

Rhenium- and Gold-Catalyzed Coupling of Aromatic Aldehydes with Trimethyl(phenylethynyl)silane: Synthesis of Diethynylmethanes**

Yoichiro Kuninobu,* Eri Ishii, and Kazuhiko Takai*

Recently, synthetic reactions using a combination of two metal complexes have received considerable attention because they lead to products that cannot be synthesized with only one of the catalysts.^[1] We report herein on the rhenium-^[2,3] and gold-catalyzed^[4] synthesis of diethynylmethanes^[5,6] by reactions of aldehydes with trimethyl(phenylethynyl)silane.

As a preliminary investigation, reactions of propargyl or benzyl alcohols with allyl- or alkynylsilanes were carried out (Table 1).^[7–9] Reaction of propargyl alcohol **1a** with allyltrimethylsilane (**2a**) in the presence of a rhenium catalyst, $[\text{ReBr}(\text{CO})_3(\text{thf})_2]$ (2.5 mol %), at 25 °C afforded enyne **3a** in quantitative yield (Table 1, entry 1). A propargyl alcohol with an alkyl group at the terminal position of the acetylene moiety, **1b**, and another with dimethyl groups at the propargyl position, **1c**, also gave the corresponding enynes **3b** and **3c** quantitatively (Table 1, entries 2 and 3). Enyne **3d** was obtained in 69 % yield by using a secondary propargyl alcohol **1d** (Table 1, entry 4), a result that deserves special mention because efficient transformations of secondary propargyl alcohols bearing an alkyl group at the propargyl position with organosilanes are usually difficult.^[2b,7c] The reaction between benzyl alcohol **4** and allylsilane **2a** gave 4-phenylpent-1-ene (**5**) in 95 % yield (Table 1, entry 5). Reaction of propargyl alcohols **1a** or **1b** with trimethyl(phenylethynyl)silane (**2b**) afforded diethynylmethanes **6a** and **6b** in 76 % and 67 % yields, respectively (Table 1, entries 6 and 7). However, the reactions of propargyl alcohols **1c** or **1d** with **2b** did not give the corresponding coupling products, but 1,3-diphenylbut-1-yne (**7**) was afforded in 56 % yield by the treatment of benzyl alcohol **4** with **2b** (Table 1, entry 8).

As shown in entries 6 and 7 (Table 1), diethynylmethanes (one kind of polyethynylmethane) were formed. Such poly-

Table 1: Reactions of propargyl alcohols with silanes.^[a]

Alcohol +		Me ₃ Si—CH=CH ₂ 2a or Me ₃ Si—C≡C—Ph 2b	$[\text{ReBr}(\text{CO})_3(\text{thf})_2]$ (2.5 mol %) CH ₂ Cl ₂ , 25 °C, 3 h	Adduct
Entry	Alcohol	Silane	Product	Yield [%] ^[b]
1		2a		99 (> 99)
2		2a		99 (> 99)
3		2a		96 (99)
4 ^[c]		2a		69 (72)
5 ^[d]		2a		95 (98)
6	1a	2b		76 (79)
7 ^[e]	1b	2b		67 (73)
8 ^[f]	4	2b		56 (57)

[a] Silane (2.0 equiv). [b] Isolated yields (yields from ¹H NMR analysis are reported in parentheses). [c] 1,2-Dichloroethane was used as solvent, 80 °C, 24 h, **2a** (4.0 equiv). [d] 1,2-Dichloromethane was used as solvent, 50 °C, 24 h. [e] 1,2-Dichloroethane was used as solvent, 80 °C, 24 h. [f] 1,1,2-Trichloroethane was used as solvent, 115 °C, 24 h, **2a** (4.0 equiv).

ethynylmethanes are interesting compounds as high-carbon-containing materials,^[10] and several synthetic methods have been reported. To construct the skeleton in one pot, we used stable alkynylsilanes^[11] as the alkynyl component.

Treatment of benzaldehyde (**8a**) with trimethyl(phenylethynyl)silane (**2b**) in the presence of a catalytic amount of the rhenium complex, $[\text{ReBr}(\text{CO})_3(\text{thf})_2]$ (2.5 mol %), produced only a trace amount of the desired diethynylmethane **6a**. However, when a gold salt, AuCl (5.0 mol %), was added to the reaction mixture, the yield of **6a** increased

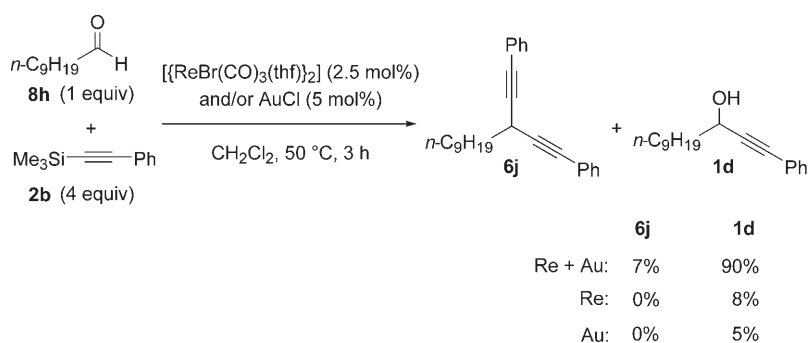
[*] Dr. Y. Kuninobu, E. Ishii, Prof. Dr. K. Takai
Division of Chemistry and Biochemistry
Okayama University
Tsushima, Okayama 700-8530 (Japan)
Fax: (+81) 86-251-8094
E-mail: kuninobu@cc.okayama-u.ac.jp
ktakai@cc.okayama-u.ac.jp

[**] Financial support through a Grant-in-Aid for Scientific Research on Priority Areas (no. 18037049, "Advanced Molecular Transformations of Carbon Resources") from the Ministry of Education, Culture, Sports, Science, and Technology of Japan, and a Grant-in-Aid for Young Scientists (B) (no. 18750088) from the Japan Society for the Promotion of Science is gratefully acknowledged. We thank Dr. Masaichi Saito (Department of Chemistry, Saitama University) for acquiring HR-MS spectra.

Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

dramatically (72% yield). Because the reaction did not occur in the presence of AuCl only, we conclude that this combination of catalysts is important to promote the reaction.^[12]

The yield of **6a** increased slightly with use of twice the amounts of rhenium and gold catalysts (Table 2, entry 1). The yields of diethynylmethanes **6c** and **6d** decreased when using aromatic aldehydes that bear an electron-donating group (Table 2, entries 2 and 3).^[13] In contrast, an aromatic aldehyde with an electron-withdrawing group gave diethynylmethane **6e** and propargyl alcohol



Scheme 1. Effect of either or both catalysts on the reaction of **8h** with **2b**. Yields from ¹H NMR analysis are provided.

Table 2: Reactions of aldehydes with **2b**.^[a]

Entry	Aldehyde	T [°C]	Product	Yield [%] ^[b]
1 ^[c]	8a : R = H	25	6a	80
2 ^[d]	8b : R = <i>p</i> -MeO	50	6c	43
3 ^[c]	8c : R = <i>p</i> -Me	50	6d	60
4	8d : R = <i>p</i> -CF ₃	25	6e	33
			1e	66
5 ^[e]	8e : R = <i>p</i> -Br	50	6f	66
6 ^[e]	8f : R = <i>o</i> -Me	50	6g	79
7 ^[c]	8g	50	6h	55

[a] Aldehyde (1.0 equiv), acetylene (4.0 equiv). [b] Isolated yield. [c] [(ReBr(CO)₃(thf))₂] (5.0 mol%), AuCl (10 mol%). [d] 24 h. [e] [(ReBr(CO)₃(thf))₂] (2.5 mol%), AuCl (10 mol%).

1e in 33% and 66% yields, respectively (Table 2, entry 4). A bromine atom at the *para* position of the aldehyde remained intact during the reaction (Table 2, entry 5).^[14] Diethynylmethane **6g** was obtained in 79% yield by using *ortho*-tolualdehyde (**8f**) with no sign of steric hindrance (Table 2, entry 6). 2-Naphthalenecarboxaldehyde (**8g**) afforded the corresponding diethynylmethane **6h** in 55% yield (Table 2, entry 7). However, aliphatic aldehydes (see below) and trimethyl(oct-1-ynyl)silane^[15] gave the corresponding diethynylmethanes in low yields.

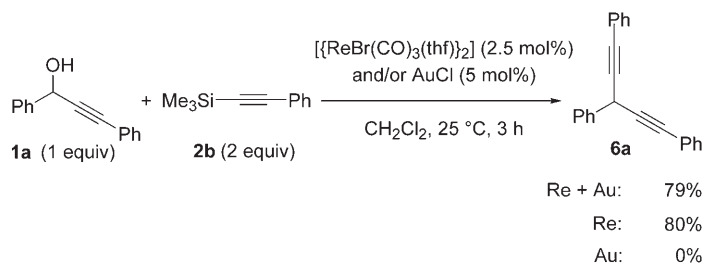
To obtain information of the reaction mechanism, we carried out several reactions. The reaction between decanal (**8h**) and trimethyl(phenylethynyl)silane (**2b**) in the presence of [(ReBr(CO)₃(thf))₂] gave the corresponding diethynylmethane **6j** and propargyl alcohol **1d** in 7% and 90% yields, respectively (Scheme 1).

We examined the reaction with each catalyst. By using [(ReBr(CO)₃(thf))₂] or AuCl as the sole catalyst, propargyl alcohol **1d** was obtained in low yields. The results suggest that both the rhenium and gold complexes are necessary for promoting the formation of propargyl alcohol efficiently.

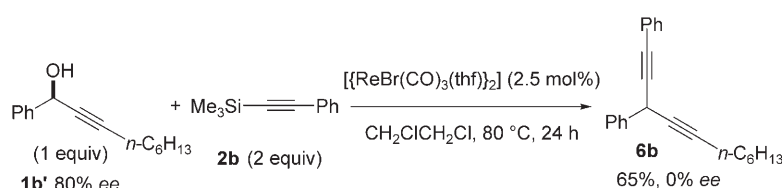
Next, the reaction between propargyl alcohol **1a** and **2b** was carried out with [(ReBr(CO)₃(thf))₂] and/or AuCl (Scheme 2). These results show that the gold salt does not disturb the addition.

Substitution of a hydroxy group at benzylic positions with allylsilanes has been reported to occur with a combined catalyst of [(dppm)ReOCl₃] (dppm: bis(diphenylphosphino)methane) and NH₄PF₆ (or AgSbF₆) in nitromethane at 65 °C by Toste and Luzung.^[2b] Compared with the results reported therein, this reaction proceeds with a rhenium complex of lower oxidation state and under milder reaction conditions.

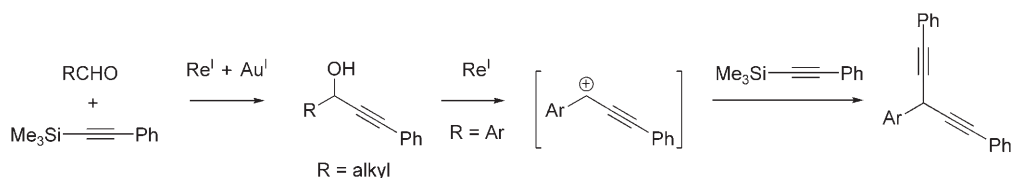
Reaction of optically active propargyl alcohol **1b'** with trimethyl(phenylethynyl)silane (**2b**) in the presence of [(ReBr(CO)₃(thf))₂] led to formation of racemic diethynylmethane **6b**. This result indicates clearly that the formation of diethynylmethanes proceeds through a propargyl cation (Scheme 3).



Scheme 2. Effect of either or both catalysts on the reaction of **1a** with **2b**. Yields from ¹H NMR analysis are provided.



Scheme 3.



Scheme 4. Proposed mechanism for the formation of diethynylmethanes.

The proposed reaction mechanism is shown in Scheme 4: 1) A combination of $[\text{ReBr}(\text{CO})_3(\text{thf})_2]$ and AuCl acts as an effective Lewis acid for promoting ethynylation of aldehydes with trimethyl(phenylethynyl)silane; 2) the rhenium complex promotes substitution of a hydroxy group by a phenylethynyl group. In the reaction step, a propargyl cation is formed as an intermediate.

In summary, we have demonstrated the rhenium-catalyzed transformations of propargyl and benzyl alcohols using organosilanes, as well as the rhenium- and gold-catalyzed synthesis of diethynylmethanes. To the best of our knowledge, the results shown here are the first example of the formation of diethynylmethanes by coupling reactions between aldehydes and alkynylsilanes. This reaction proceeds via propargyl alcohols as intermediates. A combination of the rhenium and gold complexes promotes the first ethynylation step, and the rhenium complex accelerates the second ethynylation.

Experimental Section

General procedure for the reaction of a propargyl alcohol with organosilane: A mixture of a propargyl alcohol (0.250 mmol), trimethyl(phenylethynyl)silane (87.2 mg, 0.500 mmol), and $[\text{ReBr}(\text{CO})_3(\text{thf})_2]$ (5.3 mg, 6.1 μmol) in dichloromethane (1.0 mL) was stirred for 3 h at 25°C. Then, the solvent was removed in vacuo and the products were isolated by silica gel column chromatography.

General procedure for the reaction of an aldehyde with trimethyl(2-phenylethynyl)silane: A mixture of an aldehyde (0.250 mmol), trimethyl(phenylethynyl)silane (174 mg, 1.00 mmol), $[\text{ReBr}(\text{CO})_3(\text{thf})_2]$ (5.3 mg, 6.1 μmol), and AuCl (2.9 mg, 13 μmol) in dichloromethane (1.0 mL) was stirred for 3 h at 25°C. Then, the solvent was removed in vacuo and the products were isolated by silica gel column chromatography.

Received: January 15, 2007

Published online: March 23, 2007

Keywords: aldehydes · cross-coupling · gold · rhenium

- [1] Eds.: M. Shibasaki, Y. Yamamoto, *Multimetallic Catalysts in Organic Synthesis*, Wiley-VCH, Weinheim, **2004**.
- [2] a) F. E. Kühn, A. Scherbaum, W. A. Herrmann, *J. Organomet. Chem.* **2004**, 689, 4149–4164; b) M. R. Luzung, F. D. Toste, *J. Am. Chem. Soc.* **2003**, 125, 15760–15761; c) K. A. Nolin, R. W. Ahn, F. D. Toste, *J. Am. Chem. Soc.* **2006**, 128, 12462–12463; d) H. Kusama, H. Yamabe, Y. Onizawa, T. Hoshino, N. Iwasawa, *Angew. Chem.* **2005**, 117, 472–474; *Angew. Chem. Int. Ed.* **2005**, 44, 468–470; e) L. L. Ouh, T. E. Müller, Y. K. Yan, *J. Organomet. Chem.* **2005**, 690, 3774–3782.
- [3] We recently reported on rhenium-catalyzed reactions; see: a) Y. Kuninobu, A. Kawata, K. Takai, *J. Am. Chem. Soc.* **2005**, 127,

- 13498–13499; b) Y. Kuninobu, A. Kawata, K. Takai, *Org. Lett.* **2005**, 7, 4823–4825; c) Y. Kuninobu, Y. Tokunaga, A. Kawata, K. Takai, *J. Am. Chem. Soc.* **2006**, 128, 202–209; d) Y. Kuninobu, Y. Nishina, M. Shouho, K. Takai, *Angew. Chem.* **2006**, 118, 2832–2834; *Angew. Chem. Int. Ed.* **2006**, 45, 2766–2768; e) Y. Kuninobu, A. Kawata, K. Takai, *J. Am. Chem. Soc.* **2006**, 128, 11368–11369; f) Y. Kuninobu, Y. Nishina, C. Nakagawa, K. Takai, *J. Am. Chem. Soc.* **2006**, 128, 12376–12377.
- [4] For recent reviews of gold-catalyzed transformations, see: a) A. S. K. Hashmi, *Angew. Chem.* **2005**, 117, 7150–7154; *Angew. Chem. Int. Ed.* **2005**, 44, 6990–6993; b) A. S. K. Hashmi, G. J. Hutchings, *Angew. Chem.* **2006**, 118, 8064–8105; *Angew. Chem. Int. Ed.* **2006**, 45, 7896–7936.
- [5] For previous reports on gallium trichloride promoted diethynylation, see: a) R. Amemiya, K. Suwa, J. Toriyama, Y. Nishimura, M. Yamaguchi, *J. Am. Chem. Soc.* **2005**, 127, 8252–8253; b) R. Amemiya, M. Yamaguchi, *Eur. J. Org. Chem.* **2005**, 5145–5150; c) R. Amemiya, Y. Miyake, M. Yamaguchi, *Tetrahedron Lett.* **2006**, 47, 1797–1800. However, these reactions need stoichiometric amounts of gallium chloride and heating at 130–170°C.
- [6] For copper(I)-catalyzed synthesis of 1,4-diynes by the reactions of propargyl halides with trimethylsilylacetylenes, see: F. Montel, R. Beaudegnies, J. Kessabi, B. Martin, E. Muller, S. Wendeborn, P. M. Jung, *Org. Lett.* **2006**, 8, 1905–1908.
- [7] Metal-catalyzed couplings of propargyl alcohols with organosilanes are still rare.^[2b] See also: a) M. Georgy, V. Boucard, J.-M. Campagne, *J. Am. Chem. Soc.* **2005**, 127, 14180–14181; b) Y. Nishibayashi, A. Shinoda, Y. Miyake, H. Matsuzawa, M. Sato, *Angew. Chem.* **2006**, 118, 4953–4957; *Angew. Chem. Int. Ed.* **2006**, 45, 4835–4839; c) Z.-p. Zhan, J.-l. Yu, H.-j. Liu, Y.-y. Cui, R.-f. Yang, W.-z. Yang, J.-p. Li, *J. Org. Chem.* **2006**, 71, 8298–8301; d) Z.-p. Zhan, W.-z. Yang, R.-f. Yang, J.-l. Yu, J.-p. Li, H.-j. Liu, *Chem. Commun.* **2006**, 3352–3354.
- [8] For metal-catalyzed couplings of benzyl alcohols with organosilanes, see: a) M. Braun, W. Kotter, *Angew. Chem.* **2004**, 116, 520–523; *Angew. Chem. Int. Ed.* **2004**, 43, 514–517; b) M. Yasuda, T. Saito, M. Ueba, A. Baba, *Angew. Chem.* **2004**, 116, 1438–1440; *Angew. Chem. Int. Ed.* **2004**, 43, 1414–1416; c) T. Saito, M. Yasuda, A. Baba, *Synlett* **2005**, 1737–1739; d) T. Saito, Y. Nishimoto, M. Yasuda, A. Baba, *J. Org. Chem.* **2006**, 71, 8516–8522.
- [9] For ruthenium-catalyzed carbon–carbon bond formation using propargyl alcohols, see: a) Y. Nishibayashi, M. Yoshikawa, Y. Inada, M. Hidai, S. Uemura, *J. Am. Chem. Soc.* **2002**, 124, 11846–11847; b) Y. Nishibayashi, Y. Inada, M. Yoshikawa, M. Hidai, S. Uemura, *Angew. Chem.* **2003**, 115, 1533–1536; *Angew. Chem. Int. Ed.* **2003**, 42, 1495–1498.
- [10] a) F. Diederich, Y. Rubin, *Angew. Chem.* **1992**, 104, 1123–1146; *Angew. Chem. Int. Ed. Engl.* **1992**, 31, 1101–1123; b) F. Diederich, *Nature* **1994**, 369, 199–207; c) U. H. F. Bunz, *Angew. Chem.* **1994**, 106, 1127–1131; *Angew. Chem. Int. Ed. Engl.* **1994**, 33, 1073–1076; d) M. B. Nielsen, F. Diederich, *Synlett* **2002**, 544–552.
- [11] There have been some reports on reactions using alkynylsilanes as an alkynyl component; see: a) L. Birkofer, A. Ritter, H. Uhlenbrauck, *Chem. Ber.* **1963**, 96, 3280–3288; b) A. B. Holmes, C. L. D. Jennings-White, A. H. Schulthess, B. Akinde, D. R. M. Walton, *J. Chem. Soc. Chem. Commun.* **1979**, 840–842; c) I.

- Kuwajima, E. Nakamura, K. Hashimoto, *Tetrahedron* **1983**, 39, 975–982; d) R. B. Lettan II, K. A. Scheidt, *Org. Lett.* **2005**, 7, 3227–3230.
- [12] We examined the catalytic activity of several catalyst combinations containing the rhenium complex. AuCl₃ (52 %), AuBr₃ (65 %), and FeCl₃ (52 %) were effective for the reaction (yields shown in parentheses). However, other combinations of the Re complex with potential catalysts did not improve the yield of **6a**: AgOTf: 9 %; CuCl: 8 %; PdCl₂: 11 %; PtCl₂: 19 %.
- [13] The structure of the diethynylmethane was determined by comparison of the spectral data of **6d** with the reported data. See: G. W. Kabalka, M.-L. Yao, S. Borella, *Org. Lett.* **2006**, 8, 879–881.
- [14] Aldehyde **8e** was recovered in 34 % yield.
- [15] 9-Phenyl-7,10-heptadecadiyne (**6i**) was obtained in 23 % yield.
-