

Platinum chloride/Xphos-catalyzed regioselective hydrosilylation of functionalized terminal arylalkynes

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Abstract

Totally regioselective hydrosilylation of functionalized terminal arylalkynes was achieved using PtCl₂ associated with the air-stable and bulky Xphos ligand with various silanes. Regardless of the electronic nature of the substituents on the aromatic ring, a single β-(*E*)-vinylsilane was obtained in excellent yields.

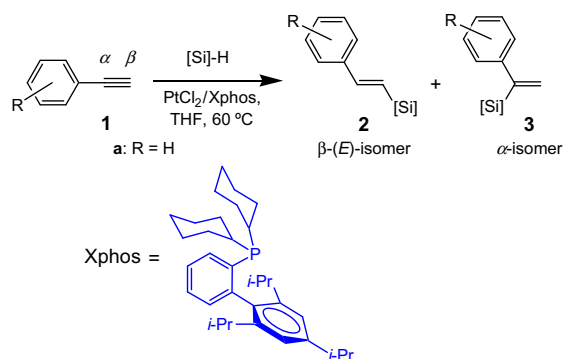
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Keywords: Hydrosilylation; Alkynes; Regioselectivity; Platinum; Phosphane ligands; Xphos

Functionalized β-(*E*)-styrylsilanes **2**, which have emerged as powerful intermediates in organic synthesis,¹ can in principle be accessed by metal-catalyzed hydrosilylation of terminal arylalkynes.² Although the platinum catalyzed hydrosilylation of alkynes is well documented, however, the reaction with functionalized terminal arylalkynes to provide β-(*E*)-styrylsilanes has received scant attention.³ Recently, significant progress with non-substituted phenylacetylene in terms of regioselectivity has been made for the β-(*E*)-styrylsilane formation⁴ using the pre-formed [Pt(CH₂=CHSiMe₂)₂O] in conjunction with air-sensitive, pyrophoric, and difficult-to-handle P(*t*Bu)₃. The remaining challenge is to obtain high β-(*E*)-selectivity from functionalized arylalkynes without compromising reagent stability and practicality. Herein, we report that PtCl₂/Xphos provides an efficient catalyst system for the hydrosilylation of a wide variety of functionalized phenylacetylenes **1** with various silanes.

Previously, we reported that platinum oxide proved to be a versatile catalyst for the hydrosilylation of internal

arylalkynes.⁵ Unfortunately, in the case of terminal alkynes, the regioselectivity of the H–Si bond addition was found to be weak.⁶ Therefore, we anticipated that the tuning of platinum complex catalysts would affect the regioselectivity of H–Si bond addition. The hydrosilylation regioselectivity of **1a** with HSiEt₃ was studied under several reaction conditions (platinum catalysts, ligands, and solvents) according to Scheme 1. The best results in term of yield and selectivity were achieved when commercially available PtCl₂ (5 mol %) and Xphos ligand (10 mol %) were used in THF. Accordingly, **2a** was exclusively formed

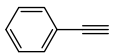
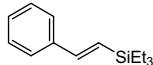
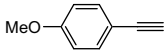
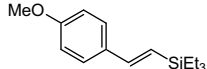
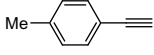
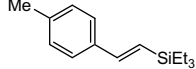
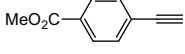
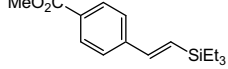
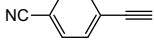
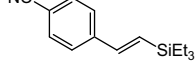
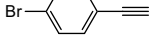
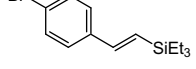
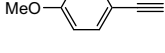
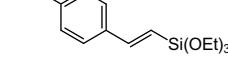
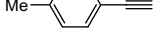
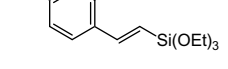
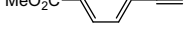
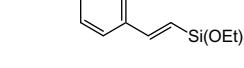
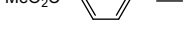
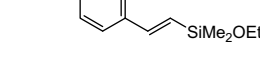
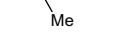
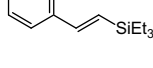
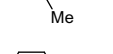
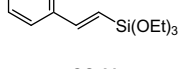
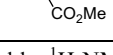
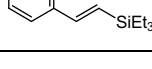


Scheme 1.

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Table 1
 PtCl₂/Xphos-catalyzed hydrosilylation of terminal alkynes **1**⁷

Entry	Alkyne 1		HSiR ₃	α:β ^a Ratio	Vinylsilanes ^b 2	Yield ^c (%)
1		1a	HSiEt ₃	0:100	2a 	98
2		1b	HSiEt ₃	0:100 ^d	2b 	91
3		1c	HSiEt ₃	0:100	2c 	91
4		1d	HSiEt ₃	0:100	2d 	86
5		1e	HSiEt ₃	0:100	2e 	80
6		1f	HSiEt ₃	0:100	2f 	94
7		1b	HSi(OEt) ₃	2:98	2g 	65
8		1c	HSi(OEt) ₃	2:98	2h 	83
9		1d	HSi(OEt) ₃	30:70	2i 	67
10		1d	HSiMe ₂ OEt	3:97	2j 	68 ^e
11		1g	HSiEt ₃	0:100	2k 	98
12		1g	HSi(OEt) ₃	0:100	2l 	75
13		1h	HSiEt ₃	19:81	2m 	83 ^f

^a Determined by ¹H NMR and GC.

^b All of the reported compounds exhibited spectral data in agreement with the assigned structures.

^c Isolated yield.

^d A 18:82 α:β mixture was obtained in the absence of Xphos ligand.

^e Reaction was performed at room temperature.

^f Isolated yield of the vinylsilane α:β mixture after column chromatography.

and the analysis of the crude reaction mixture by ¹H NMR spectroscopy and GC revealed no trace of either **3a** or the β-(Z)-vinylsilane demonstrating that the H–Si bond addition proceeded exclusively in a *syn* fashion. To the best of our knowledge, this is the first example of terminal

arylalkyne hydrosilylation being catalyzed by PtCl₂ catalyst associated with stable and commercially available monodentate Xphos ligand.

Next, we used the PtCl₂/Xphos catalyst system for evaluating the scope of this hydrosilylation with a range of

functionalized terminal alkynes (Table 1). *para*-Substituted arylalkynes **1b–f** were cleanly hydrosilylated with Et₃SiH in the presence of the PtCl₂/Xphos couple to their corresponding β -(*E*)-adducts with excellent yields whatever is the nature (electron donating or electron withdrawing group) of the substituent (entries 2–6). Replacement of Et₃SiH by (EtO)₃SiH resulted in similar yields and β -(*E*)-selectivities (entries 7 and 8) except in the case of arylalkyne **1d** with a *para* electron withdrawing group (entry 9). Fortunately, we were pleased to observe that the replacement of (EtO)₃SiH by HSiMe₂OEt led to β -(*E*) vinylsilane **2j** with an excellent regioselectivity (entry 10).

With the *ortho*-substituted alkyne **1g**, again a total β -regiocontrol was observed with either Et₃SiH or (EtO)₃SiH (entries 11 and 12). This result clearly demonstrated that the regioselectivity of the H–Si bond addition is governed by steric effects induced by Xphos ligand rather than *ortho*-directing effect (ODE) as we previously reported.^{5,6,8} To support this explanation, the hydrosilylation of *ortho* methoxyphenylacetylene was conducted without Xphos and produced a 38:62 ratio of α : β regioisomers. With *ortho*-methoxycarbonyl phenylacetylene **1h**, the PtCl₂-catalyzed hydrosilylation was less selective and led to a regioisomeric mixture with a preference for the β -isomer (α : β = 19:81, entry 13) indicating that ODE,⁵ which is opposed to steric effects, rebalances the isomeric distribution, thus increasing the amounts of α -adduct.

In conclusion, we have established that PtCl₂/Xphos is an efficient catalyst system for the hydrosilylation of functionalized terminal alkynes with various silanes. This quite simple procedure is characterized by functional group compatibility and a good generality. Additionally, our results demonstrated that commercially available and air-stable Xphos ligand associated to the PtCl₂ catalyst constitutes an attractive catalytic system for the univocal synthesis of β -(*E*)-vinylsilanes from terminal arylalkynes and should find many applications in organic synthesis.

Acknowledgment

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- Typical procedure*: Under nitrogen atmosphere, PtCl₂ (0.05 mmol) and Xphos (0.1 mmol) in THF (0.5 mL) were heated at 60 °C for 15 min. Then, terminal alkyne (1 mmol) and triethylsilane or triethoxysilane (1.5 mmol) were successively added via a syringe, and the mixture was stirred at 60 °C for 1 h. After evaporation of the solvent, the residue was purified by column chromatography to yield β -(*E*)-vinylsilane **2**.
Vinylsilane 2a: Yield: colorless oil, 91%. TLC: *R*_f 0.5 (Et₂O/cyclohexane, 5/95, SiO₂). IR (neat, cm⁻¹): 2952, 2909, 2874, 2835, 1606, 1570, 1508, 1463, 1441, 1416, 1378, 1332, 1303, 1294, 1250, 1171, 1106, 1037, 1014, 986, 843, 789, 749, 717. ¹H NMR (300 MHz, CDCl₃): δ 0.57 (q, 6H, *J* = 7.8 Hz), 0.90 (t, 9H, *J* = 7.8 Hz), 3.72 (s, 3H), 6.17 (d, 1H, *J* = 19.3 Hz), 6.70–6.82 (m, 3H), 7.30 (d, 2H, *J* = 8.7 Hz). ¹³C NMR (75 MHz, CDCl₃): δ 3.7 (3CH₂), 7.6 (3CH₃), 55.4 (OCH₃), 114.0 (2CH), 123.1 (CH), 127.6 (2CH), 131.7 (C), 144.3 (CH), 159.6 (C). MS (ESI): 248 (M⁺). Anal. Calcd for C₁₅H₂₄OSi (248.44): C, 72.52; H, 9.74. Found: C, 72.48; H, 9.82.
Vinylsiloxane 2g: Yield: yellow oil, 65%; ratio α : β (2/98 of isomers). TLC: *R*_f 0.50 (Et₂O/cyclohexane, 30/70, SiO₂). IR (neat, cm⁻¹): 3288, 2974, 2891, 2883, 1606, 1572, 1508, 1465, 1442, 1418, 1390, 1293, 1250, 1169, 1099, 1071, 1032, 994, 956, 832, 797, 776, 748, 709, 685, 640. ¹H NMR (300 MHz, CDCl₃): δ 1.20 (t, 9H, *J* = 7.0 Hz), 3.72 (s, 3H), 3.80 (q, 6H, *J* = 7.0 Hz), 5.92 (d, 1H, *J* = 19.5 Hz), 6.80 (d, 2H, *J* = 8.3 Hz), 7.08 (d, 1H, *J* = 19.5 Hz), 7.34 (d, 2H, *J* = 8.3 Hz). ¹³C NMR (75 MHz, CDCl₃): δ 18.3 (3CH₃), 55.3 (3CH₂), 58.7 (OCH₃), 113.9 (2CH), 114.7 (CH), 128.3 (2CH), 130.6 (C), 133.7 (CH), 160.3 (C). MS (ESI): 319 (M+Na)⁺. Anal. Calcd for C₁₅H₂₄O₄Si (219.40): C, 60.78; H, 8.16. Found: C, 60.65; H, 8.15.
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