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Tetrahedron Letters 49 (2008) 2429–2431
Tetrahedron Letters

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

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Received 26 November 2007; revised 7 February 2008; accepted 11 February 2008
Available online 14 February 2008

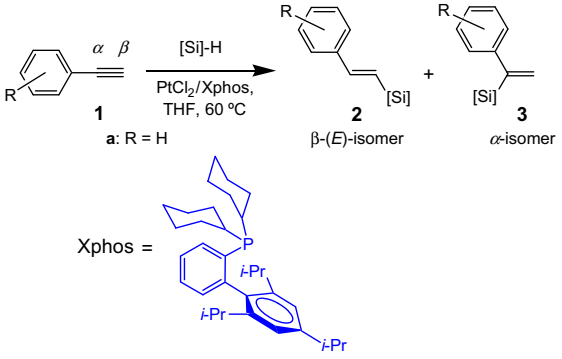
Abstract

Totally regioselective hydrosilylation of functionalized terminal arylalkynes was achieved using $PtCl_2$ 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.

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 formation[4] using the preformed $[Pt(CH_2{=}CHSiMe_2)_2O]$ in conjunction with air-sensitive, pyrophoric, and difficult-to-handle $P(t\mathrm{Bu})_3$. The remaining challenge is to obtain high β-(*E*)-selectivity from functionalized arylalkynes without compromising reagent stability and practicality. Herein, we report that $PtCl_2$/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 $HSiEt_3$ 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 $PtCl_2$ (5 mol %) and Xphos ligand (10 mol %) were used in THF. Accordingly, **2a** was exclusively formed



Scheme 1.

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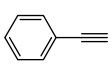
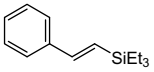
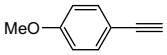
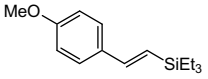
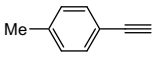
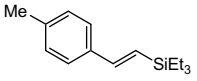
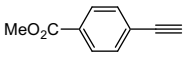
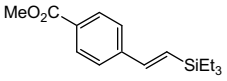
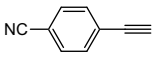
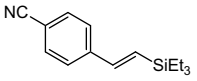
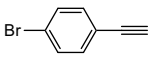
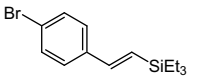
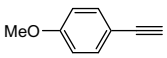
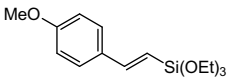
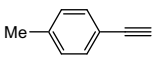
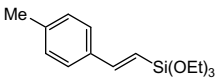
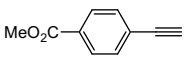
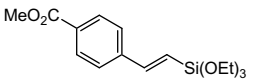
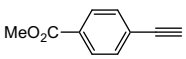
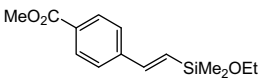
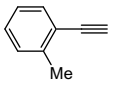
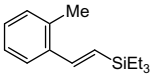
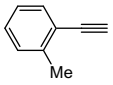
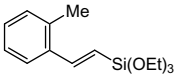
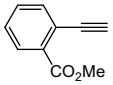
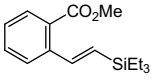
doi:10.1016/j.tetlet.2008.02.060

Table 1
$PtCl_2$/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**	$HSiMe_2OEt$	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 $PtCl_2$ catalyst associated with stable and commercially available monodentate Xphos ligand.

Next, we used the $PtCl_2$/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 Et_3SiH in the presence of the $PtCl_2$/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 Et_3SiH 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 $HSiMe_2OEt$ 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 Et_3SiH 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 $PtCl_2$-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 $PtCl_2$/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 $PtCl_2$ 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

The CNRS is gratefully acknowledged for financial support of this research.

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7. *Typical procedure:* Under nitrogen atmosphere, $PtCl_2$ (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 (Et_2O/cyclohexane, 5/95, SiO_2). 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, $CDCl_3$): 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). ^{13}C NMR (75 MHz, $CDCl_3$): δ 3.7 ($3CH_2$), 7.6 ($3CH_3$), 55.4 (OCH_3), 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 $C_{15}H_{24}OSi$ (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 (Et_2O/cyclohexane, 30/70, SiO_2). 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, $CDCl_3$): 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). ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.3 ($3CH_3$), 55.3 ($3CH_2$), 58.7 (OCH_3), 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 $C_{15}H_{24}O_4Si$ (219.40): C, 60.78; H, 8.16. Found: C, 60.65; H, 8.15.

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