

Efficient Pd(0)-Catalyzed Hydrosilylation of Alkynes with Triorganosilanes

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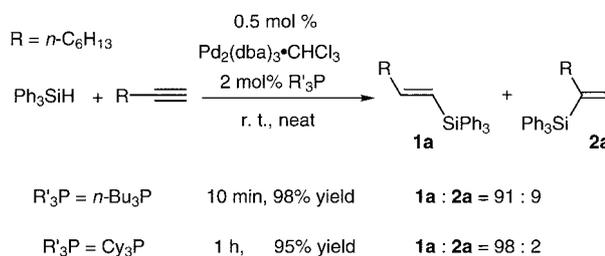
Abstract: An electron-rich Pd(0) complex, a Pd₂(dba)₃·CHCl₃–tricyclohexylphosphine combination catalyzes highly efficient hydrosilylation of alkynes at room temperature with Ph₃SiH or Ph₂MeSiH without solvents. The regioselectivity of this process is higher than that with the conventional Pt(0)-catalyzed hydrosilylation.

Key words: hydrosilylation, palladium, phosphine, alkyne, alkene

Transition metal-catalyzed hydrosilylation of alkenes and alkynes has been extensively investigated, and have found widespread application ranging from asymmetric synthesis to material science.¹ Most of hydrosilylation exploit transition metal catalysts based on platinum and rhodium complexes.^{2–5} Palladium catalysts also effect hydrosilylation with Cl₃SiH,⁶ and they are particularly important for enantioselective hydrosilylation with chiral phosphine ligands.⁷ However, palladium–phosphine complexes are not generally employed for hydrosilylation with triorganosilane because of low catalytic activity. Herein we wish to report that an electron rich Pd(0)-catalyst,⁸ a combination of Pd₂(dba)₃·CHCl₃–trialkylphosphine, efficiently catalyzes stereoselective hydrosilylation of alkynes with triorganosilanes at room temperature. The regioselectivity with this protocol is superior to that with the reported procedure under Pt(0)-catalysis.⁹

A mixture of Pd₂(dba)₃·CHCl₃ (0.005 mmol), tributylphosphine (0.02 mmol), and 1-octyne (1.2 mmol) was stirred for 10 min. To the mixture, triphenylsilane (1.0 mmol) was introduced at room temperature. After 10 min, purification of the reaction mixture provided (*E*)-1-octenylsilane **1a** in 89% yield (Scheme 1). The *Z*-isomer was not detectable in the reaction mixture. A small amount of the regioisomer **2a**, 2-silyl-1-octene, was also obtained (9%). The palladium catalyst can be reduced to 0.05 mol%. The low catalyst loading also achieved quantitative conversion within 10 min at room temperature.

To enhance the regioselectivity, we examined various phosphine ligands in the reaction with 1-octyne as the substrate. Triarylphosphines such as triphenylphosphine exhibited low catalytic activity. Although tris(2,4,6-trimethoxyphenyl)phosphine had improved activity, the regioselectivity was not acceptable (*vide infra*). Triethylphosphite achieved quantitative conversion in 6 h, but af-



Scheme 1

forded unsatisfactory regiocontrol (**1a/2a** = 79:21). After several experiments, we found tricyclohexylphosphine furnished 1-alkenylsilanes with high regioselectivity (**1a/2a** = 98:2) (Scheme 1). Unfortunately, no reaction proceeded with tri(*tert*-butyl)phosphine. As the palladium source, Pd₂(dba)₃·CHCl₃ proved to be the best among Pd₂(dba)₃·CHCl₃, Pd(OAc)₂, PdCl₂(PhCN)₂, [PdCl(η³-C₃H₅)₂], and PdCl₂(Ph₃P)₂.

With the optimized catalytic system in our hand, we examined the hydrosilylation reaction of various alkynes with Ph₃SiH, Ph₂MeSiH, and PhMe₂SiH. Table 1 summarizes the results.¹⁰ Several characteristics of this process are noteworthy. A variety of alkynes afforded the desired products in good yields. Olefin, ester, and silyl ether functionalities are compatible under the reaction conditions. Triphenylsilane is the most reactive among three silanes, and afforded excellent yields except for phenylacetylene (entry 1). As for regiocontrol, both Ph₃SiH and Ph₂MeSiH exhibited almost the same selectivity. The reaction of 3,3-dimethyl-1-butyne required the use of 5.0 equiv of the alkyne because of the low solubility of Ph₃SiH in 3,3-dimethyl-1-butyne (entry 8). Hydrosilylation with PhMe₂SiH is not so efficient as Ph₃SiH and Ph₂MeSiH (entry 13).¹¹ Unfortunately, the use of internal alkynes such as 6-dodecyne yielded none of the alkenylsilane under the same conditions (entry 14).

In the course of the optimization study, we found an intriguing phenomenon: the use of water as a reaction solvent enhances the reactivity of Pd(0)-catalyzed hydrosilylation of 1-octyne (Scheme 2).¹² A better yield was achieved in water than even the neat conditions with a Pd₂(dba)₃·CHCl₃–tris(2,4,6-trimethoxyphenyl)phosphine combination as the catalyst.^{13,14} No observable reaction proceeded in CH₂Cl₂. We also observed the similar enhancement in hydrosilylation with Pd(Ph₃P)₄. However, the difference in the yield of the product was not sig-

nificant under the optimized conditions with the Pd(0)/Cy₃P system.

The Pd₂(dba)₃·CHCl₃–tributylphosphine combination allows efficient hydrosilylation of alkenes at room temperature (Scheme 3). None of 1-alkenylsilanes, which could

Table 1 Hydrosilylation Reaction of Various Alkynes

Entry	Alkyne	Si	Yield (%)	Selectivity (1/2)
1	Ph-C≡C-H	Ph ₃ Si	55	95/5
2 ^b	<i>t</i> -Bu-C≡C-H	Ph ₃ Si	95	>99/1
3		Ph ₃ Si	90	97/3
4		Ph ₃ Si	89	97/3
5		Ph ₃ Si	88	97/3
6		Ph ₃ Si	91	97/3
7 ^c	<i>n</i> -C ₆ H ₁₃ -C≡C-H	Ph ₂ MeSi	82	98/2
8 ^d	<i>t</i> -Bu-C≡C-H	Ph ₂ MeSi	98	>99/1
9 ^e		Ph ₂ MeSi	85	94/6
10		Ph ₂ MeSi	68	>99/1
11 ^e		Ph ₂ MeSi	91	95/1
12		Ph ₂ MeSi	100	96/4
13 ^d	<i>t</i> -Bu-C≡C-H	Ph ₂ MeSi	36	>99/1
14	<i>n</i> -C ₅ H ₁₁ -C≡C- <i>n</i> -C ₅ H ₁₁	Ph ₃ Si	trace	–

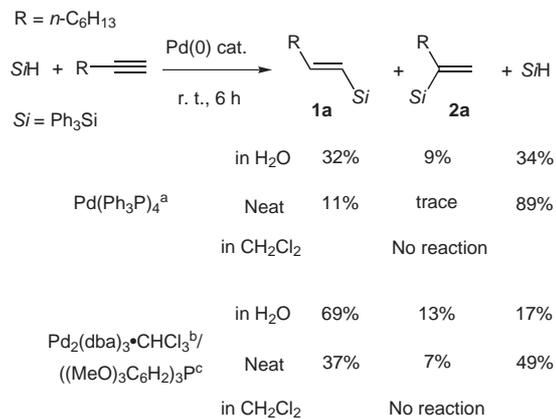
^a Alkyne (1.2 mmol), silane (1.0 mmol), Pd₂(dba)₃·CHCl₃ (0.005 mmol), Cy₃P (0.02 mmol), room temperature, 1 h.

^b 1 min.

^c 10 min.

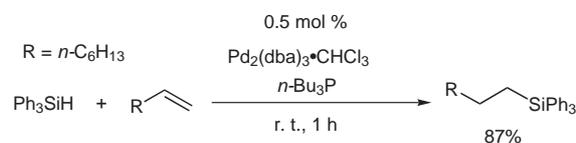
^d 3,3-Dimethyl-1-butyne (2.5 mmol) was employed.

^e 2 h.



^a 5 mol% ^b 0.5 mol% ^c 2 mol%

Scheme 2



Scheme 3

be derived via dehydrogenative silylation, was detected in the reaction mixture.

In conclusion, we have developed an efficient hydrosilylation protocol with Pd₂(dba)₃·CHCl₃–tricyclohexylphosphine combination. This catalytic system effects rapid hydrosilylation with excellent regiocontrol at room temperature, and tolerates a variety of functionalities.

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- (10) **Experimental Procedure:** The reaction of dodec-1-en-11-yne with Ph₃SiH is representative. In a 30 mL round-bottomed flask, Pd₂(dba)₃·CHCl₃ (5.2 mg, 0.005 mmol) and tricyclohexylphosphine (5.6 mg, 0.02 mmol) were placed under argon atmosphere, and dodec-1-en-11-yne (0.26 mL, 1.2 mmol) was introduced via a syringe. The mixture was stirred well for 10 min to make it homogeneous. To the mixture, triphenylsilane (260 mg, 1.0 mmol) was added at room temperature. Triphenylsilane was soon dissolved and the mixture became homogeneous. After 1 h, the reaction mixture was submitted on silica gel purification to provide (*E*)-1-triphenylsilyl-dodeca-1,11-diene (369 mg, 0.87 mmol) in 87% yield along with a minor amount of 2-triphenylsilyl-dodeca-1,11-diene (3%).
- (11) None of alkenylsilanes were obtained with triethylsilane.
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- (13) **Experimental Procedure for Aqueous Reaction:** In a round-bottomed flask, Pd₂(dba)₃·CHCl₃ (5.2 mg, 0.005 mmol), tris(2,4,6-trimethoxyphenyl)phosphine (10.7 mg, 0.02 mmol), and 1-octyne (0.30 mL, 2.0 mmol) were mixed well. To the mixture, distilled water (5 mL, non-degassed) was introduced and the mixture was stirred vigorously (1500 rpm) for 5 min. Triphenylsilane (260 mg, 1.0 mmol) was then added, and the heterogeneous mixture was stirred vigorously for 6 h. Extractive workup and purification provided (*E*)-1-triphenylsilyl-1-octene (256 mg, 0.69 mmol) along with 2-triphenylsilyl-1-octene (13%).
- (14) An addition of a small amount of water (0.1 mL) to the neat reaction did not enhance the reactivity. Therefore, the amount of water is essential.