DOI: 10.1002/adsc.200700334

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

Takahiro Nishimura,[a,*] Xun-Xiang Guo,[a] Kohei Ohnishi,[a] and Tamio Hayashi[a,*]

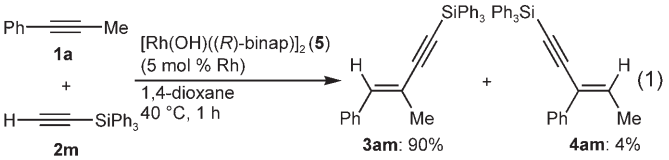
[a] Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan
Fax: (+81)-75-753-3988; e-mail: tnishi@kuchem.kyoto-u.ac.jp or thayashi@kuchem.kyoto-u.ac.jp

Received: July 9, 2007; Published online: November 27, 2007

Supporting information for this article is available on the WWW under http://asc.wiley-vch.de/home/.

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.

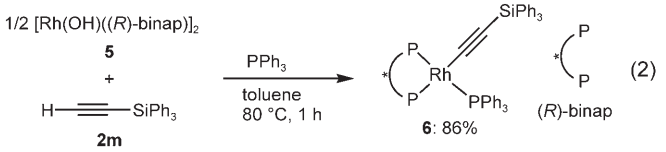
Keywords: alkynes; alkynylation; dimerization; rhodium



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 $[Rh(OH)((R)\text{-binap})]_2$[6] (**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 indicates 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 $[Rh(OH)((R)\text{-binap})]_2$ (**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 ^{31}P NMR spectrum of the complex **6** in C_6D_6 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



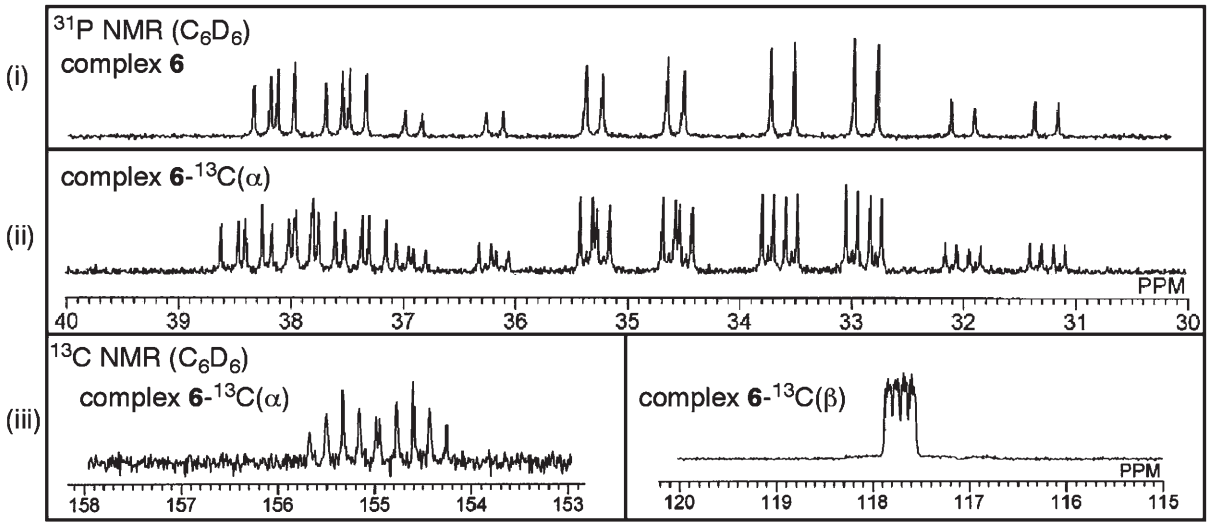
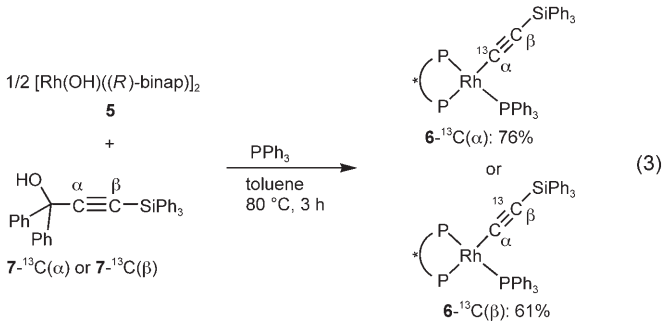


Figure 1. ^{31}P and ^{13}C NMR spectra (at 202 MHz for ^{31}P and 125 MHz for ^{13}C in C_6D_6 at room temperature) of alkynylrhodium complexes. (i) ^{31}P NMR spectrum of complex **6**. (ii) ^{31}P NMR spectrum of **6**-$^{13}C(\alpha)$. (iii) ^{13}C NMR spectra of **6**-$^{13}C(\alpha)$ [*left*, C(α)]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

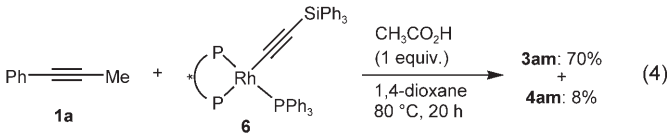
the silylethynyl group incorporated with ^{13}C at either the α or β position.[13] The ^{13}C-labeled (90% ^{13}C) rhodium complexes, **6**-$^{13}C(\alpha)$ and **6**-$^{13}C(\beta)$, were obtained in high yields by the elimination reaction with specifically ^{13}C-labeled propargylic alcohols **7**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



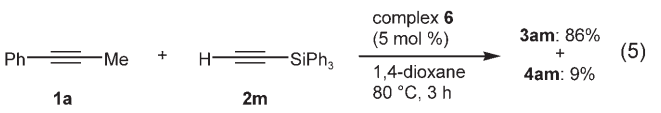
(3)

^{31}P NMR spectrum of the complex **6**-$^{13}C(\alpha)$ in C_6D_6 consisted of three dddds, where each peak has an additional coupling with $^{13}C(\alpha)$, the coupling constants ($^2J_{C,P}$) 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**-$^{13}C(\alpha)$ appeared at 155.0 ppm as dddd where the coupling constant between rhodium and ^{13}C ($^1J_{Rh,C(\alpha)}$) is 43 Hz [Figure 1, (iii)]. In the ^{13}C NMR spectrum of **6**-$^{13}C(\beta)$ (dddd, 117.7 ppm), all four coupling constants including $^2J_{Rh,C(\beta)} = 10$ Hz are much smaller than those observed for **6**-$^{13}C(\alpha)$. 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 temperature 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 mixture showed that the alkynylrhodium complex **6** is a dominant species while the catalytic hydroalkynylation is proceeding.



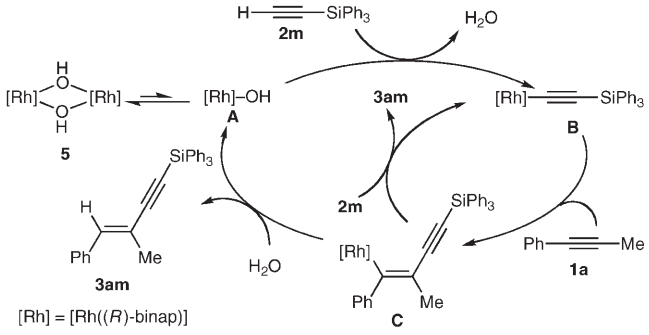
(4)



(5)

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



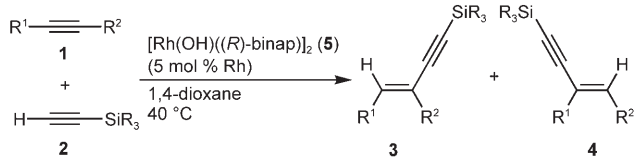
Scheme 1. Proposed catalytic cycle.

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, $[Rh(OH)((R)\text{-binap})]_2$ (**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 $[Rh(OH)(cod)]_2$ 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-butynoate **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 alkynylrhodium(I) complex was isolated and investigated for its structure and reactivity.

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

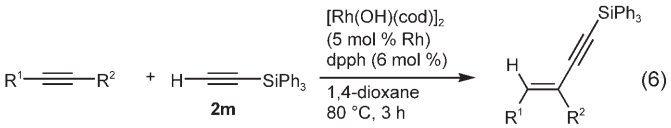


1b: R^1 = Ph, R^2 = Et
1c: R^1 = Ph, R^2 = $CH_2OCH_2OCH_3$
1d: R^1 = Ph, R^2 = CH_2OH
1e: R^1 = Ph, R^2 = $C(CH_3)_2OH$
1f: R^1 = 1-cyclohexenyl, R^2 = Me

2m: R = Ph
2n: R = Et
2o: R = ^{i}Pr

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: $[Rh(OH)((R)\text{-binap})]_2$ (**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 ^{1}H NMR.
[d] The reaction was conducted in 2.0 mmol scale with $[Rh(OH)((R)\text{-binap})]_2$ (**5**) (2 mol% of Rh) at 80 °C.
[e] Performed at 60 °C.
[f] Alkyne **2m** (0.4 mmol) was used.



(6)

1g: R^1 = R^2 = Pr
1h: R^1 = R^2 = CH_2OMe
1i: R^1 = CO_2Me, R^2 = Me

3gm: 78%
3hm: 95%
3im: 70% (6 h)

Experimental Section

Typical Procedure

To a solution of $[Rh(OH)((R)\text{-binap})]_2$ (**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%).

Acknowledgements

This work was supported in part by a Grant-in-Aid for Scientific Research on Priority Areas "Advanced Molecular Transformations of Carbon Resources" from the Ministry of Education, Culture, Sports, Science and Technology, Japan

References

[1] B. M. Trost, *Science* **1991**, *254*, 1471; B. M. Trost, *Angew. Chem. Int. Ed.* **1995**, *34*, 259; K. C. Nicolaou, W. M. Dai, S. C. Tsay, V. A. Estevez, W. Wrasidlo, *Science* **1992**, *256*, 1172.

[2] For recent examples of dimerization of terminal alkynes, see: Rh a) W. Weng, C. Guo, R. Çelenligil-Çetin, B. M. Foxman, O. V. Ozerov, *Chem. Commun.* **2006**, 197; b) C.-C. Lee, Y.-C. Lin, Y.-H. Liu, Y. Wang, *Organometallics* **2005**, *24*, 136; Ir c) R. Ghosh, X. Zhang, P. Achord, T. J. Emge, K. Krogh-Jespersen, A. S. Goldman, *J. Am. Chem. Soc.* **2007**, *129*, 853; d) M. V. Jiménez, E. Sola, F. J. Lahoz, L. A. Oro, *Organometallics* **2005**, *24*, 2722; e) T. Ohmura, S. Yorozuya, Y. Yamamoto, N. Miyaura, *Organometallics* **2000**, *19*, 365; Ru f) X. Chen, P. Xue, H. H. Y. Sung, I. D. Williams, M. Peruzzini, C. Bianchini, G. Jia, *Organometallics* **2005**, *24*, 4330; g) Y. Gao, R. J. Puddephatt, *Inorg. Chim. Acta* **2003**, *350*, 101; h) M. Bassetti, S. Marini, J. Díaz, M. P. Gamasa, J. Gimeno, Y. Rodríguez-Álvarez, S. García-Granda, *Organometallics* **2002**, *21*, 4815; Ni i) S. Ogoshi, M. Ueta, M. Oka, H. Kurosawa, *Chem. Commun.* **2004**, 2732; Pd j) C. Yang, S. P. Nolan, *J. Org. Chem.* **2002**, *67*, 591; k) M. Rubina, V. Gevorgyan, *J. Am. Chem. Soc.* **2001**, *123*, 11107; other metals; l) K. Komeyama, T. Kawabata, K. Takehira, K. Takaki, *J. Org. Chem.* **2005**, *70*, 7260; m) M. Nishiura, Z. Hou, Y. Wakatsuki, T. Yamaki, T. Miyamoto, *J. Am. Chem. Soc.* **2003**, *125*, 1184; n) M. Nishiura, Z. Hou, *J. Mol. Catal. A* **2004**, *213*, 101.

[3] Cross-dimerization of terminal alkynes, see: a) H. Katayama, H. Yari, M. Tanaka, F. Ozawa, *Chem. Commun.* **2005**, 4336; b) J. Wang, M. Kapon, J. C. Berthet, M. Ephritikhine, M. S. Eisen, *Inorg. Chim. Acta* **2002**, *334*, 183; c) M. Akita, H. Yasuda, A. Nakamura, *Bull. Chem. Soc. Jpn.* **1984**, *57*, 480.

[4] For examples of the addition of terminal alkynes to electron-deficient alkynes, see: a) B. M. Trost, M. T. Sorum, C. Chan, A. E. Harms, G. Rühter, *J. Am. Chem. Soc.* **1997**, *119*, 698, and references cited therein; b) L. Chen, C.-J. Li, *Tetrahedron Lett.* **2004**, *45*, 2771; c) T. Hirabayashi, S. Sakaguchi, Y. Ishii, *Adv. Synth. Catal.* **2005**, *347*, 872; d) U. Lücking, A. Pfaltz, *Synlett* **2000**, 1261.

[5] For an example of the addition of terminal alkynes to internal alkynes, see: C. S. Yi, N. Liu, *Organometallics* **1998**, *17*, 3158. Very recently, Miura reported rhodium-catalyzed cross dimerization of silylacetylenes and internal alkynes: T. Katagiri, H. Tsurugi, A. Funayama, T. Satoh, and M. Miura, *Chem. Lett.* **2007**, *36*, 830. Although the present reaction in this manuscript is similar to that reported by Miura, we have studied mechanistic aspects of the reaction including characterization of the intermediates in the catalytic cycle as well as its synthetic aspects.

[6] T. Hayashi, M. Takahashi, Y. Takaya, M. Ogasawara, *J. Am. Chem. Soc.* **2002**, *124*, 5052.

[7] Similar regioselectivity was observed in the rhodium(I)-catalyzed hydroarylation of alkynes with arylboronic acids, see: T. Hayashi, K. Inoue, N. Taniguchi, M. Ogasawara, *J. Am. Chem. Soc.* **2001**, *123*, 9918.

[8] The *E* geometry (>98%) was confirmed by NOE experiments.

[9] a) H. Werner, *Coord. Chem. Rev.* **2004**, *248*, 1693, and references cited therein; b) W. T. Boese, A. S. Goldman, *Organometallics* **1991**, *10*, 782; c) J. Ohshita, K. Furumori, A. Matsuguchi, M. Ishikawa, *J. Org. Chem.* **1990**, *55*, 3277; d) I. P. Kavalev, K. V. Yevdakov, Y. A. Strelenko, M. G. Vinogradov, G. I. Nikishin, *J. Organomet. Chem.* **1990**, *386*, 139.

[10] For an example of an alkynylrhodium(I) complex containing 1,5-cyclooctadiene and tricyclohexylphosphine, see: M. J. Fernández, M. A. Esteruelas, M. Covarrubias, L. A. Oro, *J. Organomet. Chem.* **1990**, *381*, 275.

[11] For examples of isolated alkynylrhodium(I) complexes, see: a) M. Schäfer, J. Wolf, H. Werner, *Organometallics* **2004**, *23*, 5713; b) H. Werner, J. Wolf, F. J. Garcia Alonso, M. L. Ziegler, O. Serhadli, *J. Organomet. Chem.* **1987**, *336*, 397.

[12] A. Funayama, T. Satoh, M. Miura, *J. Am. Chem. Soc.* **2005**, *127*, 15354.

[13] An alkynylruthenium-complex containing a ^{13}C-enriched alkynyl group, see: Y.-S. Yen, Y.-C. Lin, S.-L. Huang, Y.-H. Liu, H.-L. Sung, Y. Wang, *J. Am. Chem. Soc.* **2005**, *127*, 18037.

[14] A. Kina, H. Iwamura, T. Hayashi, *J. Am. Chem. Soc.* **2006**, *128*, 3904.

[15] The addition of 1-octyne did not give the cross-dimerization product.

[16] The $[Rh(OH)(cod)]_2$/dpph catalyst can also be applied to the addition to unsymmetrical arylacetylenes to give the corresponding enynes in high yields, although their regioselectivity was lower. For example, the addition of **2m** to **1c** gave a 92% yield of the hydroalkynylation products consisting of **3cm** (53%) and **4cm** (47%).

