

A highly regio- and stereoselective transition metal-catalyzed hydrosilylation of terminal alkynes under ambient conditions of air, water, and room temperature

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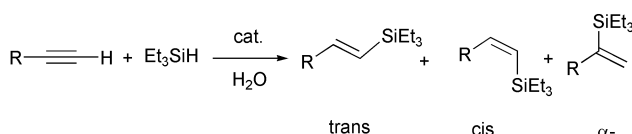
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A highly efficient and stereoselective hydrosilylation of terminal alkynes was developed at room temperature in air and water.

Catalytic hydrosilylation of alkynes is an important process generating vinylsilanes that are important reagents for a number of organic transformations such as Hiyama-type coupling,¹ coupling with aldehydes,² and applications in controlling various cation-cyclization processes.³ Since the first report of catalytic hydrosilylation of alkynes using Speier's catalyst,⁴ many catalysts have been developed for related transformations.⁵ Generally, these catalytic reactions are carried out in an inert gas atmosphere and under anhydrous conditions. Recently, there has been significant interest in developing carbon-carbon bond formation reactions in water.⁶ Among these reactions is the addition of vinylboronic acids to aldehydes.⁷ Recently, we reported a transition metal-catalyzed addition of vinylsilane derivatives to aldehydes and α,β -unsaturated carbonyl compounds,⁸ as well as coupling of vinylsilane derivatives with aryl halides⁹ in air and water. A limitation of this method is the requirement for preforming vinylsilane derivatives under the standard anhydrous conditions. A method for hydrosilylation of alkynes in aqueous media would be highly desirable. Herein, we wish to report a highly effective as well as regio- and stereoselective hydrosilylation of terminal alkynes under ambient conditions of air, water, and room temperature (Scheme 1).

To begin our study, phenylacetylene was reacted with triethylsilane in water, with a variety of catalysts being examined (Table 1). The use of H_2PtCl_6 as a catalyst led to 86% isolated yield of the hydrosilylation product as a mixture of *trans* and *cis* geometrical isomers in 3 h at room temperature



Scheme 1

Table 1 Catalyst-screening for alkyne-hydrosilylation in water

Entry	Alkyne	Catalyst	<i>trans/cis/α</i>	Yield (%) ^a
1	Phenylacetylene	H_2PtCl_6	74 : 26 : 0	86
2	Phenylacetylene	Pt(DVDS)	91 : 9 : 0	93
3	Phenylacetylene	Pt(DVDS)-P	100 : 0 : 0	98
4	Phenylacetylene	$\text{RhCl}(\text{PPh}_3)_3$	85 : 18 : 0	90
5	Phenylacetylene	$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$	77 : 23 : 0	88
6	Phenylacetylene	$\text{Rh}(\text{COD})(\text{PPh}_3)\text{PF}_6$	81 : 19 : 0	91
7	Phenylacetylene	$\text{Rh}(\text{COD})_2\text{BF}_4$	84 : 16 : 0	92
8	Phenylacetylene	$\text{Ru}(\text{CO})\text{HCl}(\text{PPh}_3)_3$	—	0
9	Phenylacetylene	$\text{Ru}(\text{Cp})_2$	—	0

All reactions were carried out at room temperature on a 1 mmol scale in 3 h.^a Isolated yields are reported. *trans/cis/α*-ratios were measured by ¹H NMR and/or GCMS.

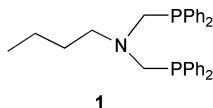
(entry 1). The use of Pt(DVDS) (DVDS: 1,3-divinyl-1,1,3,3-tetramethyldisiloxane) complex as a catalyst resulted in an increase in both the product yield and the *trans/cis* ratio under the same reaction conditions (entry 2). Notably, the use of Pt(DVDS)-P [P: *bis*(diphenylphosphinomethylene)butylamine (1)¹⁰] as catalyst led to a near quantitative yield and a 100% stereoselectivity (*trans*) (entry 3). Rhodium-based catalysts [$\text{RhCl}(\text{PPh}_3)_3$, $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, $\text{Rh}(\text{COD})(\text{PPh}_3)\text{PF}_6$, and $\text{Rh}(\text{COD})_2\text{BF}_4$] were also effective, but they led to both lower yields and lower *trans/cis* selectivity. No reaction was observed with $\text{Ru}(\text{CO})\text{HCl}(\text{PPh}_3)_3$ and $\text{Ru}(\text{Cp})_2$ as catalysts under the same reaction conditions. In addition, no α -addition product was observed in any of these cases. Subsequently, various terminal acetylenes were hydrosilylated under the standard conditions catalyzed by Pt(DVDS)-P (Table 2).¹¹ The corresponding results catalyzed by Pt(DVDS) without the phosphine ligand are also included in parentheses for comparison. Although both catalysts provided excellent yields of the hydrosilylation product in each case, the use of Pt(DVDS)-P as catalyst provided better *trans* selectivity in all cases and complete *trans* selectivity was observed with most terminal alkynes (entries 1, 7, 9, 11, 13, 15). Notably, the presence of a

Table 2 Catalytic hydrosilylation of alkynes in air and water

Entry	Alkyne	<i>trans/cis/α</i> ^a	Yield (%) ^b
1	$\text{C}_9\text{H}_{11}\text{—}\equiv$	100 : 0 : 0	97
2		(91 : 9 : 0)	(96)
3	$\text{C}_4\text{H}_9\text{—}\equiv$	96 : 4 : 0	92
4		(80 : 20 : 0)	(91)
5		95 : 5 : 0	90
6		(81 : 19 : 0)	(90)
7		100 : 0 : 0	92
8		(73 : 27 : 0)	(92)
9		100 : 0 : 0	98
10		(74 : 26 : 0)	(98)
11		100 : 0 : 0	95
12		(67 : < 1 : 33)	(93)
13		100 : 0 : 0	93
14		(82 : 18 : 0)	(93)
15		100 : 0 : 0	95
16		(93 : 7 : 0)	(89)
17		91 : 9 : 0	95
18		(55 : 45 : 0)	(96)
19		35 : 65 : 0	92
20		(45 : 55 : 0)	(92)
21		93 : 7 : 0	95
22		(86 : 14 : 0)	(93)

Pt(DVDS)-P as catalyst; results of using Pt(DVDS) as catalyst are in parentheses.^a Determined by ¹H NMR and/or GCMS. ^b Isolated yields.

hydroxyl group did not affect the reaction (entries 7–12). Except in entry 12, no α -product was observed with either catalyst in any case. Interestingly, the use of trimethylsilylacetylene (entries 19, 20) led to a switch of the *trans/cis* selectivity. It is not yet clear what caused this selectivity change.



In conclusion, a highly effective and stereoselective hydrosilylation of terminal alkynes was developed under ambient conditions of air, water, and at room temperature. Hydroxylated alkynes could be hydrosilylated directly. In all cases except for trimethylsilylacetylene, *trans*-products were obtained exclusively or selectively. Synthetic applications of the reaction are currently under investigation.

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- Preparation of ligand **1**: [cf. Y. Uozumi and Y. Nakai, *Org. Lett.*, 2002, **4**, 2997] To a three-necked 100 mL round bottomed flask, paraformaldehyde (0.23 g, 7.1 mmol) and 20 mL of degassed methanol were added under a flow of nitrogen gas. Then, 1.35 mL of diphenylphosphine were introduced to the reaction mixture via a syringe. After the mixture was stirred at room temperature for 2 h, butylamine (250 mg, 3.53 mmol) dissolved in methanol (10 mL) and toluene (20 mL) was added via a syringe. The mixture was heated to 60–70 °C and stirred overnight. Removal of all volatiles after cooling gave the product as a viscous liquid (yield, 89%). ¹H NMR (CDCl₃, 400 MHz, ppm): δ 7.54–7.21 (m, 20H), 3.61 (d, J = 3.2 Hz, 4H), 2.88 (t, J = 7.6 Hz, 2H), 1.39 (m, 2H), 1.21 (m, 2H), 0.83 (t, J = 7.2 Hz, 3H). ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 131.8, 131.7, 131.4, 131.3, 129.0, 128.9, 128.7, 128.6, 56.6, 56.5, 56.4, 56.3, 28.8, 28.6, 20.6, 20.4, 14.3, 14.2. ³¹P (CDCl₃) δ –27.47. HRMS for (M⁺ – PPh₂): calc'd. 284.1562, found 284.1567.
- A general reaction procedure follows: to a mixture of triethylsilane (1 mmol) and terminal alkyne (1 mmol) in 3 mL of water, under vigorous stirring at room temperature, were slowly added 30 μ L of Pt(DVDS)–P complex (in xylene) [the complex was prepared by reacting Pt(DVDS) with equimolar ligand **1** at 65 °C for 15 min]. The stirring was continued for 3 h after complete addition of the catalyst solution. Then the reaction mixture was extracted with ether and the solvent was removed *in vacuo*. The crude product was purified by column chromatography on silica gel (eluent: hexane–ethyl acetate) to afford the product.