Selective Hydrosilylation of 1-Alkynes Using Iridium Catalyst with Biphosphinine Ligand

Yoshihiro Miyake, Eigo Isomura, and Masahiko Iyoda*
Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397

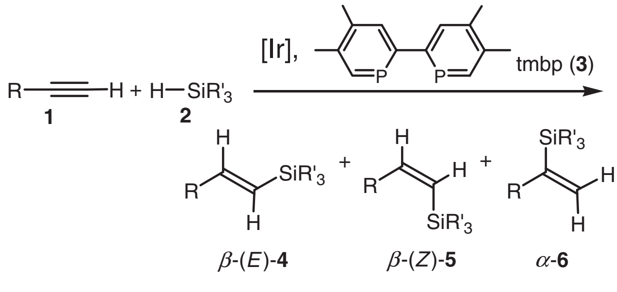
(Received April 28, 2006; CL-060506; E-mail: iyoda-masahiko@c.metro-u.ac.jp)

The iridium-catalyzed hydrosilylation of alkynes in the presence of 4,4′,5,5′-tetramethylbiphosphinine (tmbp) has been explored. The hydrosilylation of alkynes in the presence of tmbp proceeds effectively to give β-(*E*)-vinylsilanes highly selectively in moderate to high yields, whereas a similar hydrosilylation in the absence of tmbp produces β-(*Z*)-vinylsilanes selectively. The stereoselectivity of these reactions suggests the importance of the electron-withdrawing properties of tmbp coordinated to iridium.

The hydrosilylation of alkynes with transition-metal catalysts is a simple and valuable method for the synthesis of alkenyl silanes, which are widely used for organic synthesis.[1] Thus, regio- and stereoselective reactions are indispensable for the synthetic use of alkenyl silanes. For the hydrosilylation of the terminal alkyne **1** with the silane **2**, three possible alkenylsilanes can be obtained, i.e., the β-(*E*)-adduct **4** (syn-addition), the β-(*Z*)-adduct **5** (anti-addition), and the α-adduct **6** (Scheme 1). As has been reported,[2] the anti-addition product **5** is formed by the insertion of the alkyne into an M–Si bond, followed by the isomerization of a vinyl complex[2a] to give **5** via a less sterically hindered intermediate. In addition to the steric effect, electron density at metal centers strongly affects the regioselectivity of the hydrosilylation of alkynes.[2b,3,4]

Ligands containing sp^2-hybridized phosphorus atom have a strong π-acceptor property because of their remarkable tendency to engage in metal-to-phosphorus π back donation, comparable to that of the carbonyl ligand.[5] Thus, these compounds are expected to decrease the electron density at metal centers. Recently, the characteristic catalytic activities of transition-metal complexes with diphosphinidene–cyclobutene ligands have been reported.[6] Although phosphinines, which are phosphorus analogues of pyridines, function as π-acceptor ligands, catalytic transformations using transition-metal complexes bearing phoshinine ligands have been limited until now.[5a,5e,7] We report herein the iridium-catalyzed hydrosilylation of **1** with a high stereoserectivity using 4,4′,5,5′-tetramethyl-2,2′-biphosphinine (tmbp, **3**).[8,9]

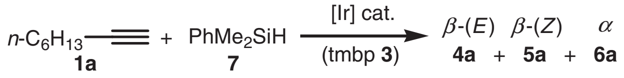
First, the hydrosilylation of 1-octyne (**1a**) was attempted and typical results are shown in Table 1. After some preliminary experiments, we found that $[\mathrm{Ir(COD)_2}][\mathrm{BF_4}]$ and $[\mathrm{Ir}(\eta^5\text{-}\mathrm{C_9H_7})(\mathrm{COD})]$ ($\eta^5\text{-}\mathrm{C_9H_7} = \eta^5$-indenyl) are ideal catalysts for the hydrosilylation of alkynes. Thus, the treatment of 1 equiv. of **1a** with 0.5 equiv. of $\mathrm{PhMe_2SiH}$ (**7**) in THF at 40 °C for 24 h in the presence of $[\mathrm{Ir(COD)_2}][\mathrm{BF_4}]$ (0.005 equiv.) produced corresponding vinylsilanes (**4a**, **5a**, and **6a**) in 94% total yield with β-(*Z*)-**5a** as the major product (Table 1, Entry 1). However, **3** retarded the iridium-catalyzed hydrosilylation of **1a**, and the reaction of **1a** with **7** under similar conditions led to the recovery of **1a** (95%) (Entry 2). In contrast, the hydrosilylation of **1a** with **7** in the presence of $[\mathrm{Ir}(\eta^5\text{-}\mathrm{C_9H_7})(\mathrm{COD})]$ gave different results. Although the reaction of **1a** with **7** in the presence of $[\mathrm{Ir}(\eta^5\text{-}\mathrm{C_9H_7})(\mathrm{COD})]$ (0.005 equiv.) in toluene at 80 °C for 24 h formed the vinyl silanes **4a**–**6a** in 34% total yield with *Z*-selectivity (Entry 3), a similar reaction in the presence of 0.006 equiv. of tmbp **3** produced the vinyl silanes in 96% total yield with **4a** as the major product (Entry 4). The reactions of **1a** with **7** (1–2 equiv.) in the presence of $[\mathrm{Ir}(\eta^5\text{-}\mathrm{C_9H_7})(\mathrm{COD})]$ (0.005 equiv.) and **3** (0.006 equiv.) also produced the vinyl silanes in 96–97% with a high selectivity of **4a** (89–93%) (Entries 5 and 6). The results in Table 1 show that the combination of $[\mathrm{Ir}(\eta^5\text{-}\mathrm{C_9H_7})(\mathrm{COD})]$ with **3** in toluene at 80 °C produces vinylsilanes in high yield with high *E*-selectivity, whereas the iridium-catalyzed hydrosilylation of **1a** with **7** in the absence of **3** forms vinylsilanes in moderate to high yield with *Z*-selectivity.



Scheme 1. Iridium-catalyzed hydrosilylation.

On the basis of the optimized conditions (Table 1, Entry 5), the hydrosilylation of various alkynes was examined (Table 2).[10] Similarly to that of **1a**, the reaction of phenylacetylene (**1b**) and its derivatives **1c** and **1d** with **7** in the presence of $[\mathrm{Ir}(\eta^5\text{-}$

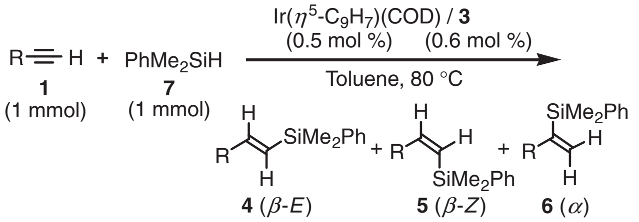
Table 1. Iridium-catalyzed hydrosilylation of 1-octyne[a]

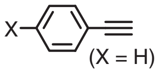
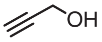
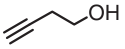
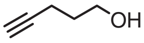
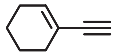


Entry	Ir catalyst	Solvent	Temp. /°C	Silane ratio/%[b]			Yield[c] /%
				4a	5a	6a	
1[d]	$[\mathrm{Ir(COD)_2}][\mathrm{BF_4}]$	$\mathrm{CH_2Cl_2}$	40	1	98	1	94
2	$[\mathrm{Ir(COD)_2}][\mathrm{BF_4}]$-**3**	$\mathrm{CH_2Cl_2}$	40	—	—	—	0
3[d]	Ir(η^5-Ind)(COD)	Toluene	80	21	67	12	34
4	Ir(η^5-Ind)(COD)-**3**	Toluene	80	94	4	2	96
5[e]	Ir(η^5-Ind)(COD)-**3**	Toluene	80	93	4	3	96
6[f]	Ir(η^5-Ind)(COD)-**3**	Toluene	80	89	7	4	97

[a]Reaction conditions: **1a** (1.0 mmol), **7** (0.5 mmol), and Ir complex (0.005 mmol) in the presence or absence of **3** (0.006 mmol) for 24 h. [b]Ratio was determined on the basis of ^{1}H NMR data. [c]GLC yield based on **7**. [d]Without **3**. [e]**7** (1.0 mmol) was used. [f]**7** (2.0 mmol) was used.

Table 2. Iridium-catalyzed hydrosilylation of 1-alkynes



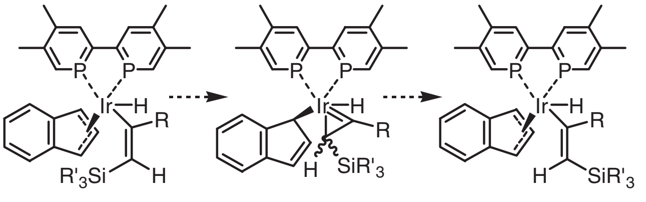
Entry	Alkyne		Time/h	Ratio/% 4	5	6	Yield[a]/%
1	 (X = H)	**1b**	14	84	16	0	88
2	X = Cl	**1c**	24	85	13	2	84
3	X = OMe	**1d**	20	91	7	2	86
4	t-Bu—≡	**1e**	20	100	0	0	59
5	TMS—≡	**1f**	17	100	0	0	59
6		**1g**	33	93	1	6	44
7		**1h**	60	97	0	3	91
8		**1i**	32	95	1	4	92
9		**1j**	129	83	17	0	67

[a]Isolated yield based on 1-alkyne **1**.

C_9H_7)(COD)] (0.5 mol %) and **3** (0.6 mol %) at 80 °C for 14–24 h produced vinylsilanes in 84–88% yields with *E*-selectivity (84–91%) (Table 2, Entries 1–3). The bulky acetylenes **1e** and **1f** underwent a similar reaction to give the corresponding *E*-adducts **4e** and **4f** in moderate yields (Entries 4 and 5). The reactions of the alkynyl alcohols **1g**–**1i** with **7** at 80 °C for 32–60 h also produced *E*-adducts **4g**–**4i** with high selectivity, although **1g** was obtained in low yield presumably owing to the interaction of the iridium catalyst with hydroxy group of **1g**. The enyne **1j** selectively reacted with its acetylenic bond to produce **4j** and **5j** with *E*-selectivity. In spite of the vinylsilane formation from terminal acetylenes, internal acetylenes such as diphenyl acetylenes, 1-phenyl-1-propyne, and 4-octyne were unreactive under these conditions.

To obtain information on the mechanism of the iridium-catalyzed hydrosilylation of alkynes in the presence of **3**, the reaction of 2-deuteriophenylacetylene (PhCCD, **1b**-d_1) with **7** was carried out under the same conditions shown in Table 2 (Supporting Information).[11] The reaction produced **4d**-d_1 and **5d**-d_1 (88:12) in 84% total yield, and deuterium remained only at the β-position of the phenyl group. The deuterium content of **1b**-d_1 was maintained in **4d**-d_1 and **5d**-d_1. Therefore, such hydrosilylation proceeded without a shift of deuterium in its transition state or intermediate formation.

In the hydrosilylation of terminal acetylenes, the first step is the oxidative addition of [Ir(η^5-C_9H_7)(COD)] to **2**, yielding η^3-indenyl iridium(III) species. The insertion of **1** into an Ir–Si bond produces the vinyl iridium species **8** (Scheme 2). Since **8** is thermodynamically unstable in the absence of **3**, the isomerization of **8** via **9** forms the less hindered intermediate **10**, and the reductive elimination of **10** produces the *Z*-adduct **5**. However, **3** has a strong π-acceptor property and can accelerate such reductive elimination. Therefore, the reductive elimination of **8** is expected to proceed smoothly to give **4** faster than the isomerization of **8** to **9**.



8 **9** **10**

Scheme 2. Possible intermediates **8**–**10** for the hydrosilylation of **1** to yield β-(*Z*)-**5**.

This work was supported by a Grant-in-Aid for Scientific Research from JSPS. We are grateful to Ms. Sayaka Watanabe and Mr. Takeshi Narita for experimental assistance.

References and Notes

1 a) I. Ojima, in *The Chemistry of Organic Silicon Compounds*, ed. by S. Patai, Z. Rappoport, Wiley, New York, **1989**, p. 1479. b) T. Hiyama, T. Kusumoto, in *Comprehensive Organic Synthesis*, ed. by B. M. Trost, I. Fleming, Pergamon Press, Oxford, **1991**, Vol. 8, p. 763. c) B. Marciniec, in *Comprehensive Handbook on Hydrosilylation*, Pergamon Press, Oxford, **1992**, p. 130. d) J. A. Reiche, D. H. Bery, *Adv. Organomet. Chem.* **1998**, *43*, 197. e) B. M. Trost, Z. T. Ball, *Synthesis* **2005**, 853.

2 a) R. S. Tanke, R. H. Crabtree, *J. Am. Chem. Soc.* **1990**, *112*, 7984. b) I. Ojima, N. Clos, R. J. Donovan, P. Ingallina, *Organometallics* **1990**, *9*, 3127.

3 For recent examples, see: a) A. Mori, E. Takahisa, Y. Yamamura, T. Kato, A. P. Mudalige, H. Kajiro, K. Hirabayashi, Y. Nishihara, T. Hiyama, *Organometallics* **2004**, *23*, 1755. b) J. W. Faller, D. G. Alliessi, *Organometallics* **2002**, *21*, 1743, and references cited therein.

4 R. Takeuchi, S. Nitta, D. Watanabe, *J. Org. Chem.* **1995**, *60*, 3045.

5 For reviews, see: a) M. Doux, A. Moores, N. Mézailles, L. Ricard, Y. Jean, P. Le. Floch, *J. Organomet. Chem.* **2005**, *690*, 2407. b) P. Le Floch, F. Mathey, *Coord. Chem. Rev.* **1998**, *178–180*, 771. c) F. Mathey, *Acc. Chem. Res.* **1992**, *112*, 4686. d) M. Yoshifuji, *J. Chem. Soc., Dalton Trans.* **1998**, 3343. e) L. Weber, *Angew. Chem., Int. Ed.* **2002**, *41*, 563.

6 For representative examples, see: a) T. Minami, H. Okamoto, S. Ikeda, T. Tanaka, F. Ozawa, M. Yoshifuji, *Angew. Chem., Int. Ed.* **2001**, *40*, 4501. b) F. Ozawa, H. Okamoto, S. Kawagishi, S. Yamamoto, T. Minami, M. Yoshifuji, *J. Am. Chem. Soc.* **2002**, *124*, 10968.

7 a) B. Breit, R. Winde, T. Mackewitz, R. Paciello, K. Harms, *Chem. Eur. J.* **2001**, *7*, 3106. b) M. T. Reetz, X. Li, *Angew. Chem., Int. Ed.* **2005**, *44*, 2962.

8 P. Rosa, N. Mézailles, F. Mathey, P. Le Floch, *J. Org. Chem.* **1998**, *63*, 4826.

9 For the preparation of tmbp (**3**), see the Supporting Information.

10 For the general procedure of the hydrosilylation shown in Table 2, see the Supporting Information.

11 For the hydrosilylation of deuteriophenylacetylene (**1b**-d_1), see the Supporting Information.

Published on the web (Advance View) June 27, 2006; doi:10.1246/cl.2006.836