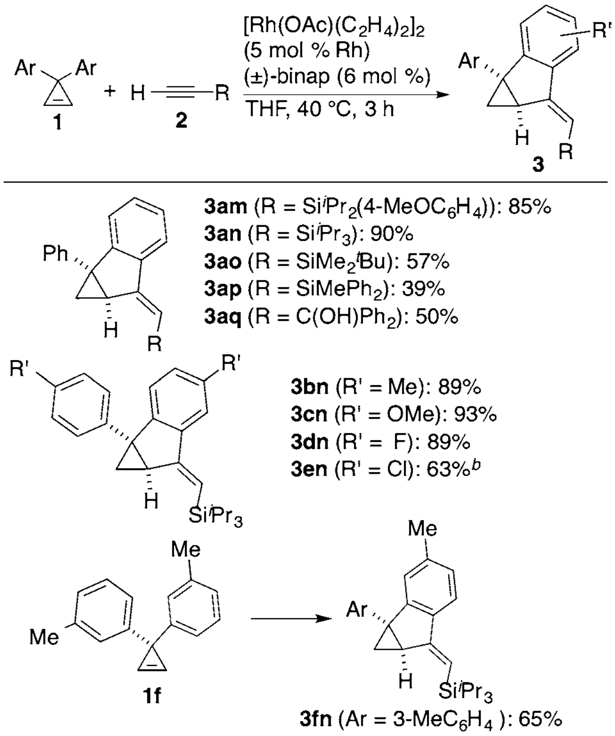


entry	ligand	**3am**[b] (%)	**4am**[b] (%)
1	(±)-binap	81 (80)[c]	6
2	dppe	4	7
3	dppp	1	2
4	dppb	1	1
5	dppf	3	3
6	xantphos	0	0
7[d]	(±)-binap	88 (85)[c]	5

[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).

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]

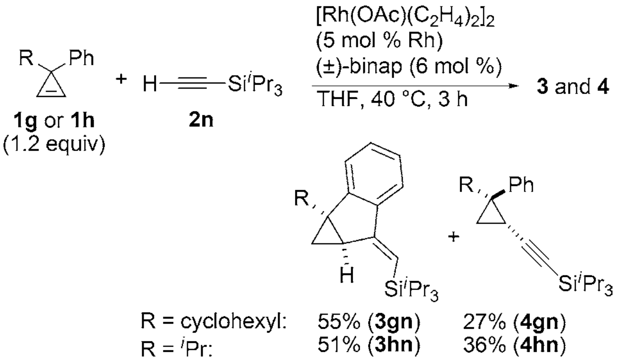
Scheme 2. Rh-Catalyzed Addition of Alkyne 2 to 3,3-Diarylcyclopropenes 1[a]



[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.

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

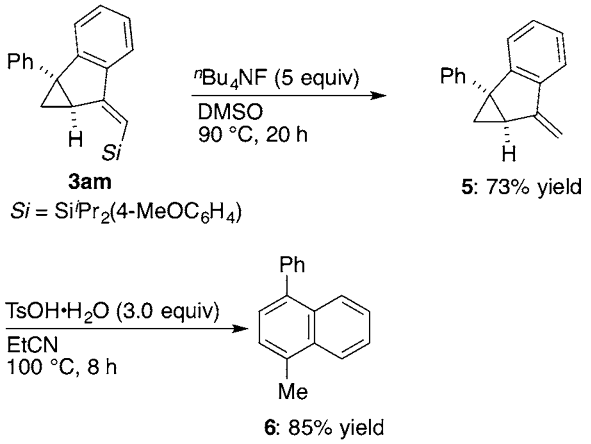
Scheme 3. Rh-Catalyzed Addition of Alkyne 2n to Unsymmetrically Substituted Cyclopropenes



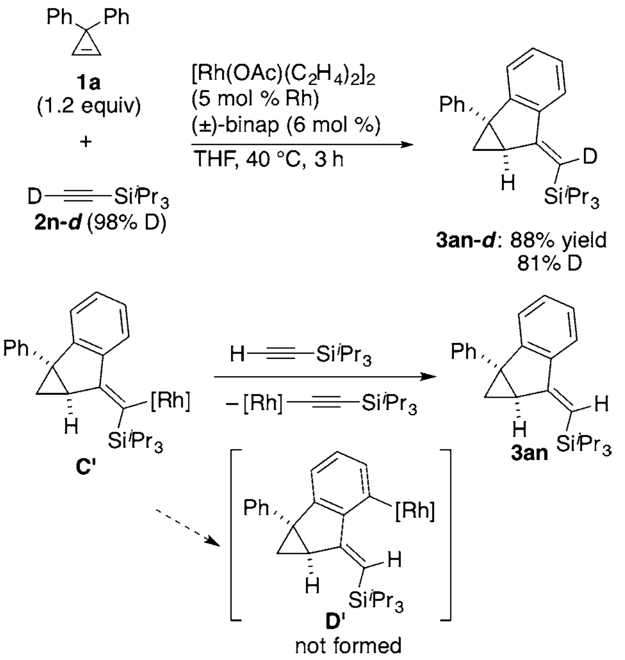
The silyl group at the alkene moiety of **3am** can be removed by treatment of **3am** with tetrabutylammonium fluoride (TBAF) in dimethyl sulfoxide (DMSO) at 90 °C for 20 h. The reaction gave **5** in 73% yield (Scheme 4). The resulting cyclic compound **5** was further converted into 1,4-disubstituted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

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

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.