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Tri(*t*-butyl)phosphine-assisted selective hydrosilylation of terminal alkynes

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Abstract

A highly efficient and regio-/stereoselective method of hydrosilylating terminal alkynes was developed using Pt(DVDS)-tri(*t*-butyl)phosphine catalyst system at room temperature. *Trans*-products or *alpha*-products were obtained almost exclusively depending on the alkynes and silanes employed.

Keywords: Hydrosilylation; Terminal alkynes; Tri(*t*-butyl)phosphine; Platinum

Catalytic hydrosilylation of alkynes is one of the most convenient and straightforward methods for the synthesis of vinylsilanes that are important building blocks in organic synthesis [1–3]. Because the hydrosilylation of terminal alkynes usually give a primary mixture of three isomeric vinylsilanes (*β*–*Z*, *β*–*E*, and *α*, Scheme 1), the major consideration in this conversion is the regio- and stereoselectivities.

Many catalyst systems, such as Pt [4], Ru [5], Rh [6], Pd [7], etc., have been developed for hydrosilylating alkynes since the first report using Speier's catalyst [8]. It was found that the control of the selectivity, in most cases, was capriciously affected by various factors such as types of alkynes and silanes, metal species and reaction conditions including solvent, temperature and reaction time [5], etc.

Among the aforementioned catalyst systems, platinum is still a better choice for the highly efficient formation of stereospecific vinylsilanes, for that it is generally applicable, convenient and easy accessible. The reactions are usually clean and no detectable byproducts can be found, although the vinylsilane isomer distribution may vary. Other conventional metal catalysts, like rhodium, ruthenium and palladium, usually show certain catalytic activity toward cyclotrimerization and/or dimerization of alkynes thus result in unsatisfactory yields, or they are only effective to certain activated silanes (such as trichloro-, trialkoxyl, and di/triphenylsilanes) [9]. Recently we found the regio-/stereoselectivity of Pt-catalyzed hydrosilylation can be greatly improved by addition of certain kind of bulky ligand [10]. Tri(*t*-butyl)phosphine, which is readily available and have been proven to be highly efficient for a one-pot hydrocarbonation [11], could be an excellent candidate for this purpose. Herein, we report a rapid and efficient room-temperature method for the highly stereo- and regioselective hydrosilylation of terminal alkynes using the Pt(DVDS)/P(*t*-Bu)$_3$ catalyst system.

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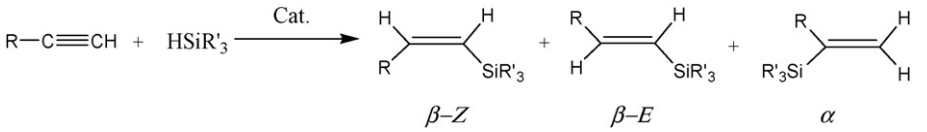
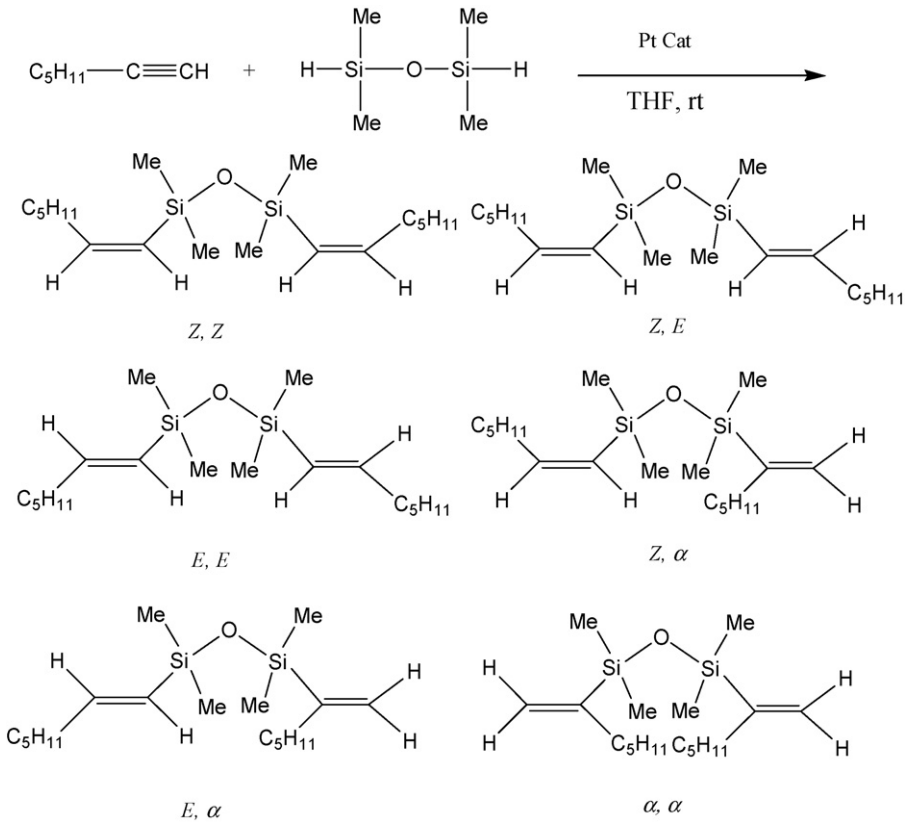


Scheme 1.

To begin our study, 1-heptyne was reacted with 1,1,3,3-tetramethyldisiloxane in THF with a variety of phosphorus ligands being examined. 1,1,3,3-tetramethylsiloxane can combine with two equivalents of 1-heptyne, giving six possibilities of product isomers as shown in Scheme 2. The effect of ligand on the catalytic selectivity can be well observed from the product isomer distribution.

As shown in Table 1, the use of H_2PtCl_6 as a catalyst led to 69% isolated yield of the hydrosilylation products as an isomer mixture. Five isomers were present with the *E*,*E*-isomer as the main component (53%). In all cases, the least possible α,α-isomer was not found. 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 yield of the products and the *E*,*E* isomer ratio under the same reaction conditions. The use of HMPT, PPh_3 and P(*o*-MeC_6H_4)$_3$ increased the yields but the selectivity were still not good. $P(OEt)_3$ and $P(OPh)_3$ were totally unacceptable because of the low yield and poor selectivity under this condition. Notably, the employment of P(*t*-Bu)$_3$ as ligand resulted in both excellent yield and improved selectivity, giving only three isomers with the *E*,*E*-isomer ratio up to 91%. Thus Pt(DVDS)/P(*t*-Bu)$_3$ was selected as catalyst for the following hydrosilylation of various terminal alkynes.

Under the optimized conditions, a variety of alkynes bearing various functional groups were hydrosilated with triethylsilane, and triphenylsilane (Table 2). Hydrosilylation of heptyne with triethylsilane catalyzed by Pt(DVDS) without the phosphine ligand was also included for comparison (in parentheses, entries 1 and 2). The use of Pt(DVDS)/P(*t*-Bu)$_3$ as catalyst provided excellent yields in all cases. When triethylsilane was used, very high *trans* selectivity was



Scheme 2.

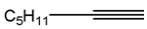
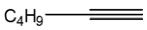
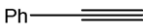
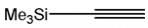
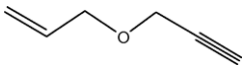
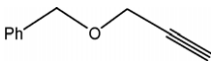
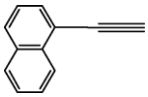
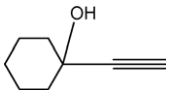
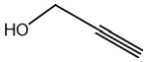
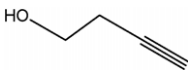
Table 1
Hydrosilylation of 1-heptyne with 1,1,3,3-tetramethylsiloxane using different Pt complexes[a].

Catalyst	Yield (%)	Product isomer[b] (%)			Others
		Z,*Z*	*Z*,*E*	*E*,*E*	
H_2PtCl_6	69	3	34	53	10
Pt(DVDS)	89	2	21	72	5
w/HMPT	93	1	15	78	6
w/PPh_3	96	2	22	68	8
w/P(*o*-$C_6H_4CH_3)_3$	94	3	25	65	7
w/P(OEt)$_3$	26	2	24	70	4
w/P(OPh)$_3$	30	2	26	63	9
w/P(*t*-Bu)$_3$	93	0	8	90	2

[a] In THF 0.5 mL, 2 mmol of heptyne, 1 mmol of tetramethyldisiloxane, rt, 30 min, catalyst, 1 mol.%.
[b] Determined by GC–MS.

observed for entries 1, 5, 7 and 21 and exclusively *trans* selectivity were realized with most other terminal alkynes (entries 3, 11, 13, 15, 17 and 19). Except in entry 9, the substrate trimethylsilylacetylene gave a moderate selectivity under this condition. When triphenylsilane was used, almost complete *alpha* selectivity (>99%) was observed with alkylacetylene (entries 2, 4 and 6), and complete *alpha* selectivity was observed with aromatic acetylene (entries 8 and

Table 2
Catalytic hydrosilylation of alkynes[a].

Entry	Akyne	Silane	Yield (%)[b]	*Z*/*E*/α[c]
1		Et_3SiH	95(87)	2/98/0 (1/77/6)
2		Ph_3SiH	95(89)	0/t/>99 (13/78/9)
3		Et_3SiH	94	0/100/0
4		Ph_3SiH	95	0/t/>99
5		Et_3SiH	97	2/98/0
6		Ph_3SiH	98	0/t/>99
7		Et_3SiH	97	4/94/2
8		Ph_3SiH	99	0/0/100
9		Et_3SiH	86	12/77/11
10		Ph_3SiH	92	0/6/94
11		Et_3SiH	96	0/100/0
12		Ph_3SiH	97	t/>99/0
13		Et_3SiH	97	0/100/0
14		Ph_3SiH	98	t/>99/0
15		Et_3SiH	96	0/100/0
16		Ph_3SiH	92	0/0/100
17		Et_3SiH	93	0/100/0
18		Ph_3SiH	92	t/>99/0
19		Et_3SiH	93	0/100/0
20		Ph_3SiH	95	0/100/0
21		Et_3SiH	92	t/>99/0
22		Ph_3SiH	94	0/100/0

[a] In THF, 1.1 mmol of alkyne, 1 mmol of silane, rt, catalyst 1 mol.%.
[b] Isolated yields.
[c] Determined by ^{1}H NMR and/or GC–MS; t means trace.

16). Very high *alpha* selectivity (94%) could also be obtained with trimethylacetylene (entry 10). Similar *alpha* selectivity has been reported previously for a $Pd(PPh_3)_2Cl_2$-catalyzed hydrostannylation [12,13]. With the other alkynes, including allyl propargyl ether (entry 12), benzyl propargyl ether (entry 14), 1-ethynylcyclohexan-1-ol (entry 15), propargyl alcohol (entry 20) and 3-butyn-1-ol (entry 22), interestingly, almost complete or complete *trans* vinyltriphenylsilane products were obtained. It is not quite clear what caused this selectivity change at the moment. The oxygen atom in the substrate might be responsible for this observation. Finally, in common with most hydrosilylation of alkynes, the presence of a hydroxyl or alkenyl group can tolerate in this protocol (entries 11, 12 and 17–22).

In conclusion, a highly effective and regio- and stereoselective hydrosilylation of terminal alkynes was developed by using the Pt(DVDS)–P(*t*-Bu)$_3$ complex as catalyst. In most cases, only *trans* products or *alpha* products were obtained exclusively or selectively.

1. Experimental

A xylenes solution of Pt(DVDS) and P(*t*-Bu)$_3$ were obtained from Aldrich. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity 400 or 300 MHz spectrometer. ^{1}H NMR spectra are referenced to the residual $CHCl_3$ peak (δ 7.27) in $CDCl_3$, and ^{13}C NMR spectra are referenced to $CDCl_3$ (δ 77.23). GC–MS data were recorded on a Varian Saturn 2100 GC/MS System. Combustion analyses were performed on a PE 2400 elemental analyzer.

1.1. In situ synthesis of metal complexes

To a xylenes solution of Pt(DVDS) (1 mL containing 2% Pt) was added P(*t*-Bu)$_3$ (1.0 equiv. per Pt). The mixture was stirred at 65 °C for 10 min, and cooled to room temperature. This solution was stored under argon and used within 1 month.

1.2. Reaction of 1-heptyne with 1,1,3,3-tetrmethyldisiloxane

To 1-heptyne (2 mmol) solution of THF (0.5 mL) was added 1,1,3,3-tetrmethyldisiloxane (1 mmol) under argon. The reaction mixture was stirred at 20 °C for 30 min after addition of the catalyst (1 mol.%). The crude reaction mixture was concentrated in vacuum and was purified by column chromatography on silica gel column. (GC–MS: retention time for the isomeric products from hydrosilylation of 1-heptyne with 1,1,3,3-tetramethyldisiloxane (min): *Z*,*Z*: 12.0; *Z*,*E*: 12.11, *E*,*E*: 12.27; *Z*,α: 12.39; *E*,α: 12.5)

1.3. General procedure for the hydrosilylation reactions

To an alkyne (1 mmol) solution of THF (1 mL) was added silane (1.1 equiv.) under argon. And the reaction mixture was stirred at 20 °C for 20–30 min after addition of the catalyst (1 mol.%). The crude reaction mixture was concentrated in vacuum and was purified by column chromatography on silica gel column.

1.4. (E,E)-1,1,3,3-tetramethyl-1,3-bis(1-heptenyl)disiloxane

^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.12 (s, 12H), 0.90 (t, 6H, J = 8.8 Hz), 1.28–1.43 (m, 12H), 2.08–2.14 (m, 4H), 5.61 (dt, 2H, J = 18.7, 1.3 Hz), 6.11 (dt, 2H, J = 18.7 Hz, 6.2 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 1.1, 14.3, 22.8, 28.5, 31.7, 36.8, 129.5, 148.3. Anal. Calcd. for $C_{18}H_{38}OSi_2$: C, 66.18; H, 11.73. Found: C, 65.84; H, 11.98.

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