Cross-Coupling

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

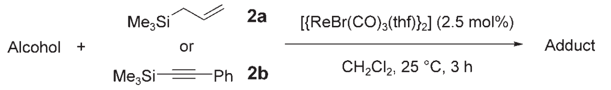
Yoichiro Kuninobu, Eri Ishii, and Kazuhiko Takai**

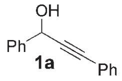
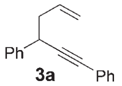
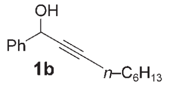
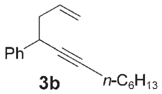
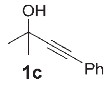
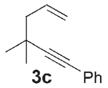
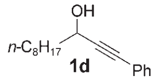
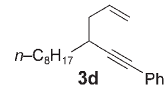
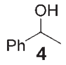
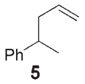
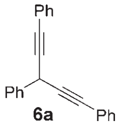
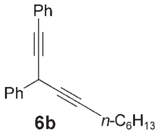
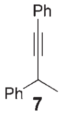
Recently, synthetic reactions using a combination of two metal complexes have received considerable attention because they lead to products that cannot be synthesized with only one of the catalysts.[1] We report herein on the rhenium-[2,3] and gold-catalyzed[4] synthesis of diethynylmethanes[5,6] by 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, [{ReBr(CO)$_3$(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 polyethynylmethanes 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.

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



Entry	Alcohol	Silane	Product	Yield [%][b]
1	 **1a**	**2a**	 **3a**	99 (>99)
2	 **1b**	**2a**	 **3b**	99 (>99)
3	 **1c**	**2a**	 **3c**	96 (99)
4[c]	 **1d**	**2a**	 **3d**	69 (72)
5[d]	 **4**	**2a**	 **5**	95 (98)
6	**1a**	**2b**	 **6a**	76 (79)
7[e]	**1b**	**2b**	 **6b**	67 (73)
8[f]	**4**	**2b**	 **7**	56 (57)

[a] Silane (2.0 equiv). [b] Isolated yields (yields from ^{1}H 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).

Treatment of benzaldehyde (**8a**) with trimethyl(phenylethynyl)silane (**2b**) in the presence of a catalytic amount of the rhenium complex, [{ReBr(CO)$_3$(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

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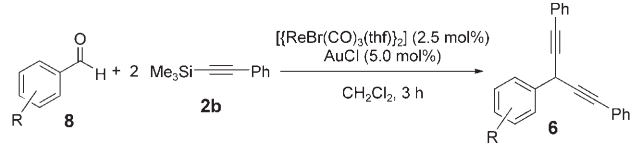
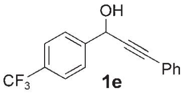
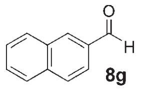
dramatically (72 % yield). Because the reaction did not occur in the presence of AuCl only, we conclude that this combination of catalysts is important to promote the reaction.[12]

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 **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.

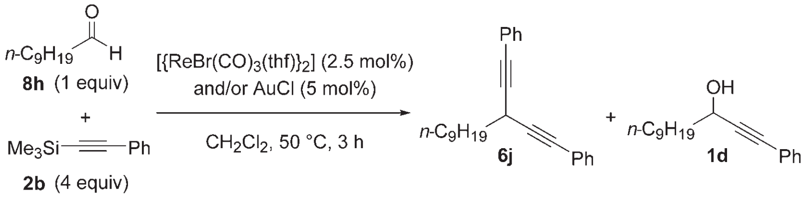
Table 2: Reactions of aldehydes with **2b**.[a]



Entry	Aldehyde	T [°C]	Product	Yield [%][b]
1[c]	**8a**: R = H	25	**6a**	80
2[d]	**8b**: R = p-MeO	50	**6c**	43
3[c]	**8c**: R = p-Me	50	**6d**	60
4	**8d**: R = p-CF$_3$	25	**6e**	33
			 **1e**	66
5[e]	**8e**: R = p-Br	50	**6f**	66
6[e]	**8f**: R = o-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%).

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).



	6j	1d
Re + Au:	7%	90%
Re:	0%	8%
Au:	0%	5%

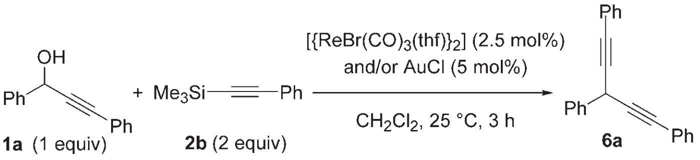
Scheme 1. Effect of either or both catalysts on the reaction of **8h** with **2b**. Yields from ^{1}H NMR analysis are provided.

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.

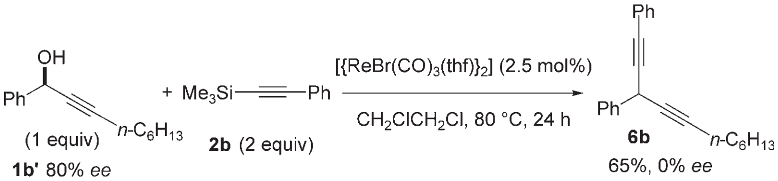
Substitution of a hydroxy group at benzylic positions with allylsilanes has been reported to occur with a combined catalyst of [(dppm)ReOCl$_3$] (dppm: bis(diphenylphosphino)methane) and NH$_4$PF$_6$ (or AgSbF$_6$) in nitromethane at 65 °C by Toste and Luzung.[2b] Compared with the results reported therein, 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).

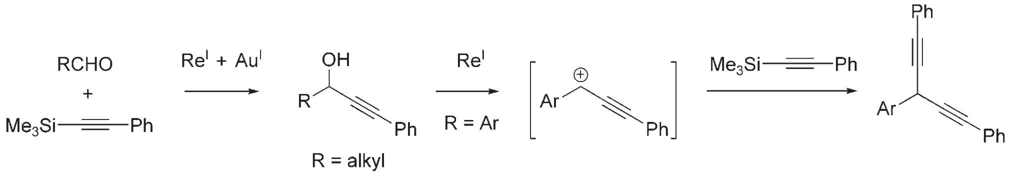


Re + Au: 79%
Re: 80%
Au: 0%

Scheme 2. Effect of either or both catalysts on the reaction of **1a** with **2b**. Yields from ^{1}H 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 [{ReBr(CO)$_3$(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 [{ReBr(CO)$_3$(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), [{ReBr(CO)$_3$(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.

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[12] We examined the catalytic activity of several catalyst combinations containing the rhenium complex. $AuCl_3$ (52%), $AuBr_3$ (65%), and $FeCl_3$ (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%; $PdCl_2$: 11%; $PtCl_2$: 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.