

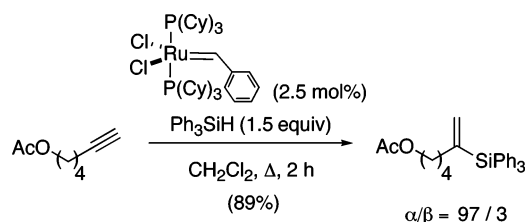
Hydrosilylation of Terminal Alkynes with Alkylidene Ruthenium Complexes and Silanes

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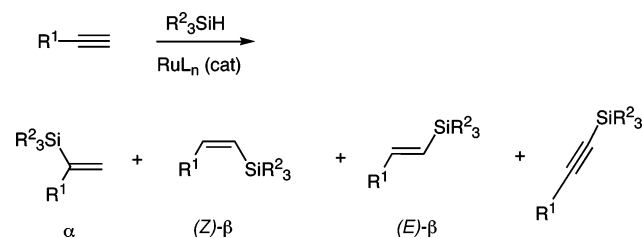


Ruthenium alkylidene complexes **1–3** mediate hydrosilylation of alkynes with silanes. When triethoxy- or triphenylsilanes are used as silylating agents, the reaction affords α -substituted vinylsilanes as major products.

A number of transition metal complexes promote the oxidative addition of Si–H to alkynes,^{1,2} affording (*E*)- β -vinylsilanes as the major products. Ruthenium catalysts produce, however, low or even opposite selectivity, affording (*Z*)- β - or α -vinylsilanes, as the major isomers, and silyl alkynes formed by dehydrogenative silylation (Scheme 1).^{1,2} The selectivity in these Ru-mediated reactions are influenced by the catalyst, substrate, hydrosilylating agent and solvent. For example, a [RuCl₂(*p*-cymene)]₂ catalyst that affords (*Z*)- β -vinylsilanes as the major isomer^{3a} can induce a reverse selectivity as the α -adduct is obtained when a hydroxyl group is present in the vicinity of the alkyne.^{3b} This polar group directs the hydrosilylation probably by chelation of the metal.

With the exception of the cationic [Cp**Ru*(MeCN)₃]-PF₆^{4a,b} and Cp**Ru*H₃(PPh₃)₄^{4c} which afford selectively α -vinylsilanes without the presence of a directing group, no method has been developed for the preparation of the elusive Markovnikov product with Ru-based catalysts. As

SCHEME 1



part of our program on the non-metathetic activity of ruthenium-alkylidene complexes,⁵ we were interested in reexamining the hydrosilylation of terminal alkynes with silanes using complexes **1–3** (Scheme 2).^{6,7}

The butyn-3-ol derivative **4** was selected as a suitable substrate, in which the bulky *t*-butyldimethylsilyl protecting group suppresses efficiently the directing effect of the polar hydroxyl group. The addition of triethylsilane

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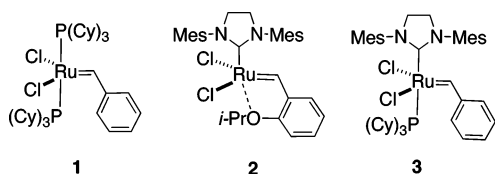
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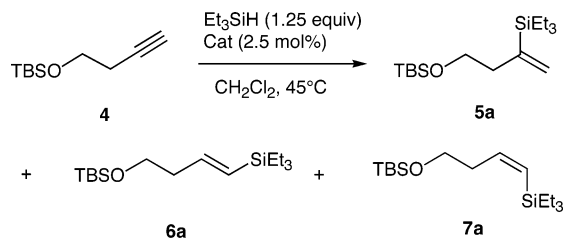
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SCHEME 2



SCHEME 3

TABLE 1^a

	catalyst	time (h)	yield (%)	ratio ^b 5a/6a/7a
1	RuCl(PPh ₃) ₃	12	9	7/81/12
2	RuCl ₃ ·xH ₂ O	12	38	63/24/13
3	[RuCl ₂ (<i>p</i> -cymene)] ₂	1	71	7/3/90
4	1	1.5	86	77/3/20
5	2	2	56	33/16/51
6	3	10	71	19/5/76

^a Conditions: **4** (1.08 mmol) in CH₂Cl₂ (2 mL), TESH (1.5 equiv), catalyst (5 mol %), reflux.

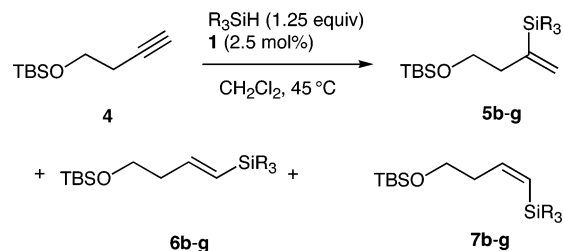
(TESH) to **4** was examined in the presence of ruthenium complexes (2.5 mol %), as reported in Table 1, and TESH (1.25 equiv) in refluxing CH₂Cl₂.

All the ruthenium complexes were found to be active in the hydro-silylation of **4**, affording products **5a–7a** (Scheme 3), although in markedly different selectivity and efficiency. Catalyst RuCl(PPh₃)₃ afforded traces of products (9%) in favor of the (*E*)-isomer (ratio of **5a/6a/7a** = 7/81/12)⁸ (Table 1, entry 1), and RuCl₃·xH₂O provided a modest α -selectivity (ratio of **5a/6a/7a** = 63/24/13) and products were obtained in low yield (38%) (Table 1, entry 2). Better yield was obtained when [RuCl₂(*p*-cymene)]₂ was utilized. As expected on the basis of literature precedents,^{3a} the reaction afforded good β -selectivity in favor of the (*Z*)-isomer **7a** (ratio of **5a/6a/7a** = 7/3/90, yield = 71%) (Table 1, entry 3). Furthermore, ruthenium(II) alkylidene complexes **1–3** showed remarkable efficiency in hydro-silylation. Among them, **1** and **2** performed the reaction rapidly although in opposite selectivity (catalyst **1**: 86% yield, ratio of **5a/6a/7a** = 77/3/20; catalyst **2**: 56% yield, ratio of **5a/6a/7a** = 33/16/51) (Table 1, entries 4 and 5).⁹ Finally, Grubbs second generation catalyst **3**, was less active as **7a** was obtained as the major isomer in a slow process (10 h versus 2 h; yield = 71%, ratio of **5a/6a/7a** = 19/5/76) (Table 1, entry 6). It is worth noting that no reaction was observed in the absence of catalyst.

It was observed that the regioselectivity of the hydro-silylation is dependent on the conversion rates and the reaction times. For example, when the reaction in the presence of **1** was stopped after 45 min, the conversion

(8) Product ratio was established by GC–MS from crude reaction sample.

SCHEME 4

TABLE 2^a

	silane	time (h)	yield (%)	ratio 5b/6/7	
1	<i>i</i> Pr ₃ SiH	b	24	0	— — —
2	<i>t</i> Bu(Me) ₂ SiH	c	12	75	30/0/70
3	Ph ₃ SiH	d	1.5	98	97/0/3
4	EtMe ₂ SiH	e	8	70	56/18/26
5	(EtO) ₃ SiH	f	1.5	76	87/7/7
6	Me ₂ (2-Thi)SiH	g	2	80	58/21/21

^a Conditions: **4** (1.08 mmol) in CH₂Cl₂ (2 mL), silane (1.5 equiv), **1** (5 mol %), reflux.

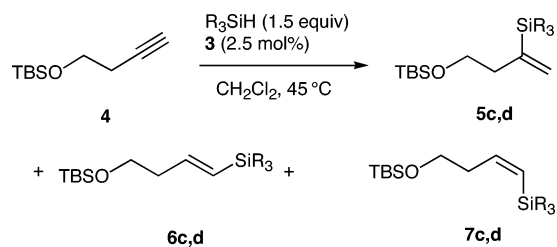
in **4** was 54% and the ratio of products **5a/6a/7a** was 98/0/2.⁸ When the reaction was achieved for 15 h, the ratio of **5a/6a/7a** decreased to 49/13/38.⁸ No further variation in the product distribution over this period of time was observed.

The best yield and α -selectivity were obtained with catalyst **1**. Consequently, this catalyst was selected for further studies. The effect of the hydrosilylating agent on the regiochemistry of the addition was examined under the conditions used previously, for example, catalyst **1** (2.5 mol %) and silanes (1.25 equiv), in refluxing CH₂Cl₂ (Scheme 4). The reactivities of electron-poor silanes, such as (EtO)₃SiH, and electron-rich alkyl- and arylsilanes were compared. Results are reported in Table 2.

No conversion of the alkyne **4** to vinylsilane was observed when tri-isopropylsilane (TIPSH) was used (Table 2, entry 1). *tert*-Butyldimethylsilane (TBSH) produced the (*Z*)-product **7c** as the major isomer in a slow reaction process (12 h; yield = 75%, ratio of **5c/6c/7c** =

(9) To a solution of **4** (200 mg, 1.08 mmol, 1 equiv) in degassed dichloromethane (2 mL) were added, under inert atmosphere at room temperature, TESH (0.26 mL, 1.62 mmol, 1.5 equiv) and **1** (44 mg, 54 μ mol, 5 mol %). The resulting mixture was stirred at reflux. After the total conversion of the starting material, the solution was concentrated under reduced pressure, and the crude product was purified by flash chromatography on silica gel using a gradient of eluent (pentane/ethyl acetate). Colorless oil (279 mg, 0.93 mmol, 86%, mixture of isomers **5a/6a/7a** 77/3/20); IR (neat): 2950, 1460, 1260, 1190 cm⁻¹. (**5a**): *R*_f 0.57 (pentane/ethyl acetate 95/1); ¹H NMR (300 MHz, CDCl₃) δ 5.61 (dt, *J* = 3.0, 1.5 Hz, 1H), 5.30 (d, *J* = 3.0 Hz, 1H), 3.58 (d, *J* = 7.9, 7.5 Hz, 2H), 2.34–2.26 (m, 2H), 0.86 (t, *J* = 7.9 Hz, 9H), 0.83 (s, 9H), 0.54 (q, *J* = 7.9 Hz, 6H), 0.00 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 145.4, 127.3, 63.0, 39.3, 25.9, 18.4, 7.3, 2.8, –5.2; MS (EI, 70 eV) *m/z*: 285 (M⁺ – 15), 271 (M⁺ – 29), 243 (21), 215 (26), 189 (55), 161 (100), 115 (64), 87 (46). (**6a**): *R*_f 0.57 (pentane/ethyl acetate 95/1); ¹H NMR (300 MHz, CDCl₃) δ 6.58 (dt, *J* = 18.4, 6.8 Hz, 1H), 5.57 (dt, *J* = 18.8, 1.5 Hz, 1H), 3.61 (t, *J* = 6.4 Hz, 2H), 2.29 (qd, *J* = 6.4, 1.5 Hz, 2H), 0.87 (t, *J* = 8.0 Hz, 9H), 0.84 (s, 9H), 0.54 (q, *J* = 7.9 Hz, 6H), 0.00 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 144.9, 128.2, 62.7, 40.6, 25.9, 18.3, 7.4, 3.4, –5.3; MS (EI, 70 eV) *m/z*: 285 (M⁺ – 15), 271 (M⁺ – 29), 243 (58), 161 (45), 115 (100), 87 (73). (**7a**): *R*_f 0.57 (pentane/ethyl acetate 95/1); ¹H NMR (300 MHz, CDCl₃) δ 6.33 (dt, *J* = 14.3, 7.2 Hz, 1H), 5.45 (dt, *J* = 14.3, 1.1 Hz, 1H), 3.59 (t, *J* = 6.8 Hz, 2H), 2.28 (tdd, *J* = 7.2, 6.8, 1.5 Hz, 2H), 0.89 (t, *J* = 7.9 Hz, 9H), 0.84 (s, 9H), 0.56 (q, *J* = 7.9 Hz, 6H), 0.00 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 146.0, 127.3, 63.0, 37.7, 25.9, 18.4, 7.5, 4.6, –5.3; MS (EI, 70 eV) *m/z*: 285 (M⁺ – 15), 271 (M⁺ – 29, 79), 243 (37), 161 (35), 147 (25), 133 (25), 115 (100), 87 (70), 73 (86), 59 (34).

SCHEME 5

TABLE 3^a

R ₃ SiH	time (h)	yield (%)	ratio 5/6/7
1 <i>t</i> BuMe ₂ SiH c	12	51	48/1/51
2 Ph ₃ SiH d	8	80	55/0/45

^a Conditions: **4** (1.08 mmol) in CH₂Cl₂ (2 mL), silane (1.5 equiv), **3** (5 mol %), reflux.

30/0/70) (Table 2, entry 2). In all other experiments a clear preference for α -selective addition was observed (Table 2, entries 3–6). Triphenylsilane produced almost quantitatively the desired α -vinylsilane **5d** (yield = 98%, ratio of **5d/6d/7d** = 97/0/3) (Table 2, entry 3).¹⁰ The addition of dimethylethylsilane to the alkyne **4** was shown to be less selective (yield = 70%, ratio of **5e/6e/7e** = 56/18/26, Table 2, entry 4). The hydrosilylation of **4** with triethoxysilane also yielded the α -product with good selectivity (yield = 76%, ratio of **5f/6f/7f** = 86/7/7, Table 2, entry 5). Finally, dimethyl-(2-thiyl)-silane (Me₂(2-Thi)-SiH)¹¹ afforded a roughly 3:1:1 mixture of isomers in 80% yield (ratio of **5g/6g/7g** = 58/21/21) (Table 2, entry 6). Longer reaction times correlated with the decrease of the α -adduct **5** in favor of the β -(*Z*)-product **7**.

It is interesting to compare the selectivity of the hydrosilylation of the alkyne **4** with different silanes in the presence of catalyst **3** (Table 3). Contrary to reactions with **1**, this catalyst afforded a roughly 1:1 mixture of α - and β -isomers **5** and **7** in a slow reaction process when TBSH or Ph₃SiH was used (Scheme 5).

The addition of triphenylsilane to terminal alkynes **8–11** was further investigated in the presence of catalyst **1** (2.5 mol %) in refluxing CH₂Cl₂ (Scheme 6). Under these conditions, the reaction afforded almost exclusively the desired α -products **12–15**. The reaction is chemoselective and can be performed in the presence of enones (Scheme 6, eq 4) without reducing either the olefin or the carbonyl function.^{5b} In addition, it is compatible with the presence of esters (Scheme 6, eqs 2 and 3).

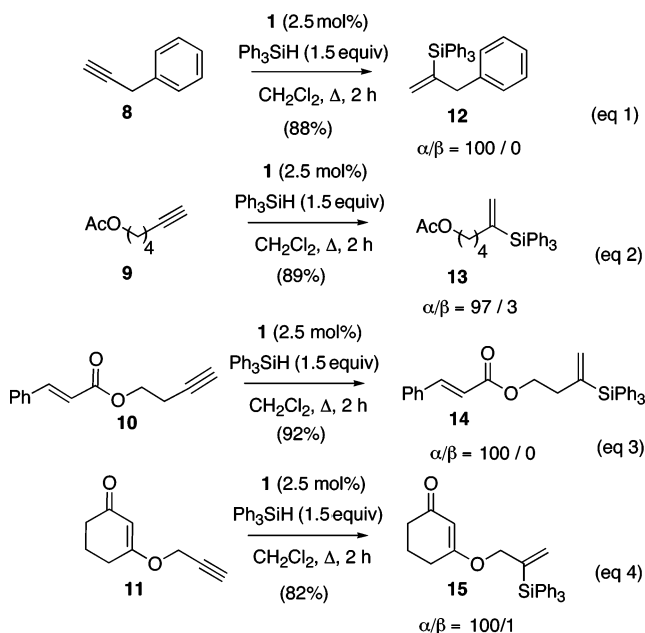
The mechanism of the hydrosilylation of alkynes catalyzed by ruthenium alkylidene complexes is the subject of speculation. Unfortunately, we were unable to characterize any of the intermediates by different NMR techniques. Presently, we can only speculate on the plausible intermediates involved in the process. The catalyst can mediate the hydrosilylation of alkynes by a modified Harrod–Chalk mechanism¹² or by an analogous process described recently by Markó and co-workers for

(10) No variation in the regioselectivity was observed in this hydrosilylation even after 15 h.

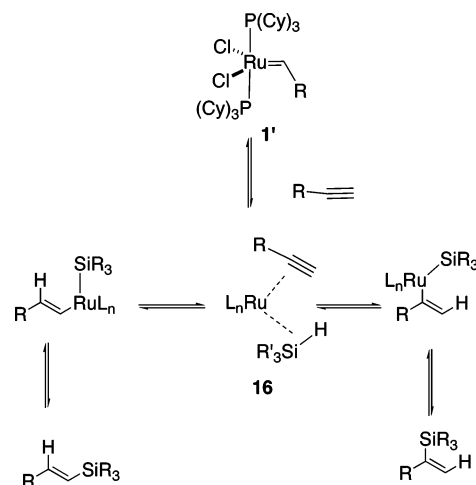
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SCHEME 6



SCHEME 7



carbene–Pt complexes.¹³ The departure of the P(Cy)₃ ligand from the Ru–alkylidene complex can generate a transient 16-electron metal complex (RuL_n), which may react simultaneously with the alkyne and with the silane to produce intermediate **16** (Scheme 7). The addition of the Ru–H bond to the alkyne, followed by reductive elimination of the metal, are probably the elementary steps involved in the catalytic cycle. The pronounced α -selectivity can be the result of stereoelectronic factors when the reaction is run under kinetic conditions. When the mixture is allowed to equilibrate, steric factors may compensate for the stereoelectronic factors, thus increasing the amount of the β -products.

Supporting Information Available: Experimental procedures for the hydrosilylation reaction, characterization of the products, and ¹H and ¹³C NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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