

Rhodium-Catalyzed Hydroalkynylation of Internal Alkynes with Silylacetylenes: An Alkynylrhodium(I) Intermediate Generated from the Hydroxorhodium(I) Complex $[\text{Rh}(\text{OH})(\text{binap})]_2$

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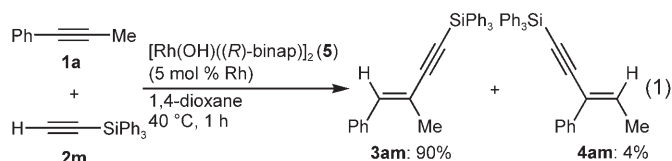
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Abstract: A highly selective hydroalkynylation of internal alkynes with silylacetylenes giving 1,3-enynes was realized by use of a hydroxorhodium catalyst. As a key intermediate in the catalytic cycle, an alkynylrhodium(I) complex was isolated and investigated for its structure and reactivity.

Keywords: alkynes; alkynylation; dimerization; rhodium

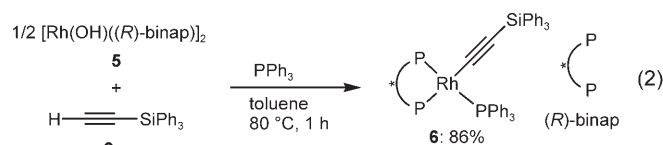
As a straightforward and economical method for preparing conjugate enynes, which are important building blocks in organic synthesis,^[1] the catalytic dimerization of alkynes has attracted considerable attention. Although several protocols have been developed for the homo-dimerization of terminal alkynes,^[2,3] there are only a few examples of selective cross-dimerization between terminal alkynes and internal ones,^[4,5] mainly because the terminal alkynes are highly reactive towards homo-dimerization or oligomerization. Here we describe that a hydroxorhodium(I) complex efficiently catalyzes the addition of silylacetylenes to internal alkynes giving conjugate enynes with high selectivity and that its catalytic cycle involves an alkynylrhodium(I) complex as a key intermediate.

A hydroxorhodium(I) complex coordinated with binap was found to be highly effective in catalyzing the addition of silylacetylenes to internal alkynes to give high yields of the cross-dimerization products with high selectivity. Thus, the reaction of 1-phenyl-1-propyne (**1a**) with (triphenylsilyl)ethyne (**2m**) (**1a/2m** = 1/1.5) in the presence of a catalytic amount of $[\text{Rh}(\text{OH})((R)\text{-binap})]_2$ (**5**) (5 mol % Rh) in 1,4-dioxane at 40 °C for 1 h gave a 90 % yield of (*E*)-1-triphenylsilyl-3-methyl-4-phenylbut-1-yn-3-ene (**3am**) together with a minor amount (4 %) of its regioisomer (*E*)-**4am** [Eq. (1)].^[7] The formation of (*E*)-isomers in-



dicates that the hydroalkynylation took place in a *syn* fashion.^[8]

In previous studies on the rhodium-catalyzed dimerization of terminal alkynes, alkynylrhodium(III) hydride or vinylidene-rhodium species have been proposed as key intermediates.^[2a,b,9] In our studies, we succeeded in isolating and characterizing an alkynylrhodium(I) complex, which gave us significant insights into the mechanism of the present hydroalkynylation. Thus, treatment of $[\text{Rh}(\text{OH})((R)\text{-binap})]_2$ (**5**) with silylacetylene **2m** and triphenylphosphine in toluene at 80 °C for 1 h brought about the selective formation of alkynylrhodium(I) complex **6** coordinated with binap and triphenylphosphine, which was isolated in 86 %



yield [Eq. (2)].^[10,11] The ³¹P NMR spectrum of the complex **6** in C₆D₆ showed three ddd peaks (32.6, 35.5, and 37.8 ppm) [Figure 1, (i)], which are characteristic for square planar rhodium complexes coordinated with three non-equivalent phosphorus atoms.^[6] The complex **6** was also formed in the reaction of hydroxorhodium **5** with propargylic alcohol **7** in place of **2m**, which should proceed *via* β-alkynyl elimination on an alkoxorhodium intermediate.^[12] The alkynyl complex **6** was fully characterized by introduction of

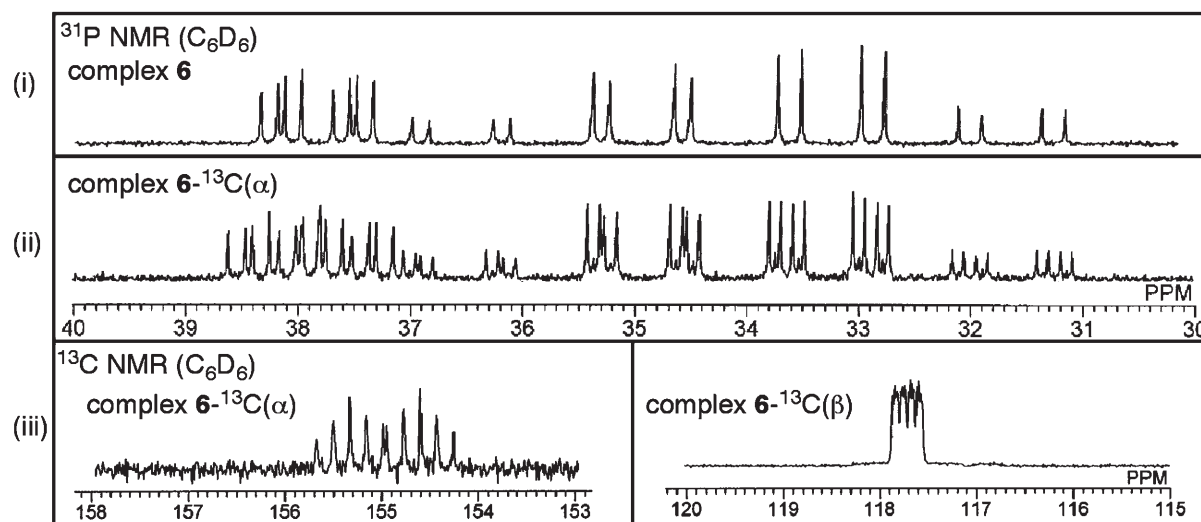
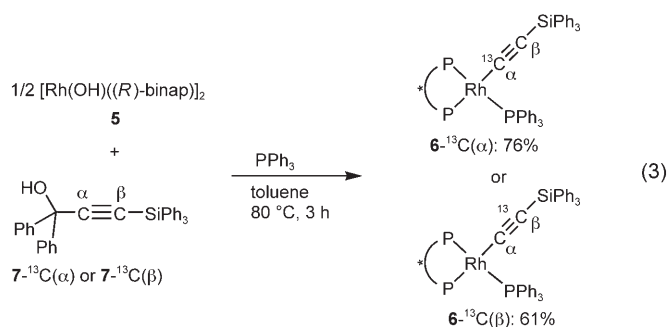


Figure 1. ^{31}P and ^{13}C NMR spectra (at 202 MHz for ^{31}P and 125 MHz for ^{13}C in C_6D_6 at room temperature) of alkynylrhodium complexes. (i) ^{31}P NMR spectrum of complex **6**. (ii) ^{31}P NMR spectrum of **6**- $^{13}\text{C}(\alpha)$. (iii) ^{13}C NMR spectra of **6**- $^{13}\text{C}(\alpha)$ [left, C(α)] and **6**- $^{13}\text{C}(\beta)$ [right, C(β)].

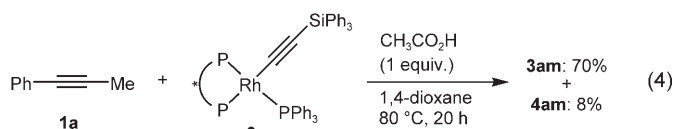
the silylethynyl group incorporated with ^{13}C at either the α or β position.^[13] The ^{13}C -labeled (90 % ^{13}C) rhodium complexes, **6**- $^{13}\text{C}(\alpha)$ and **6**- $^{13}\text{C}(\beta)$, were obtained in high yields by the elimination reaction with specifically ^{13}C -labeled propargylic alcohols **7** [Eq. (3)]. The



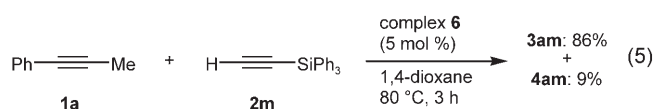
^{31}P NMR spectrum of the complex **6**- $^{13}\text{C}(\alpha)$ in C_6D_6 consisted of three dddd, where each peak has an additional coupling with $^{13}\text{C}(\alpha)$, the coupling constants ($^2J_{\text{C,P}}$) being 21, 22, and 92 Hz for the peaks at 32.6, 35.5, and 37.8 ppm, respectively [Figure 1, (ii)]. The ^{13}C NMR signal of the complex **6**- $^{13}\text{C}(\alpha)$ appeared at 155.0 ppm as dddd where the coupling constant between rhodium and ^{13}C ($^1J_{\text{Rh,C}(\alpha)}$) is 43 Hz [Figure 1, (iii)]. In the ^{13}C NMR spectrum of **6**- $^{13}\text{C}(\beta)$ (dddd, 117.7 ppm), all four coupling constants including $^2J_{\text{Rh,C}(\beta)} = 10$ Hz are much smaller than those observed for **6**- $^{13}\text{C}(\alpha)$. These ^{31}P and ^{13}C NMR spectra clearly indicate the direct connectivity between a rhodium center and the silylethynyl group.

A stoichiometric reaction of the alkynylrhodium complex **6** with alkyne **1a** (**6**/**1a** = 1/1) in the presence

of acetic acid (1 equiv.) was found to proceed at 80 °C to give a 78 % yield of the hydroalkynylation product [**3am**/**4am** = 90/10, Eq. (4)]. The high reaction temper-



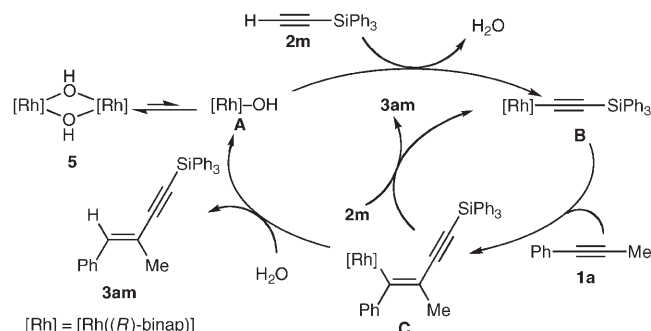
ature compared with that (40 °C) for the catalytic reaction is probably because the strongly coordinating triphenylphosphine ligand occupies a coordination site required for the activation of the alkyne prior to its insertion into the alkynyl-rhodium bond. Unfortunately, attempts to isolate a but-3-yn-1-enylrhodium intermediate before protonolysis were not successful, probably due to its instability under the reaction conditions. On monitoring the reaction of **1a** with **2m** catalyzed by complex **6** (5 mol %) at 80 °C, which gave a high yield of the hydroalkynylation products in 3 h [Eq. (5)], ^{31}P NMR spectrometry of the reaction mix-



ture showed that the alkynylrhodium complex **6** is a dominant species while the catalytic hydroalkynylation is proceeding.

On the basis of the results observed above which demonstrated the intermediacy of the alkynylrhod-

ium(I) species in the present hydroalkynylation, a catalytic cycle is proposed as illustrated in Scheme 1. A hydroxorhodium complex **A** which is in equilibrium



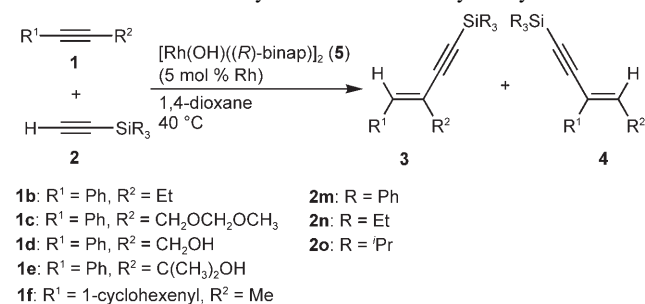
Scheme 1. Proposed catalytic cycle.

with dimeric hydroxorhodium **5**,^[14] undergoes a reaction with the terminal alkyne to form an alkynylrhodium(I) **B** and water. Insertion of the internal alkyne into the carbon-rhodium bond in **B** forms an alkenylrhodium species **C**. σ -Bond metathesis between alkenylrhodium **C** and the terminal alkyne or hydrolysis followed by alkynylation by way of **A** gives the enyne product to regenerate the alkynylrhodium intermediate **B**.^[5] The observation of the alkynylrhodium complex **6** as a dominant rhodium species during the catalytic reaction may indicate that alkynylrhodium **B** is a resting stage in the catalytic cycle.

As summarized in Table 1, $[\text{Rh}(\text{OH})((R)\text{-binap})]_2$ (**5**) efficiently catalyzed the addition of (triphenylsilyl)ethyne (**2m**) to several types of phenyl-(alkyl)acetylenes **1b–1e** to give over 90% yields of the corresponding enynes **3** with high regioselectivity (entries 1–3 and 5). The reaction of **2d** on a 2-mmol scale with a reduced amount of the rhodium catalyst (2 mol%) successfully proceeded to give enyne **3dm** in 87% yield (entry 4). The addition to alkenylacetylene **1f** also proceeded with high regioselectivity (entry 6). As a terminal acetylene, (triethylsilyl)- (**2n**) and (triisopropylsilyl)ethyne (**2o**) can be used as well,^[15] the addition to propargylic alcohol **1e** giving high yields of the corresponding enynes **3** (entries 7 and 8). For the addition to dialkylacetylenes, 4-octyne (**1g**) and 1,4-dimethoxy-2-butyne (**1h**), a rhodium complex coordinated with 1,6-bis(diphenylphosphino)hexane (dpph), generated *in situ* from $[\text{Rh}(\text{OH})(\text{cod})]_2$ and dpph, was more effective than the binap complex **5** to give enynes **3gm** and **3hm** in higher yields [Eq. (6)].^[16] The addition of **2m** to 2-butyne **1i** was also catalyzed by the dpph-rhodium catalyst.

In summary, highly selective hydroalkynylation of internal alkynes with silylacetylenes giving 1,3-enynes was realized by use of a hydroxorhodium catalyst. As a key intermediate in the catalytic cycle, an alkynyl-

Table 1. Rhodium-catalyzed addition of silylacetylenes.^[a]



Entry	Alkyne 1	Alkyne 2	Time [h]	Yield [%] ^[b]	3/4 ^[c]
1	1b	2m	1	90	97/3
2	1c	2m	2	95	95/5
3	1d	2m	2	92	98/2
4 ^[d]	1d	2m	3	87	98/2
5 ^[e]	1e	2m	4	93	94/6
6 ^[e,f]	1f	2m	12	80	93/7
7 ^[e]	1e	2n	4	92	98/2
8 ^[e]	1e	2o	4	96	98/2

^[a] Reaction conditions: $[\text{Rh}(\text{OH})((R)\text{-binap})]_2$ (**5**) (5 mol % of Rh), internal alkyne **1** (0.20 mmol), terminal alkyne **2** (0.30 mmol), 1,4-dioxane (0.4 mL) at 40 °C.

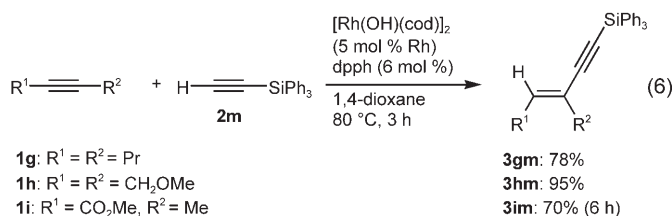
^[b] Isolated yields of **3** and **4**.

^[c] Determined by ^1H NMR.

^[d] The reaction was conducted in 2.0 mmol scale with $[\text{Rh}(\text{OH})((R)\text{-binap})]_2$ (**5**) (2 mol % of Rh) at 80 °C.

^[e] Performed at 60 °C.

^[f] Alkyne **2m** (0.4 mmol) was used.



rhodium(I) complex was isolated and investigated for its structure and reactivity.

Experimental Section

Typical Procedure

To a solution of $[\text{Rh}(\text{OH})((R)\text{-binap})]_2$ (**5**) (7.4 mg, 0.010 mmol of Rh) in 1,4-dioxane (0.40 mL) in a screw-cap test tube was added (triphenylsilyl)acetylene (85.3 mg, 0.30 mmol) and 1-phenyl-1-propyne (23.2 mg, 0.20 mmol) successively, and the tube was capped tightly. Then, the mixture was allowed to stir at 40 °C (bath temperature) for 1 h. The reaction mixture was passed through a short silica gel column eluting with Et_2O . Evaporation of the solvent followed by preparative thin-layer chromatography on silica gel (eluent: *n*-hexane/ethyl acetate = 10/1) gave a mixture of

3am and **4am** (**3am/4am** = 96/4) as a colorless oil; yield: 75.3 mg (0.19 mmol, 94 %).

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