



Selective Hydrosilylation

Hydrosilylation of Allenes Over Palladium–Gold Alloy Catalysts: Enhancing Activity and Switching Selectivity by the Incorporation of Palladium into Gold Nanoparticles

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Abstract: An efficient synthetic route to alkenylsilanes involving the hydrosilylation of allenes with supported Pd–Au alloy catalysts has been developed. The incorporation of Pd atoms into Au nanoparticles remarkably enhanced the catalytic activity and product selectivity. Pd–Au alloy catalysts with a low Pd/ Au ratio were highly effective for the hydrosilylation at an ambient temperature, and the corresponding β -alkenylsilanes were obtained as a main product in good to high yields.

Introduction

The hydrosilylation of unsaturated organic molecules is the most straightforward and convenient method for the synthesis of organosilicon compounds.^[1] Particularly, alkyne hydrosilylation by transition-metal catalysts is a well-established tool for the preparation of alkenylsilanes,^[2] which are important scaffolds due to their utility in organic synthesis, such as in Hiyama cross-coupling^[3] and Tamao-Fleming oxidation.^[4] The hydrosilylation of allenes is an alternative route for the synthesis of alkenylsilanes. In this case, considerable attention must be paid to controlling the regiochemistry of the silvlated adducts due to the presence of two contiguous π -systems in allenes (Scheme 1). In fact, previous studies have demonstrated the selective formation of allylsilanes by Pd-[5] Co-[6] or Mo-catalyzed^[7] hydrosilylation involving protonation of the allene center carbon (Scheme 1a and 1b). Despite the fact that allene hydrosilylation under Ni,^[5] Pd,^[5] Al^[8] and Au^[9] catalysis has emerged as an effective route to terminal alkenylsilanes (Scheme 1c), an synthetic route to internal alkenylsilanes via allene hydrosilylation has scarcely been explored (Scheme 1d).

On the other hand, increasing attention has recently been paid to the development of a novel environmentally friendly catalytic system.^[10] In this respect, the use of supported metal nanoparticles (NPs) as a heterogeneous catalyst is intriguing due to their high stability and high reusability, and the ease with which the catalysts can be separated from the

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 $R^{=} + H-SiR'_{3} - \frac{H-Si}{R} + H-SiR'_{3} - \frac{H-Si}{R} + H-SiR'_{3} - \frac{H-Si}{R} + H-SiR'_{3} + H-SiR'_{$

Scheme 1. Formation of allylsilanes and alkenylsilanes via the hydrosilylation of allene.

products.^[11] We recently reported that supported Pd–Au alloy NPs functioned as an efficient catalyst for the hydrosilylation of α , β -unsaturated ketones and alkynes under mild reaction conditions, whereas monometallic Pd and Au NP catalysts were totally ineffective.^[12] A detailed characterization of supported Pd–Au alloy catalysts revealed that Pd species that were atomically incorporated into Au NPs served as the main active site for efficient hydrosilylation.

Herein, we describe the hydrosilylation of allenes in the presence of supported Pd–Au alloy catalysts. The reactions took place under ambient temperature through the use of Pd–Au alloy catalysts with a low Pd/Au atomic ratio to afford internal alkenylsilanes as the main products.

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Results and Discussion

The reactions of phenylallene (**1a**) with triethylsilane (**2a**) in CH₃CN in the presence of the catalyst with different Pd/Au ratios were investigated (Scheme 2).^[13] As previously demonstrated by Stratakis et al., the reaction at 65 °C with Au/TiO₂ catalyst proceeded smoothly to give the corresponding terminal alkenylsilane (**4a**) as a main product with high selectivity. However, only a trace amount of products was obtained by the reaction with Au/TiO₂ at room temperature.

•= +	+ H−SiEt ₃	catalyst in CH ₃ CN	→	t ₃ + Ph	SiEt ₃	+ SiEt ₃
1a	2a		3a(<i>E</i>)	3a(.	Z)	4a
		_	Cat.	Condition	Yield	3a(<i>E</i>)/3a(<i>Z</i>)/4a
			Au/TiO ₂	65 °C, 3 h	85%	(7:0: 93)
			Au/TiO ₂	r.t., 4 h	4%	(6:0: 94)
			1Pd5Au/TiO ₂	r.t., 4 h	58%	(62: 9:29)
		_	Pd/TiO ₂	r.t., 4 h	0%	

Scheme 2. Hydrosilylation of phenylallene (1a) by TiO_2 -supported Au, Pd or Pd–Au catalysts.

In contrast, $1Pd5Au/TiO_2$ showed high activity even under ambient conditions to afford alkenylsilanes in total yields of 58 %. Remarkably, the incorporation of Pd atoms into Au NPs drastically changed the regiochemistry of the products, and the main product in the reaction with PdAu alloy catalysts turned out to be the internal alkenylsilane with an *E* configuration [**3a**(*E*)]. No reaction took place in the presence of Pd/TiO₂ catalyst under the present conditions.

Table 1 summarizes the effects of the Pd/Au molar ratio and the support for Pd–Au alloy on the reaction of **1a** with **2a**. As in the hydrosilylation of unsaturated ketones and alkynes we previously reported,^[12] Pd–Au catalysts with a low Pd/Au ratio showed high activity for the present catalytic reactions, and the reaction catalyzed by 1Pd5Au alloy gave the highest total yield of the products (entry 2), whereas the reaction with Pd–Au catalysts with a high Pd/Au ratio resulted in very low yields of the products (entries 4 and 5). Our detailed structural characteriza-

Table 1. Optimization of catalysts.[a]

/ Ph 1	•= + HSiEt ₃ <u>catalyst</u> in CH ₃ CN a 2a	→ /= SiEt ₃ + + Ph Pi 3a(E)	$ \begin{array}{c} \overbrace{\mathbf{A}}^{SiEt_3} + \overbrace{\mathbf{Ph}}^{SiEt_3} \\ 3a(Z) & 4a \end{array} $
Entry	Catalyst	Yield [%] ^[b]	3a (<i>E</i>)/ 3a (<i>Z</i>)/ 4 ^[b]
1	1Pd10Au/TiO ₂	7	79:6:15
2	1Pd5Au/TiO ₂	58	62:9:29
3	1Pd3Au/TiO ₂	53	61:8:31
4	1Pd1Au/TiO ₂	3	68:8:24
5	3Pd1Au/TiO ₂	0	-
6	1Pd5Au/Al ₂ O ₃	73	57:8:35
7	1Pd5Au/ZrO ₂	64	60:7:33
8	1Pd5Au/Nb ₂ O ₅	62	64:6:30
9	1Pd5Au/CeO ₂	57	64:7:29
10	1Pd5Au/SiO ₂	11	77:4:19
11	1Pt5Au/Al ₂ O ₃	23	67:0:33

[a] Reaction conditions: **1a** (0.50 mmol), **2a** (0.60 mmol), catalyst (1.0 mol-% as a total amount of Pd and Au), CH₃CN (3 mL), at room temp. [b] Yields and selectivities of the products were determined by GC analysis by using biphenyl as internal standard.

tion of supported Pd–Au alloy catalysts revealed the formation of isolated single Pd atoms on the surface of Pd–Au alloy NPs, which are believed to act as the main active site for the present allene hydrosilylation.^[14] A survey to identify the optimal support for the 1Pd5Au alloy revealed that Al₂O₃-supported Pd–Au catalysts gave the highest total yield of the products (entry 6). The reaction with 1Pt5Au/Al₂O₃ resulted in a low total yield of the products. Notably, no formation of allylsilanes was observed in the reactions with PdAu alloy catalysts.

Under the optimized reaction conditions, the reactions of a variety of allenes with triethylsilane were investigated (Table 2).

Table 2. Scope of allenes.^[a]

R ₂ R ₁	= + HSiEt ₃ -	$\xrightarrow{\text{1Pd5Au/Al}_2O_3}_{\text{CH}_3\text{CN, r.t.}} \xrightarrow{\text{R}_2}_{\text{R}_1}$	$=$ $\begin{pmatrix} SiEt_3 \\ + \end{pmatrix} \\ R_1 \\ R_1 \end{pmatrix}$	$= \left\langle \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$
Entry	Allene	Product	Yield [%] ^[b]	3(2) 4 3a(E)/3 <i>a(Z</i>)/4 ^[c]
1	 1b	3b(<i>E</i>)/3b(<i>Z</i>)/4b	79	51:6:43
2	MeO 1c	3c(<i>E</i>)/3c(<i>Z</i>)/4c	61	60:8:32
3	ci 1d	3d(<i>E</i>)/3d(<i>Z</i>)/4d	50	62:3:34
4	 1e	3e(<i>E</i>)/3e(<i>Z</i>)/4e	62	33:0:67
5	n-Hex →	3f(<i>E</i>)/3f(<i>Z</i>)/4f	71	38:2:60
6	⊤sN ──── 1g	3g(<i>E</i>)/3g(<i>Z</i>)/4g	70	56:0:44
7	pinB ■•■	3h(<i>E</i>)/3h(<i>Z</i>)/4h	60	75:0:25
8	BnO-√⊖·≕	3i(<i>E</i>)/3i(<i>Z</i>)/4i	58	81:0:19
9	_{Eto} -√⊖·≕ 1j	3j(<i>E</i>)/3j(<i>Z</i>)/4j	55	80:0:20
10	⊳⊢ Ph	3k(<i>E</i>)/3k(<i>Z</i>)/4k	43	60:15:25
11	мео ₂ с	3I(<i>E</i>)/3I(<i>Z</i>)/4I	28	79:21: -

[[]a] Reaction conditions: **1** (0.50 mmol), **2a** (0.60 mmol), $1Pd5Au/Al_2O_3$ (1.0 mol-% as a total amount of Pd and Au), CH₃CN (3 mL), at room temp. [b] Isolated yield. [c] Selectivity of the products were determined by ¹H NMR analysis. Ts = 4-toluenesulfonyl.



The reactions of allenes with an aromatic substituent gave the corresponding alkenylsilanes in good to high yields, and internal alkenylsilanes with an E-configuration were obtained as the main products (entries 1-3). Alkyl-substituted allenes were also good substrates in the present catalytic system to afford the silvlated adducts in satisfactory yields, whereas the selectivities of internal alkenylsilane were decreased (entries 4 and 5). Trisubstituted internal alkenes bearing two different heteroatoms could be synthesized in high yields by the reactions of N- or Batom-substituted allenes (entries 6 and 7). In the reaction of ester-substituted allenes, increased selectivities for internal silvlalkenes were observed without significant decreases in the total yields of the product (entries 8 and 9). Although tri-substituted alkenylsilanes can be prepared by the hydrosilylation of internal alkynes, this protocol could not be used to synthesize tetrasubstituted alkenes bearing silyl groups. Despite the unsatisfactory yield and selectivity of the product, the hydrosilylation of 1,1-substituted allene with the present PdAu alloy catalytic system provides a novel route to tetra-substituted silvlalkenes (entry 10). Internal allene 11 could participate to give the corresponding alkenylsilane **3I** in a moderate yield (entry 11).

The scope of hydrosilanes was also investigated (Table 3). Various tertiary silanes (**2a**) participated in the present catalytic system to afford the corresponding alkenylsilanes in moderate yields (entries 1–4). The reaction of diphenylsilane did not occur with the present supported PdAu catalyst (entry 5).

Table 3. Scope of hydrosilane.[a]

Ph	$=$ + HSiR ₃ $\frac{1P}{C}$	d5Au/Al ₂ C H ₃ CN, r.t.	$P_3 \rightarrow Ph$	+ Ph_SiR ₃ +	Ph
1a	2		3(E)	3(Z)	4
Entry	Hydrosilane	<i>t</i> [h]	Product	Yield [%] ^[b]	3E/3Z/4 ^[c]
1 ^[d]	HSi(<i>n</i> Bu) ₃ (2b)	5	3m(E)/3m(Z)/4m	37	65:7:28
2	HSi(OEt) ₃ (2c)	4	3n(<i>E</i>)/3n(<i>Z</i>)/4n	43	40:29:31
3	HSiMe ₂ Ph (2d)	5	30 (<i>E</i>)/ 30 (<i>Z</i>)/ 40	45	66:0:34
4 ^[d]	HSiMe ₂ tBu (2e)	8	3p(E)/3p(Z)/4p	21	80:0:20
5	H ₂ SiPh ₂ (2f)	5	3q(E)/3q(Z)/4q	0	-

[a] Reaction conditions: **1a** (0.50 mmol), **2** (0.60 mmol), 1Pd5Au/Al₂O₃ (1.0 mol-% as a total amount of Pd and Au), CH₃CN (3 mL), at room temp. [b] Isolated yield. [c] Selectivity of the products was determined by ¹H NMR analysis. [d] 2 mol-% metal was used.

The high environmental compatibility of the present catalysts is reflected in their reusability. Significant decreases in the yield of the product were not observed during three consecutive catalytic tests (Scheme 3). Filtration of the supported PdAu catalyst during the reaction of **1a** with **2a** completely retarded the further progress of the reaction. Furthermore, no leaching of either of the precious metals into the reaction mixture was observed by atomic emission spectroscopic analysis of the filtrate. These results clearly indicate that supported PdAu alloy catalyst worked heterogeneously and the reactions took place on the surface of alloy nanoparticles.

Scheme 4 shows a possible reaction mechanism for the Pd or Ni complex-catalyzed hydrosilylation of terminal allenes to the corresponding terminal alkenylsilanes, as proposed in earlier reports. Hydrosilanes and allenes are subsequently or simul-



Ph 1a (1.0 mmol)	+ HSiEt ₃ 2a (1.2 mmol)	3 <u>1Pd5Au/Al₂O3</u> CH ₃ CN (6.0 mL) r.t.		Ph SiEt ₃ + 3a(<i>E</i>)		Ph SiEt 3a(Z)	₃ + Ph SiEt ₃ 4a
			Reuse	catalyst [mg]	Time [h]	Yield [%] ^[a]	3 <i>E</i> a/3 <i>Z</i> a/4a ^[a]
			-	181	4	64	57/10/33
			1	170	6	61	57/9/34
			2	158	7	63	60/8/32

Scheme 3. Reuse of $1Pd5Au/Al_2O_3$ for the hydrosilylation of **1a** with **2a**.

taneously activated by the metal center **5** to give π -allyl metal hydride intermediate **6**, which is a key intermediate for the formation of alkenylsilanes. Subsequent reductive elimination provides terminal alkenylsilanes. In this Pd or Ni catalysis, bulky *N*-heterocyclic carbene ligands play a key role for the formation of Si-bearing π -allyl species to avoid steric repulsion between silyl group and the bulky metal center. Xie and co-workers theoretically predicted that the rate-limiting step in these catalysis is the formation of π -allyl metal hydride species.^[15] Despite such deep consideration regarding the formation of internal alkenylsilanes via allene hydrosilylation, the formation of internal alkenylsilanes was not observed in these catalysis. Thus, kinetic studies on the allene hydrosilylation with the use of supported Pd–Au catalysts were performed to gain insight into the reaction mechanism.



Scheme 4. Possible reaction pathway to a terminal alkenylsilane via allene hydrosilylation by Pd or Ni complex catalysis.

The reaction orders of substrates and catalysts in the reaction of **1a** with **2a** over 1Pd5Au/Al₂O₃ catalyst were found to be almost zero-order for both substrates and first-order for the catalyst. This suggests that the rate-limiting step in the reaction over supported PdAu catalysts should not be the formation of allyl metal species, but rather C–H bond formation (reductive elimination). A similar tendency regarding for the concentrations of substrates and catalysts was observed in the reaction over Au/Al₂O₃ catalysts, which indicates that the incorporation of Pd atom into Au NPs does not change the entire reaction mechanism, but rather promotes the rate-limiting step of C–H bond formation.

Based on these results, a possible reaction mechanism for the hydrosilylation of terminal allenes over supported PdAu alloy catalysts was depicted in Scheme 5. At first, the dissociative adsorption of hydrosilanes on adjacent Pd and Au atoms takes place to form Pd-H and Au-Si species. Subsequent silyl-metallation of the terminal C=C bond of allene gives primary Si-bearing σ -allyl Au species (**A**). Finally, surface C–H coupling provides internal alkenylsilanes **3**. In contrast, the isomerization of (**A**) generates secondary σ -allyl Au intermediate (**C**) via the forma-





tion of a π -allyl Au intermediate (**B**). Subsequent reductive elimination from Pd-H and σ -allyl Au species (**C**) furnishes terminal alkenylsilanes as a product. In this supported catalysis, the determining factor for both the reaction efficiency and the product selectivity is the reactivity of the surface hydride and allyl species. Stratakis et al. experimentally proved that allyl species on Au NPs exhibited a carbocationic character.^[9] From these facts, striking effects of the incorporation of Pd atom into Au NPs on drastic enhancement of catalytic activity and change of product selectivity are based on the formation of highly nucleophilic hydride species on Pd atoms, which in turn facilitates C–H coupling with cationic σ -allyl species on Au atoms (A) to provide internal alkenylsilanes. Conversely, hydride species formed on pure Au NPs exhibit low nucleophilicity due to the strong electron-withdrawing nature of Au atoms.^[16] As a result, isomerization of primary σ -allyl Au species (A) predominantly occurs to give stable secondary σ -allyl Au species (**C**), and subsequent C-H coupling provides terminal alkenylsilanes as a sole product. These suppositions can be supported by the fact that the reactions of allene bearing electron-withdrawing substituents showed increased selectivities for internal alkenylsilanes (Table 2, entries 8 and 9). On the other hand, the remarkable decreases in the activity of Pd-Au catalysts with high Pd/Au ratios are probably due to the generation of electron-rich Au species by excess charge-transfer from Pd to Au, which decreases the electrophilicity of cationic allyl species on Au atoms. In fact, a change in the electronic state of Au species caused by a change in the Pd/Au ratio was confirmed in XAS and XPS studies (Figures S8 and S11 in the Supporting Information).



Scheme 5. Model structure of 1Pd5Au NP and a possible reaction mechanism for hydrosilylation of allenes over supported Pd–Au catalysts.

Conclusion

In summary, the hydrosilylation of allenes over supported PdAu alloy catalysts was demonstrated. The incorporation of Pd atoms into Au NPs not only drastically enhanced the catalytic activity, but also dramatically changed the product selectivity,

and the reaction over PdAu alloy at room temperature efficiently proceeded to give the corresponding alkenylsilanes as a main product. A kinetic study revealed that the incorporation of Pd atoms into Au NPs promoted rate-limiting surface C–H coupling. Further applications of supported Pd–Au alloy catalysts in other synthetic reactions as well as a theoretical study on the detailed reaction mechanism are currently underway in our laboratory.

Experimental Section

Typical Reaction Procedure: Allenes **1b** (0.50 mmol) and CH_3CN (3.0 mL) were added to a Schlenk tube containing the supported Pd–Au catalyst (1.0 mol-% as a total amount of Pd and Au) under an argon atmosphere. The reaction was initiated by the injection of hydrosilane **2a** (0.60 mmol) at room temperature. After the allenes were completely consumed, the solid catalyst was removed by centrifugation. The remaining solution was concentrated under reduced pressure and purified through silica gel column chromatography (hexane) to give the product in a total yield of 79 %.

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