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Ruthenium-catalyzed hydrosilylation of terminal alkynes: stereodivergent synthesis of (*E*)- and (*Z*)-alkenylsilanes

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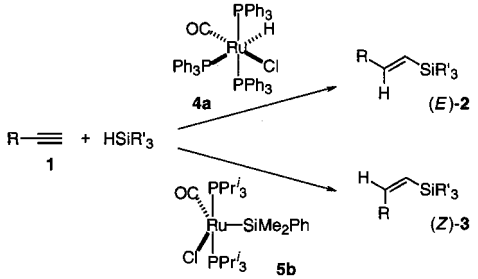
Abstract

Stereodivergent hydrosilylation of terminal alkynes (RC≡CH; R = Ph, *p*-tolyl, Cy, *n*-hexyl) with hydrosilanes ($HSiMe_2Ar$; Ar=Ph, 3,5-$(CF_3)_2C_6H_3$, 4-$CF_3C_6H_4$, 4-$MeOC_6H_4$) has been examined using ruthenium catalysts. (*E*)-selective reactions giving (*E*)-RCH=CHSiMe$_2$Ar proceed in over 99% selectivity in the presence of a catalytic amount of $RuHCl(CO)(PPh_3)_3$. On the other hand, (*Z*)-selective reactions are successfully conducted in 91–99% selectivity by using $Ru(SiMe_2Ph)Cl(CO)(PPr^i_3)_2$ as the catalyst. All reactions readily proceed at room temperature in high yields. (*E*)- and (*Z*)-styrylsilanes having a $SiMe_2[C_6H_3$–3,5-$(CF_3)_2]$ group serve as good cross-coupling reagents with *p*-iodotoluene in the presence of tetrabutylammonium fluoride and $[Pd(\eta^3$-allyl)Cl$]_2$ catalyst. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Hydrosilylation; Alkynes; Ruthenium catalysts; Stereodivergent synthesis; Alkenylsilanes

1. Introduction

Transition metal-catalyzed hydrosilylation of terminal alkynes is one of the simplest and efficient ways of synthesizing alkenylsilanes [1]. While the reaction generally adopts a *syn*-addition process to afford (*E*)-alkenylsilanes, *anti*-addition giving (*Z*)-alkenylsilanes has also been documented [2]. Considering great utility of alkenylsilanes in organic synthesis [3], it is desirable to establish the catalytic systems which enable to prepare both stereoisomers independently. Such stereodivergent hydrosilylation of terminal alkynes has been documented with rhodium catalysts [4,5]. However, since the mechanistic reasons for variation of stereoselectivity dependent on reaction conditions have not been well-understood, exact control of the stereochemistry of catalytic hydrosilylation is still a difficult task in most cases. We herein report that both (*E*)- and (*Z*)-isomers of alkenylsilane can be prepared in high selectivity by proper choice of ruthenium catalysts (Eq. (1)).



(1)

The present study has been conducted on the basis of recent our mechanistic findings [6,7]. We have succeeded in identifying almost complete array of elementary processes that are responsible for ruthenium-catalyzed hydrosilylation of 1-trimethylsilyl-1-buten-3-yne [6]. The essence of the results can be illustrated as shown in Scheme 1 using terminal alkyne (**1**) as a substrate. The mechanism consists of two catalytic cycles A and B, which are connected with each other by processes (v) and (vi), respectively. Cycle A starting from alkyne-insertion into a ruthenium hydride (**4**) forms (*E*)-alkenylsilane (**2**), whereas cycle B involving a silylruthenium intermediate (**5**) affords (*Z*)-alkenylsilane (**3**). The latter cycle invokes essentially the same

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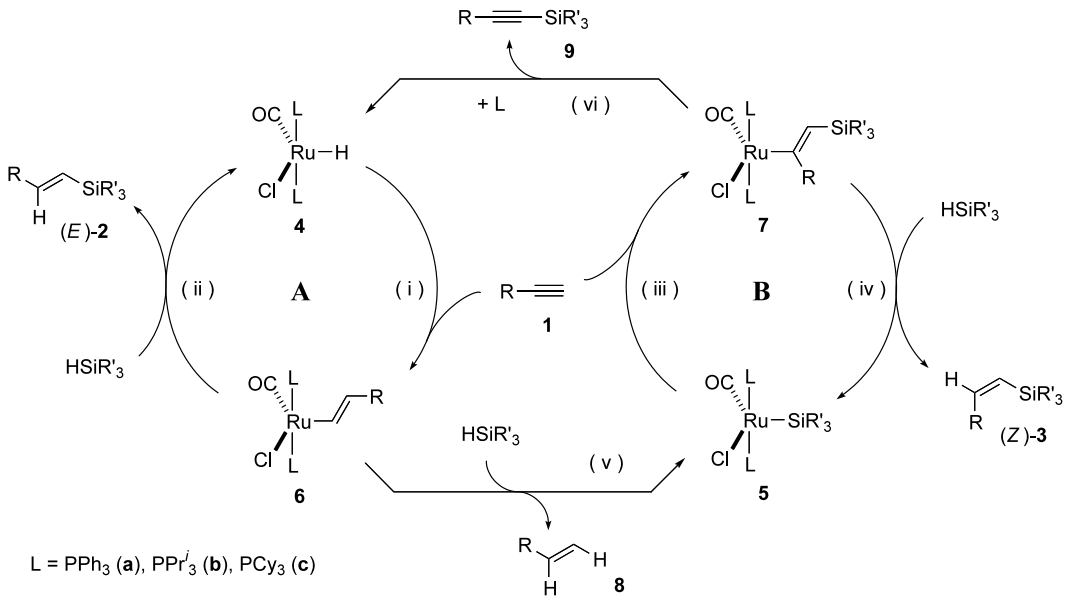
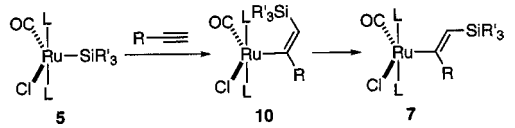


Scheme 1. Mechanisms of (*E*)- and (*Z*)-selective hydrosilylation of terminal alkynes catalyzed by ruthenium complexes [6].

elementary processes as previously proposed for rhodium- and iridium-catalyzed systems [8] and later for ruthenium-catalyzed reactions [9,10]. Thus the reaction of **5** with alkyne forms a formal *trans*-insertion complex **7**, and this has been shown to proceed via a common *cis*-insertion process, followed by cis to trans isomerization of the resulting β-silylalkenyl ligand (Eq. (2)) [8,10]. Reflecting the geometry of alkenyl ligand in **7**, the hydrosilylation product **3** has the (*Z*)-configuration.



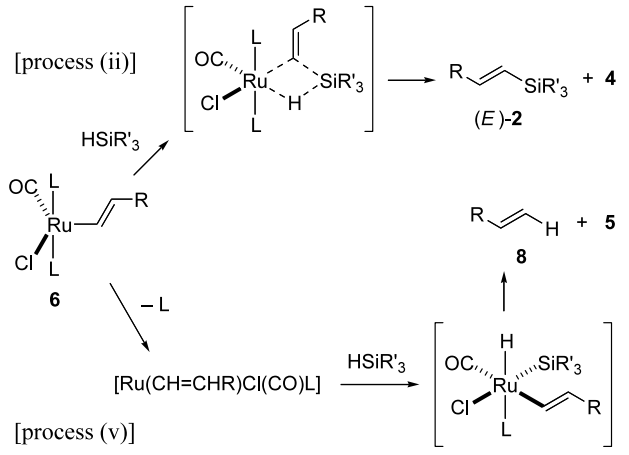
(2)

Thus far most of the rhodium- and ruthenium-catalyzed reactions have been discussed only on the basis of the mechanism corresponding to cycle B, where the (*E*)- and (*Z*)-alkenylsilanes are afforded by the reactions of *cis*- and *trans*-β-silylalkenyl complexes (e.g. **10** and **7** in Eq. (2)) with hydrosilane, respectively [8–10]. On the other hand, Scheme 1 clearly shows the possibility of (*E*)-selective reaction according to cycle A. Therefore, we have considered that (*E*)- and (*Z*)-selective hydrosilylation reactions may be accomplished by selective operation of cycle A and B, respectively. Since the ruthenium-catalyzed hydrosilylation of terminal alkynes so far reported is entirely (*Z*)-selective [9–11], we first examined if the (*E*)-selective cycle A is revolved selectively.

2. Results and discussion

2.1. (E)-Selective hydrosilylation catalyzed by $RuHCl(CO)(PPh_3)_3$ (4a)

Of the elementary processes in cycle A, insertion of terminal alkyne into **4** (process (i)) is known to proceed rapidly at room temperature, giving 1-alkenyl complex **6**, exclusively [12]. On the other hand, the subsequent reaction of **6** with hydrosilane follows two courses [6,7]. When C–Si bond formation giving (*E*)-alkenylsilane **2** is operative (process (ii)), the resulting **4** resumes cycle A. On the other hand, when C–H bond formation of process (v) takes place, the catalytic cycle shifts from A



Scheme 2. Two types of processes for the reaction of alkenylruthenium **6** with hydrosilane [7].

Table 1
(*E*)-Selective hydrosilylation of terminal alkynes catalyzed by $RuHCl(CO)(PPh_3)_3$ (**4a**) [a]

Run	RC≡CH (**1**)	$HSiR'_3$	Time (h)	(*E*)-**2**/(*Z*)-**3** ratio [b]	Yield (%) [b] (**2**+**3**)
1	PhC≡CH	$HSiMe_2Ph$	10	99/1	94
2 [c]	PhC≡CH	$HSiMe_2Ph$	1	>99/1	100
3	PhC≡CH	$HSiMe_2[C_6H_3$–3,5-$(CF_3)_2]$	1	>99/1	98
4	PhC≡CH	$HSiMe_2(C_6H_4$–4-$CF_3)$	2	>99/1	98
5[c]	PhC≡CH	$HSiMe_2(C_6H_4$–4-OMe)	1	99/1	97
6	PhC≡CH	$HSiFPh_2$	0.5	99/1	97
7 [c]	PhC≡CH	$HSi(OEt)_3$	4	95/5	96
8	*p*-TolC≡CH	$HSiMe_2[C_6H_3$–3,5-$(CF_3)_2]$	1	>99/1	100
9	CyC≡CH	$HSiMe_2[C_6H_3$–3,5-$(CF_3)_2]$	2	99/1	94
10 [c]	*n*-HexC≡CH	$HSiMe_2Ph$	2	99/1	80 [d]

[a] All reactions were run at room temperature in CH_2Cl_2. Unless otherwise noted, initial concentration of the components are as follows: $[\mathbf{4a}]_0 = 10$ mM, $[RC{\equiv}CH]_0 = 0.20$ M, $[HSiR'_3]_0 = 0.20$ M.
[b] Determined by GLC using anisole as an internal standard. Yield is based on the amount of alkyne employed.
[c] The reaction was performed with a 5-fold excess amount of hydrosilane ($[HSiR'_3]_0 = 1.0$ M) relative to alkyne.
[d] The regioisomer *n*-Hex$(PhMe_2Si)C{=}CH_2$ was also obtained in 14% yield.

to B. Accordingly, selective operation of cycle A may be achieved by course-control of the reaction of **6** with hydrosilane.

We have recently found that PPh_3-coordinated **6**, $Ru(CH{=}CHR)Cl(CO)(PPh_3)_2$ (R = Ph, Bu^t, CH=$CHSiMe_3$) reacts with $HSiMe_2Ph$ mainly by process (ii) [7]. It has been also confirmed by kinetic examinations that process (ii) and the competing process (v) adopt completely different mechanisms from each other (Scheme 2). Thus, process (ii) proceeds via direct association of **6** with hydrosilane without dissociation of phosphine ligand (L). In contrast, process (v) involves prior dissociation of L, which is followed by the sequence of oxidative addition of hydrosilane and reductive elimination of C–H coupling product **8**. Therefore, we chose $RuHCl(CO)(PPh_3)_3$ (**4a**) having three PPh_3 ligands as the catalyst. We have anticipated that free PPh_3, which is released upon the alkyne-insertion into **4a** (process (i)), may effectively suppress process (v) to cause highly selective cycle A.

Table 1 lists the results. All reactions were examined in CH_2Cl_2 at room temperature using 5 mol% of **4a**. The reaction of phenylacetylene with an equimolar amount of $HSiMe_2Ph$ was completed in 10 h to give (*E*)- and (*Z*)-PhCH=CHSiMe_2Ph in 93 and 1% yield (GLC), respectively (run 1). Also detected in the catalytic solution were $PhCH{=}CH_2$ (4%) and PhC≡CSiMe_2-Ph (2%), which correspond to **8** and **9** in Scheme 1, respectively. The reaction was significantly accelerated by the use of $HSiMe_2Ph$ in excess to phenylacetylene (run 2). Moreover, the by-production of styrene and silylacetylene was effectively suppressed under this condition. Consequently, (*E*)-PhCH=CHSiMe_2Ph was obtained in almost quantitative yield.

(*E*)-Selective hydrosilylation of phenylacetylene was also successful with various hydrosilanes, giving the corresponding (*E*)-styrylsilanes in high selectivity (runs 3–6). There is a tendency that the more electron-withdrawing substituent on silicon leads to the higher reactivity and selectivity. $HSiMe_2[C_6H_3$–3,5-$(CF_3)_2]$ was particularly efficient. Thus the reaction was completed within 1 h in almost perfect selectivity, using an equimolar amount of the hydrosilane (run 3). Similarly, *p*-tolylacetylene and cyclohexylacetylene were hydrosilylated in over 99% (*E*)-selectivity (runs 8, 9). The reaction of 1-octyne with $HSiMe_2Ph$ was also highly stereoselective (run 10), though the regioisomer *n*-Hex-$(PhMe_2Si)C{=}CH_2$ (14%) was formed as a by-product.

2.2. (*Z*)-Selective hydrosilylation catalyzed by silylruthenium complexes

We next examined (*Z*)-selective hydrosilylation according to cycle B (Table 2). Since the key intermediate in this cycle is silyl complex **5**, $Ru(SiMe_2Ph)Cl(CO)$-$(PPh_3)_2$ (**5a**) was isolated and employed in the catalytic hydrosilylation of phenylacetylene with $HSiMe_2Ph$. The reaction smoothly proceeded at room temperature to give (*Z*)-PhCH=CHSiMe_2Ph in 84% selectivity (run 1). The selectivity rose to 91% in the presence of an excess amount of phenylacetylene to $HSiMe_2Ph$ (run 2) [13], while considerable amounts of $PhCH{=}CH_2$ (6%) and PhC≡CSiMe_2Ph (6%) were formed in addition to styrylsilanes.

A further improvement in the product selectivity was achieved by using $Ru(SiMe_2Ph)Cl(CO)(PPr^i_3)_2$ (**5b**) instead of **5a**. This complex exhibited extremely high catalytic activity. Thus the reaction of phenylacetylene with $HSiMe_2Ph$ was completed within a few minutes at room temperature to produce 98% purity of (*Z*)-PhCH=CHSiMe_2Ph (run 3). In this run, the amounts of styrene and silylacetylene were negligible (each $< 1\%$).

Under similar conditions, (*Z*)-selective hydrosilylation could be successfully performed with a range of

hydrosilanes and terminal alkynes in high selectivity (>91%) (runs 4–6 and 8–11). The only exception of hydrosilanes tested was $HSiFPh_2$, which afforded (*Z*)-styrylsilane in 82% selectivity (run 7).

The catalytic performance of **5b** is clearly much higher than the other ruthenium catalysts so far reported [9,11]. The highly reactive nature of **5b** was further confirmed by stoichiometric reactions. Thus the treatment of **5b** with five molar amounts of phenylacetylene in $CDCl_3$ at room temperature instantly gave a β-silylalkenyl complex $Ru[C(Ph)((CHSiMe_2Ph]Cl(CO)(PPr^i_3)_2$ (**7b**). Addition of $HSiMe_2Ph$ to this solution led to rapid formation of $PhCH{=}CHSiMe_2Ph$ ((*E*)/(*Z*) = 6/94) in 87% yield.

2.3. (*Z*)-Selective hydrosilylation using hydridoruthenium precursors

We have described in Section 2.1 that the (*E*)-selective cycle A in Scheme 1 can be conducted in high selectivity by using **4a** coordinated with PPh_3 as the catalyst. On the other hand, it has been previously reported that $RuHCl(CO)(PPr^i_3)_2$ (**4b**) having PPr^i_3 ligands causes (*Z*)-selective hydrosilylation of phenylacetylene [9]. We next examined the difference between these hydride catalysts.

Table 3 lists the results of catalytic hydrosilylation of phenylacetylene using **4b** or $RuHCl(CO)(PCy_3)_2$ (**4c**) as a catalyst precursor. All reactions were run at room temperature. In agreement with the previous report [9], **4b** afforded (*Z*)-styrylsilane in high selectivity (run 1), while the catalytic activity was much lower than that of the silyl complex **5b**. The PCy_3 complex **4c** provided a comparable result (run 2). The remaining part of product was styrene in both systems. The (*Z*)-selective reaction was also successful with $HSiMe_2[C_6H_3$–3,5-$(CF_3)_2]$ and $HSiMe_2(C_6H_4$–4-$CF_3)$ instead of $HSiMe_2Ph$ (runs 3 and 4), whereas the reaction with $HSiMe_2(C_6H_4$–4-OMe) was less selective (run 5).

Similarly to **4a**, complex **4b** is known to undergo rapid insertion of phenylacetylene at room temperature [12c]. It has been also reported that the resulting $Ru(CH{=}CHPh)Cl(CO)(PPr^i_3)_2$ (**6b**) reacts with $HSiEt_3$ to give (*E*)-$PhCH{=}CHSiEt_3$ and **4b** [9]. These reactions correspond to the elementary process (i) and (ii) of cycle A, respectively. However, despite our repeated trials using several kinds of hydrosilanes, the latter reaction could not take place, at least under the present

Table 2
(*Z*)-selective hydrosilylation of terminal alkynes catalyzed by silylruthenium complexes [a]

Run	Catalyst [b]	RC≡CH (**1**)	$HSiR'_3$	Time (h)	(*E*)-**2**/(*Z*)-**3** ratio [c]	Yield (%) [c] (**2**+**3**)
1 [d]	**5a**	PhC≡CH	$HSiMe_2Ph$	1	16/84	93
2	**5a**	PhC≡CH	$HSiMe_2Ph$	8	9/91	88
3	**5b**	PhC≡CH	$HSiMe_2Ph$	Rapid	2/98	98
4	**5b**	PhC≡CH	$HSiMe_2[C_6H_3$–3,5-$(CF_3)_2]$	Rapid	2/98	98
5	**5b**	PhC≡CH	$HSiMe_2(C_6H_4$–4-$CF_3)$	Rapid	2/98	98
6	**5b**	PhC≡CH	$HSiMe_2(C_6H_4$–4-OMe)	Rapid	3/97	99
7	**5b**	PhC≡CH	$HSiFPh_2$	Rapid	18/82	98
8	**5b**	PhC≡CH	$HSi(OEt)_3$	3	4/96	88
9	**5b**	*p*-TolC≡CH	$HSiMe_2Ph$	Rapid	1/99	93
10	**5b**	CyC≡CH	$HSiMe_2Ph$	0.5	5/95	80
11	**5b**	*n*-HexC≡CH	$HSiMe_2Ph$	Rapid	9/91	98

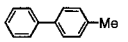
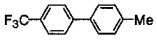
[a] All reactions were run at room temperature in CH_2Cl_2. Unless otherwise noted, initial concentration of the components are as follows: $[catalyst]_0 = 10$ mM, $[RC{\equiv}CH]_0 = 1.0$ M, $[HSiR'_3]_0 = 0.20$ M.
[b] **5a**: $Ru(SiMe_2Ph)Cl(CO)(PPh_3)_2$; **5b**: $Ru(SiMe_2Ph)Cl(CO)(PPr^i_3)_2$.
[c] Determined by GLC using anisole as an internal standard.
[d] Initial concentration: $[catalyst]_0 = 10$ mM, $[RC{\equiv}CH]_0 = [HSiR'_3]_0 = 0.20$ M.

Table 3
(*Z*)-Selective hydrosilylation of phenylacetylene catalyzed by hydridoruthenium complexes [a]

Run	Catalyst [b]	$HSiR'_3$	Time (h)	(*E*)-**2**/(*Z*)-**3** ratio [c]	Yield (%) [c] (**2**+**3**)
1	**4b**	$HSiMe_2Ph$	2	3/97	98
2	**4c**	$HSiMe_2Ph$	2	4/96	97
3	**4c**	$HSiMe_2[C_6H_3$–3,5-$(CF_3)_2]$	2	3/97	99
4	**4c**	$HSiMe_2(C_6H_4$–4-$CF_3)$	2	4/96	96
5	**4c**	$HSiMe_2(C_6H_4$–4-OMe)	3	12/88	96

[a] All reactions were run at room temperature in CH_2Cl_2. Initial concentration: $[catalyst]_0 = 10$ mM, $[PhC{\equiv}CH]_0 = 0.20$ M, $[HSiR'_3]_0 = 0.20$ M.
[b] **4b**: $RuHCl(CO)(PPr^i_3)_2$; **4c**: $RuHCl(CO)(PCy_3)_2$.
[c] Determined by GLC using anisole as an internal standard.

Table 4
Palladium-catalyzed cross-coupling between styrylsilanes and *p*-iodotoluene [a]

Run	Styrylsilane (*E*/*Z*)[c]	Yield of **11**[b] (*E*/*Z*)[c]	Other product (yield)[b]
1	PhCH=CHSiFPh$_2$ (99/1)	82% (98/2)	 (16%)
2	PhCH=CHSiMe$_2$(C$_6$H$_4$-4-CF$_3$) (99/1)	74% (99/1)	 (5%)
3	PhCH=CHSiMe$_2${C$_6$H$_3$-3,5-(CF$_3$)$_2$} (99/1)	83% (99/1)	—
4	PhCH=CHSiMe$_2${C$_6$H$_3$-3,5-(CF$_3$)$_2$} (3/97)	89% (3/97)	—

[a] All reactions were carried out using 2.5 mol% of [(η^3-allyl)PdCl]$_2$ in THF at room temperature for 1 h. Initial concentration: [*p*-iodotoluene]$_0$ = 0.20 M, [styrylsilane]$_0$ = 0.24 M, [TBAF]$_0$ = 0.24 M.
[b] Isolated yield.
[c] Determined by ^{1}H-NMR spectroscopy.

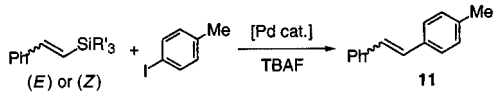
catalytic condition (i.e. at room temperature) [14]. For example, treatment of **6b** with HSiMe$_2$Ph (20 molar) in CD_2Cl_2 at room temperature afforded no trace of styrylsilane as confirmed by ^{1}H-NMR spectroscopy and GC–MS, but resulted in gradual formation of a small amount of styrene (< 10%) over several days instead.

We have recently shown that the reaction of Ru(CH=CHPh)Cl(CO)(PPh$_3$)$_2$ (**6a**) with hydrosilane giving (*E*)-styrylsilane (process (ii)) proceeds via direct association of hydrosilane with **6a** (see Scheme 2) [7]. Reflecting this mechanistic feature, the reactivity is highly sensitive to steric factors. For example, HSiMe$_2$Ph is about 17 times more reactive than HSiMePh$_2$, and HSiPh$_3$ is much less reactive than these two hydrosilanes. Therefore, it seems reasonable that the extremely poor reactivity of **6b** towards (*E*)-styrylsilane formation (process (ii) in Scheme 1) is mainly due to steric congestion around the ruthenium center, which is protected by two bulky P*Pr*$^i_3$ ligands [15,16].

Clearly, **6b** is nonproductive in the (*E*)-selective cycle A, whereas **6a** is sufficiently reactive in this cycle. Thus the strikingly different property of **4a** and **4b** in the catalytic hydrosilylation is attributed principally to the different reactivity of these alkenyl species towards C–Si bond formation (process (ii)).

2.4. Application to cross-coupling reaction

Finally, (*E*)- and (*Z*)-styrylsilanes thus prepared were subjected to the palladium-catalyzed cross-coupling reaction with *p*-iodotoluene in the presence of tetrabutylammonium fluoride (TBAF) (Eq. (3)) [17].



(3)

The results are listed in Table 4. Although the present hydrosilylation reactions preferably proceed with aryl-substituted hydrosilanes, the alkenylsilanes originally employed in the cross-coupling reactions are those without aryl-substituents on silicon, so as to avoid a side reaction giving aryl–aryl coupling products. Actually, the reaction of (*E*)-PhCH=CHSiFPh$_2$ afforded 16% yield of 4-methylbiphenyl in addition to desired (*E*)-4-methylstilbene ((*E*)-**11**) (run 1). On the other hand, introduction of CF_3 group(s) into the phenyl group on silicon was found to effectively suppress the aryl–aryl coupling (runs 2–4). Especially, the styrylsilane synthesized with HSiMe$_2$[C$_6$H$_3$–3,5-(CF$_3$)$_2$] gave only desired product ((*E*)- or (*Z*)-**11**) in high yield with retention of the starting geometry (runs 3 and 4).

3. Conclusion

We have demonstrated in this paper that (*E*)- and (*Z*)-selective hydrosilylation of terminal alkynes can be precisely performed by following cycle A and B in Scheme 1, respectively. Cycle A is operative in almost perfect selectivity using RuHCl(CO)(PPh$_3$)$_3$ (**4a**) as the catalyst, whereas cycle B proceeds very rapidly in the presence of a catalytic amount of Ru(SiMe$_2$Ph)Cl(CO)(PP*r*$^i_3$)$_2$ (**5b**). The (*E*)- and (*Z*)-styrylsilanes thus prepared using HSiMe$_2$[C$_6$H$_3$–3,5-(CF$_3$)$_2$] can be utilized as good reagents for the palladium-catalyzed cross-coupling with *p*-iodotoluene in the presence of tetrabutylammonium fluoride. Further application of these highly efficient hydrosilylation systems will be reported in due course.

4. Experimental

4.1. General remarks

All manipulations were performed under a nitrogen atmosphere using conventional Schlenk techniques. Nitrogen gas was purified by passing through a column of P_2O_5 (Merck, SICAPENT). NMR spectra were recorded on a Varian Mercury 300 (^{1}H-NMR, 300.11 MHz; ^{13}C-NMR, 75.46 MHz; ^{31}P-NMR, 121.49 MHz) spectrometer. Chemical shifts are reported in δ (ppm), referenced to the ^{1}H (of residual protons) and ^{13}C signals of deuterated solvents or to the ^{31}P signal of external 85% H_3PO_4. Mass spectra were measured with a Shimadzu QP-5000 GC-mass spectrometer (EI, 70 eV). GLC analysis was performed on a Shimadzu GC-14B instrument equipped with a FID detector and a

capillary column CBP-1 (25 m × 0.25 mm). Analytical TLC was carried out on Merck TLC aluminum sheets precoated with silica gel 60 F_{254}. Flash column chromatography was performed using Merck silica gel 60 (230–400 mesh).

CH_2Cl_2 was dried over CaH_2. THF was dried over sodium benzophenone ketyl. These solvents were distilled and stored over activated molecular sieves (MS4A) under a nitrogen atmosphere. Liquid alkynes and hydrosilanes were degassed by freeze–pump–thaw cycles prior to use. $RuHCl(CO)(PPh_3)_3$ (**4a**) [18], $RuHCl(CO)(PPr^i_3)_2$ (**4b**) [19], $RuHCl(CO)(PCy_3)_2$ (**4c**) [20], $Ru(SiMe_2Ph)Cl(CO)(PPh_3)_2$ (**5a**) [6], and $RuCl_2(CO)(PPr^i_3)_2$ [21] were synthesized according to the literatures. All other chemicals were obtained from commercial sources and used without further purification.

4.2. Preparation of $Ru(SiMe_2Ph)Cl(CO)(PPr^i_3)_2$ (**5b**)

To a solution of $RuCl_2(CO)(PPr^i_3)_2$ (100 mg, 0.192 mmol) in THF (3.2 ml) was added dropwise a 1.0 M solution of $Me_2PhSiLi$ in THF [22] (0.19 ml, 0.19 mmol) at 0 °C. The resulting orange suspension was concentrated to dryness by pumping to give an orange oily material, which was extracted repeatedly with pentane (5 × 2 ml). The combined extracts were concentrated to ca. 2 ml and allowed to stand at −70 °C overnight, giving an orange crystalline solid, which was collected by filtration, washed with cold pentane, and dried under vacuum (50 mg, 43%). ^{1}H-NMR (toluene-d_8): δ 7.90–7.87 (m, 2H, Ph), 7.21–7.08 (m, 3H, Ph), 2.57–2.42 (m, 6H, PC*H*), 1.21 (virtual triplet of doublet, $J = 7.0$ and 5.7 Hz, 18H, PCHCH_3), 1.12 (virtual triplet of doublet, $J = 7.0$ and 5.7 Hz, 18H, PCHCH_3), 0.95 (s, 6H, $SiMe_2$). ^{13}C{^{1}H}-NMR (toluene-d_8): δ 201.6 (t, $^2J_{PC} = 13$ Hz, CO), 149.3, 137.5, 134.9, 127.4, 24.5 (virtual triplet, $J = 9$ Hz, P*C*HCH$_3$), 20.7 (s, PCH*C*H$_3$), 10.3 (s, $SiMe_2$). ^{31}P{^{1}H}-NMR (toluene-d_8): δ 38.4 (s). Anal. Calc. for $C_{27}H_{53}ClOP_2RuSi$: C, 52.28; H, 8.61. Found: C, 52.07; H, 8.58%.

4.3. Catalytic hydrosilylation

A typical procedure for (*E*)-selective reaction (run 3 in Table 1) is as follows. To a Schlenk tube containing $RuHCl(CO)(PPh_3)_3$ (**4a**) (9.4 mg, 9.9 μmol) was added a solution of PhC≡CH (20.3 mg, 0.199 mmol), $HSiMe_2[C_6H_3$–3,5-$(CF_3)_2]$ (54.4 mg, 0.200 mmol), and anisole (7.6 mg, 0.070 mmol; internal standard for GLC analysis) in CH_2Cl_2 (1.0 ml) under a nitrogen atmosphere. The mixture was stirred at room temperature (r.t.) for 1 h. GLC analysis revealed the formation of (*E*)-PhCH=CHSi$Me_2[C_6H_3$–3,5-$(CF_3)_2]$ in 98% yield, along with small amounts of (*Z*)-isomer (< 1%), styrene (2%), and PhC≡CSi$Me_2[C_6H_3$–3,5-$(CF_3)_2]$ (< 1%). The solvent was removed by pumping, and the resulting orange residue was purified by flash column chromatography (SiO_2, hexane) to give a colorless oil, which was analytically pure (68 mg, 91% yield).

The (*Z*)-selective reaction (run 4 in Table 2) was similarly conducted using $Ru(SiMe_2Ph)Cl(CO)(PPr^i_3)_2$ (**5b**) in place of **4a**. (*Z*)-PhCH=CHSi$Me_2[C_6H_3$–3,5-$(CF_3)_2]$ was formed in 96% yield (GLC; 87% isolated), along with (*E*)-isomer (2%), styrene (< 1%), and PhC≡CSi$Me_2[C_6H_3$–3,5-$(CF_3)_2]$ (< 1%).

Identification data of alkenylsilanes prepared in this study are as follows.

4.3.1. (E)-PhCH=CHSiMe$_2$Ph

^{1}H-NMR ($CDCl_3$): δ 7.59–7.21 (m, 10H, Ph), 6.94 (d, $J = 19.0$ Hz, 1H, PhCH=), 6.59 (d, $J = 19.0$ Hz, 1H, =CHSi), 0.44 (s, 6H, $SiMe_2$). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 145.2, 138.5, 138.1, 133.9, 129.0, 128.5, 128.1, 127.8, 127.1, 126.5, −2.5. MS, *m*/*z* (relative intensity, %): 238[M^+, 25], 223 (45), 146 (16), 145 (100), 135 (10), 121 (35), 105 (20), 59 (12), 53 (16), 51 (10), 43 (52). Anal. Calc. for $C_{16}H_{18}Si$: C, 80.61; H, 7.61. Found: C, 80.73; H, 7.39%.

4.3.2. (E)-PhCH=CHSiMe$_2$[C$_6$H$_3$–3,5-(CF$_3$)$_2$]

^{1}H-NMR ($CDCl_3$): δ 7.95 (br, 2H, Ar), 7.86 (br, 1H, Ar), 7.48–7.45 (m, 2H, Ar), 7.39–7.27 (m, 3H, Ar), 6.99 (d, $J = 19.2$ Hz, PhCH=), 6.52 (d, $J = 19.2$ Hz, =CHSi), 0.51 (s, 6H, $SiMe_2$). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 146.9, 142.4, 137.6, 133.6, 130.8 (q, $J_{FC} = 33$ Hz), 128.7, 128.7, 126.6, 124.4, 123.6 (q, $J_{FC} = 273$ Hz), 122.9 (septet, $J_{FC} = 3$ Hz), −2.8. MS, *m*/*z* (relative intensity, %): 374 [M^+, 10], 279 (13), 278 (77), 277 (14), 257 (23), 227 (12), 209 (24), 195 (16), 145 (100), 81 (17), 77 (82), 59 (17), 51 (18), 47 (15), 43 (28). Anal. Calc. for $C_{18}H_{16}F_6Si$: C, 57.75; H, 4.31. Found: C, 57.83; H, 4.28%.

4.3.3. (E)-PhCH=CHSiMe$_2$(C$_6$H$_4$–4-CF$_3$)

^{1}H-NMR ($CDCl_3$): δ 7.70–7.59 (m, 4H, Ar), 7.47–7.26 (m, 5H, Ar), 6.96 (d, $J = 19.2$ Hz, 1H, PhCH=), 6.55 (d, $J = 19.2$ Hz, 1H, =CHSi), 0.46 (s, 6H, $SiMe_2$). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 146.0, 143.7, 137.8, 134.2, 131.0 (q, $J_{FC} = 32$ Hz), 128.6, 128.4, 126.5, 125.8, 124.2 (q, $J_{FC} = 272$ Hz), 124.3 (q, $J_{FC} = 4$ Hz), −2.7. MS, *m*/*z* (relative intensity, %): 306 [M^+, 30], 292 (11), 291 (47), 229 (30), 213 (25), 210 (22), 209 (14), 189 (39), 151 (12), 146 (19), 145 (100), 127 (39), 121 (11), 77 (34), 63 (13), 59 (17), 53 (11), 51 (18), 47 (14), 43 (35). Anal. Calc. for $C_{17}H_{17}F_3Si$: C, 66.64; H, 5.59. Found: C, 66.66; H, 5.65%.

4.3.4. (E)-PhCH=CHSiMe$_2$(C$_6$H$_4$–4-OMe)

^{1}H-NMR ($CDCl_3$): δ 7.52–7.42 (m, 4H, Ar), 7.36–7.23 (m, 3H, Ar), 6.94–6.91 (m, 2H, Ar), 6.92 (d, $J = 19.1$ Hz, 1H, PhCH=), 6.58 (d, $J = 19.1$ Hz, =CHSi), 3.82 (s, 3H, OMe), 0.41 (s, 6H, $SiMe_2$).

$^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 160.4, 145.0, 138.2, 135.4, 129.3, 128.5, 128.1, 127.5, 126.5, 113.6, 55.0, −2.3. MS, m/z (relative intensity, %): 268 [M^+, 53], 254 (18), 253 (78), 175 (34), 165 (14), 152 (11), 146 (20), 145 (100), 135 (15), 121 (15), 119 (11), 105 (12), 59 (37), 53 (11), 43 (41). Anal. Calc. for $C_{17}H_{20}OSi$: C, 76.07; H, 7.51. Found: C, 75.86, H, 7.36%.

4.3.5. (E)-PhCH=CHSiFPh$_2$

^{1}H-NMR ($CDCl_3$): δ 7.74–7.68 (m, 4H, Ph), 7.54–7.30 (m, 11H, Ph), 7.18 (d, $J = 19.2$ Hz, 1H, PhCH=), 6.74 (dd, $J = 19.2$ Hz, $^3J_{FH} = 3.5$ Hz, =CHSi). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 150.4 (d, $J_{FC} = 4$ Hz), 137.2 (s), 134.7 (d, $J_{FC} = 1$ Hz), 132.7 (d, $J_{FC} = 17$ Hz), 130.8, 129.1, 128.6, 128.1, 127.0, 120.3 (d, $J_{FC} = 17$ Hz). MS, m/z (relative intensity, %): 304 [M^+, 9], 226 (38), 201 (12), 199 (11), 181 (17), 180 (80), 179 (38), 178 (20), 165 (14), 149 (25), 125 (10), 77 (12), 51 (22), 47 (100). Anal. Calc. for $C_{20}H_{17}FSi$: C, 78.91; H, 5.63. Found: C, 80.44; H, 5.47%.

4.3.6. (E)-PhCH=CHSi(OEt)$_3$

^{1}H-NMR ($CDCl_3$): δ 7.50–7.26 (m, 5H, Ph), 7.22 (d, $J = 19.2$ Hz, 1H, PhCH=), 6.18 (d, $J = 19.2$ Hz, 1H, =CHSi), 3.89 (q, $J = 7.0$ Hz, 6H, OCH_2CH_3), 1.27 (t, $J = 7.0$ Hz, 9H, OCH_2CH_3). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 149.1, 137.6, 128.7, 128.5, 126.8, 117.6, 58.6, 18.3. MS, m/z (relative intensity, %): 266 [M^+, 6], 251 (40), 223 (17), 222 (73), 221 (17), 193 (41), 176 (63), 149 (82), 147 (92), 131 (45), 103 (47), 79 (56), 77 (28), 63 (68), 45 (100). Anal. Calc. for $C_{14}H_{22}O_3Si$: C, 63.12; H, 8.32. Found: C, 62.99; H, 8.18%.

4.3.7. (E)-p-CH$_3$C$_6$H$_4$CH=CHSiMe$_2$[C$_6$H$_3$–3,5-(CF$_3$)$_2$]

^{1}H-NMR ($CDCl_3$): δ 7.95 (br, 2H, Ar), 7.86 (br, 1H, Ar), 7.36 (d, $J = 8.1$ Hz, 2H, Ar), 7.16 (d, $J = 8.1$ Hz, 2H, Ar), 6.96 (d, $J = 19.2$ Hz, 1H, ArCH=), 6.45 (d, $J = 19.2$ Hz, 1H, =CHSi), 2.36 (s, 3H, Me), 0.49 (s, 6H, $SiMe_2$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 146.8, 142.6, 138.7, 134.9, 133.6, 130.7 (q, $J_{FC} = 33$ Hz), 129.3, 126.6, 123.6 (q, $J_{FC} = 273$ Hz), 123.0, 122.8 (septet, $^3J_{FC} = 4$ Hz), 21.3, −2.8. MS, m/z (relative intensity, %): 388 [M^+, 18], 292 (52), 277 (28), 257 (21), 241 (14), 195 (13), 159 (100), 115 (13), 77 (67), 43 (22). Anal. Calc. for $C_{19}H_{18}F_6Si$: C, 58.75; H, 4.67. Found: C, 58.73; H, 4.72%.

4.3.8. (E)-cyclo-C$_6$H$_{11}$CH=CHSiMe$_2$[C$_6$H$_3$–3,5-(CF$_3$)$_2$]

^{1}H-NMR ($CDCl_3$): δ 7.90 (br s, 2H, Ar), 7.83 (s, br, 1H, Ar), 6.13 (dd, $J = 18.9$ and 6.0 Hz, 1H, CyCH=), 5.67 (dd, $J = 18.9$ and 1.5 Hz, 1H, =CHSi), 2.12–1.98 (m, 1H, Cy), 1.80–1.60 (m, 5H, Cy), 1.36–1.02 (m, 5H, Cy), 0.37 (s, 6H, $SiMe_2$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 156.8, 143.3, 133.6, 130.5 (q, $J_{FC} = 33$ Hz), 123.7 (q, $J_{FC} = 273$ Hz), 122.6 (septet, $^3J_{FC} = 4$ Hz), 121.9, 44.1, 32.2, 26.1, 25.9, −2.7. MS, m/z (relative intensity, %): 380 [M^+, 4], 271 (100), 257 (20), 108 (76), 93 (14), 79 (28), 77 (18), 67 (20), 55 (18), 41 (35). Anal. Calc. for $C_{18}H_{22}F_6Si$: C, 56.83; H, 5.83. Found: C, 56.91; H, 5.76%.

4.3.9. (E)-n-C$_6$H$_{13}$CH=CHSiMe$_2$Ph

^{1}H-NMR ($CDCl_3$): δ 7.56–7.47 (m, 2H, Ph), 7.38–7.31 (m, 3H, Ph), 6.12 (dt, $J = 18.5$ and 6.3 Hz, 1H, CH=), 5.75 (dt, $J = 18.5$ and 1.5 Hz, 1H, =CHSi), 2.14 (dt, $J = 6.3$ and 1.5 Hz, 2H, CH_2), 1.34–1.15 (m, 8H, CH_2), 0.88 (t, $J = 7.0$ Hz, 3H, Me), 0.31 (s, 6H, $SiMe_2$). MS, m/z (relative intensity, %): 246 [M^+, 3], 231 (18), 136 (19), 135 (100), 121 (60), 162 (15), 161 (17), 107 (11), 105 (15), 59 (24). Anal. Calc. for $C_{16}H_{26}Si$: C, 77.97; H, 10.63. Found: C, 77.92; H, 10.67%.

4.3.10. (Z)-PhCH=CHSiMe$_2$Ph

^{1}H-NMR ($CDCl_3$): δ 7.56–7.53 (m, 2H, Ph), 7.49 (d, $J = 15.2$ Hz, 1H, PhCH=), 7.36–7.32 (m, 3H, Ph), 7.21 (br, 5H, Ph), 6.00 (d, $J = 15.2$ Hz, 1H, =CHSi), 0.26 (s, 6H, $SiMe_2$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 148.0, 139.6, 139.6, 133.7, 130.2, 128.8, 128.2, 127.8, 127.4, −1.1. MS, m/z (relative intensity, %): 238 [M^+, 34], 224 (15), 223 (68), 146 (24), 145 (100), 135 (16), 121 (43), 119 (13), 105 (30), 59 (16), 53 (23), 51 (13), 43 (57). Anal. Calc. for $C_{16}H_{18}Si$: C, 80.61; H, 7.61. Found: C, 80.63; H, 7.47%.

4.3.11. (Z)-PhCH=CHSiMe$_2$[C$_6$H$_3$–3,5-(CF$_3$)$_2$]

^{1}H-NMR ($CDCl_3$): δ 7.81 (br, 2H, Ar), 7.76 (br, 1H, Ar), 7.58 (d, $J = 15.0$ Hz, PhCH=), 7.18–7.13 (m, 3H, Ar), 7.10–7.05 (m, 2H, Ar), 5.95 (d, $J = 15.0$ Hz, =CHSi), 0.36 (s, 6H, $SiMe_2$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 149.9, 142.9, 139.2, 133.4, 130.5 (q, $J_{FC} = 33$ Hz), 128.2, 127.9, 127.9, 127.8, 123.6 (q, $J_{FC} = 273$ Hz), 122.5 (septet, $J_{FC} = 4$ Hz), −1.2. MS, m/z (relative intensity, %): 374 [M^+, 5], 279 (12), 278 (70), 277 (13), 257 (20), 227 (13), 209 (24), 195 (17), 145 (100), 81 (19), 77 (85), 59 (19), 51 (23), 47 (17), 43 (32). Anal. Calc. for $C_{18}H_{16}F_6Si$: C, 57.75; H, 4.31. Found: C, 57.90; H, 4.23%.

4.3.12. (Z)-PhCH=CHSiMe$_2$(C$_6$H$_4$–4-CF$_3$)

^{1}H-NMR ($CDCl_3$): δ 7.63–7.51 (m, 4H, Ar), 7.53 (d, $J = 15.0$ Hz, 1H, PhCH=), 7.26–7.16 (m, 5H, Ar), 5.97 (d, $J = 15.0$ Hz, 1H, =CHSi), 0.29 (s, 6H, $SiMe_2$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 148.9, 144.6, 139.4, 133.9, 130.7 (q, $J_{FC} = 32$ Hz), 129.0, 128.1, 127.9, 127.7, 124.3 (q, $J_{FC} = 3$ Hz), 124.2 (q, $J_{FC} = 272$ Hz), −1.2. MS, m/z (relative intensity, %): 306 [M^+, 23], 291 (42), 229 (28), 213 (23), 210 (22), 209 (13), 189 (33), 151 (12), 146 (19), 145 (100), 127 (42), 121 (11), 81 (10), 77 (35), 63 (14), 59 (17), 53 (12), 51 (21), 47 (15), 43 (37). Anal. Calc. for $C_{17}H_{17}F_3Si$: C, 66.64; H, 5.59. Found: C, 66.68; H, 5.69%.

4.3.13. (Z)-PhCH=CHSiMe$_2$(C_6H_4–4-OMe)

^{1}H-NMR ($CDCl_3$): δ 7.50–7.44 (m, 3H, Ar), 7.47 (d, $J = 15.2$ Hz, 1H, PhCH=), 7.33–7.18 (m, 4H, Ar), 6.98–6.87 (m, 2H, Ar), 5.99 (d, $J = 15.2$ Hz, =CHSi), 3.81 (s, 3H, OMe), 0.24 (s, 6H, $SiMe_2$). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 160.2, 147.8, 139.6, 135.1, 130.5, 130.4, 128.3, 127.8, 127.4, 113.6, 55.0, −0.9. MS, *m*/*z* (relative intensity, %): 268 [M$^+$, 32], 254 (11), 253 (48), 175 (21), 165 (11), 151 (32), 146 (16), 145 (100), 135 (10), 105 (9), 59 (26), 43 (29). Anal. Calc. for $C_{17}H_{20}OSi$: C, 76.07; H, 7.51. Found: C, 74.83; H, 7.50%.

4.3.14. (Z)-PhCH=CHSiFPh$_2$

^{1}H-NMR ($CDCl_3$): δ 7.63–7.57 (m, 4H, Ph), 7.42–7.30 (m, 9H, Ph and PhCH=), 7.20–7.12 (m, 3H, Ph), 6.10 (dd, $J = 15.0$ Hz, $^3J_{FH} = 8.7$ Hz, 1H, =CHSi). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 152.6 (d, $J_{FC} = 2$ Hz), 138.1, 134.4 (d, $J_{FC} = 2$ Hz), 133.4 (d, $J_{FC} = 18$ Hz), 130.5, 128.4, 128.3, 128.0, 122.7 (d, $J_{FC} = 17$ Hz). MS, *m*/*z* (relative intensity, %): 304 [M$^+$, 20], 226 (38), 201 (20), 180 (100), 179 (64), 165 (26), 149 (43), 125 (15), 77 (13), 47 (79). Anal. Calc. for $C_{20}H_{17}FSi$: C, 78.91; H, 5.63. Found: C, 79.88; H, 5.51%.

4.3.15. (Z)-p-$CH_3C_6H_4$CH=CHSiMe$_2$Ph

^{1}H-NMR ($CDCl_3$): δ 7.60–7.52 (m, 2H, Ar), 7.43 (d, $J = 15.3$ Hz, 1H, ArCH=), 7.38–7.32 (m, 3H, Ar), 7.13 (d, $J = 8.1$ Hz, 2H, Ar), 7.03 (d, $J = 8.1$ Hz, 2H, Ar), 6.94 (d, $J = 15.0$ Hz, 1H, =CHSi), 2.30 (s, 3H, Me), 0.28 (s, 6H, $SiMe_2$). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 148.0, 139.8, 137.3, 136.7, 133.7, 129.0, 128.8, 128.5, 128.2, 127.8, 21.2, −1.1. MS, *m*/*z* (relative intensity, %): 252 [M$^+$, 27], 237 (50), 159 (100), 145 (34), 135 (13), 121 (24), 105 (15), 59 (13), 53 (14), 43 (55). Anal. Calc. for $C_{17}H_{20}Si$: C, 80.89; H, 7.99. Found: C, 80.76; H, 7.88%.

4.3.16. (Z)-cyclo-C_6H_{11}CH=CHSiMe$_2$Ph

^{1}H-NMR ($CDCl_3$): δ 7.58–7.52 (m, 2H, Ph), 7.38–7.32 (m, 3H, Ph), 6.22 (dd, $J = 13.8$ and 9.9 Hz, 1H, CyCH=), 5.51 (d, $J = 13.8$ Hz, 1H, =CHSi), 2.12–1.96 (m, 1H, Cy), 1.68–1.44 (m, 5H, Cy), 1.16–0.96 (m, 5H, Cy), 0.37 (s, 6H, $SiMe_2$). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 156.5, 139.9, 133.7, 128.7, 127.7, 124.3, 42.7, 32.7, 25.8, 25.6, −0.7. MS, *m*/*z* (relative intensity, %): 244 [M$^+$, 2], 229 (11), 185 (11), 166 (40), 151 (21), 135 (100), 121 (65), 105 (17), 59 (31), 43 (69). Anal. Calc. for $C_{16}H_{24}Si$: C, 78.61; H, 9.90. Found: C, 78.73; H, 9.83%.

4.3.17. (Z)-n-C_6H_{13}CH=CHSiMe$_2$Ph

^{1}H-NMR ($CDCl_3$): δ 7.59–7.49 (m, 2H, Ph), 7.39–7.31 (m, 3H, Ph), 6.43 (dt, $J = 13.9$ and 7.5 Hz, 1H, CH=), 5.62 (dt, $J = 13.9$ and 1.3 Hz, 1H, =CHSi), 2.03 (dt, $J = 7.5$ and 1.3 Hz, 2H, CH_2), 1.38–1.12 (m, 8H, CH_2), 0.86 (t, $J = 7.2$ Hz, 3H, Me), 0.37 (s, 6H, $SiMe_2$). ^{13}C{^{1}H}-NMR: δ 151.0, 139.8, 133.7, 128.7, 127.7, 126.4, 33.8, 31.7, 29.5, 28.9, 22.6, 14.1, −0.8. MS, *m*/*z* (relative intensity, %): 246 [M$^+$, 3], 231 (29), 135 (59), 121 (100), 162 (27), 161 (33), 147 (14), 145 (20), 105 (19), 59 (48). Anal. Calc. for $C_{16}H_{26}Si$: C, 77.97; H, 10.63. Found: C, 77.84; H, 10.32%.

4.4. Reaction of Ru($SiMe_2Ph$)Cl(CO)(PPr^i_3)$_2$ ***(5b)*** *with phenylacetylene and HSiMe$_2$Ph*

An NMR sample tube was charged with **5b** (8.6 mg, 0.014 mmol) and capped with a rubber septum. The system was replaced with nitrogen gas. $CDCl_3$ (0.70 ml) and PhC≡CH (7.1 mg, 0.070 mmol) were added at r.t. NMR analysis after several minutes revealed complete conversion of **5b** into Ru[C(Ph)(CHSiMe$_2$Ph)]Cl(CO)(PPr^i_3)$_2$ (**7b**). ^{1}H-NMR ($CDCl_3$, 20 °C): δ 7.49–7.02 (m, 10H, Ph), 6.14 (t, $^4J_{PH} = 2.0$ Hz, 1H, =CH), 2.80–2.68 (m, 6H, PC*H*), 1.21 (doublet of virtual triplets, $J = 7.0$ and 6.3 Hz, 18H, PCHCH_3), 1.17 (doublet of virtual triplets, $J = 7.0$ and 6.3 Hz, 18H, PCHCH_3), −0.15 (s, $SiMe_2$). ^{13}C{^{1}H}-NMR (toluene-d_8, 0 °C): δ 207.6 (t, $^2J_{PC} = 14$ Hz, CO), 179.0 (t, $^2J_{PC} = 9$ Hz, Ru*C*Ph=), 151.8 (s, Ph), 142.6 (s, Ph), 134.0 (s, CPh = *C*Si), 128.5 (s, Ph), 127.9 (s, Ph), 127.5 (s, Ph), 126.9 (s, Ph), 24.4 (virtual triplet, $J_{app} = 9$ Hz, P*C*HCH$_3$), 20.3 (s, PCH*C*H$_3$), 19.9 (s, PCH*C*H$_3$), −0.8 (s, $SiMe_2$). ^{31}P{^{1}H}-NMR ($CDCl_3$, 20 °C): δ 33.7 (s).

After the sample solution was allowed to stand at r.t. for 3 days, two singlet signals at δ 33.7 and 37.0, which are assignable to **7b** and Ru(CH(CHPh)Cl(CO)(PPr^i_3)$_2$ (**6b**), respectively, were observed in a 2:1 ratio by ^{31}P{^{1}H}-NMR spectroscopy.

A solution of **7b** in $CDCl_3$ was similarly prepared, and $HSiMe_2Ph$ (1.9 mg, 0.014 mmol) and anisole (1.0 μl, 9.2 μmol; an internal standard for ^{1}H-NMR and GLC analysis) were added at r.t. The ^{1}H-NMR spectrum measured after a few minutes showed the formation of (*Z*)- and (*E*)-PhCH=CHSiMe$_2$Ph in 82 and 5% yield, respectively.

4.5. Palladium-catalyzed coupling of styrylsilanes with p-iodotoluene

A typical procedure (run 3 in Table 4) is as follows. PhCH=CHSiMe$_2$[C_6H_3–3,5-(CF_3)$_2$] (93.6 mg, 0.25 mmol, (*E*)/(*Z*) = 99/1) and *p*-iodotoluene (43.6 mg, 0.20 mmol) were dissolved in THF (1 ml), and added to a Schlenk tube containing [PdCl(η^3-allyl)]$_2$ (1.8 mg, 4.9 μmol). A THF solution of tetrabutylammonium fluoride (1.0 M, 0.25 ml) was added, and the mixture was stirred at r.t. for 1 h. GLC analysis revealed 100% conversion of *p*-iodotoluene. The solvent was removed by pumping and the residue was subjected to flash column chromatography (SiO_2, hexane), giving 4-methylstilbene (**11**) in 83% yield (32.3 mg, (*E*)/(*Z*) = 99/

1). The reaction of run 4 in Table 4 was similarly performed.

*4.5.1. (E)-**11***

^{1}H-NMR ($CDCl_3$): δ 7.51 (d, $J = 7.5$ Hz, 2H, Ar), 7.43 (d, $J = 8.1$ Hz, 2H, Ar), 7.34 (t, $J = 8.1$ Hz, 2H, Ar), 7.29–7.22 (m, 1H, Ar), 7.18 (d, $J = 8.4$ Hz, 2H, Ar), 7.09 (s, 2H, HC=), 2.37 (s, 3H, Me).

*4.5.2. (Z)-**11***

^{1}H-NMR ($CDCl_3$): δ 7.30–7.12 (m, 7H, Ar), 7.03 (d, $J = 8.4$ Hz, 2H, Ar), 6.56 (s, 2H, HC=), 2.31 (s, 3H, Me).

The assignment of (*E*)- and (*Z*)-isomers was based on comparison of the chemical shifts of vinylic protons with those of (*E*)- and (*Z*)-stilbenes (δ 7.12 and 6.60, respectively).

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References

[1] For reviews, see: (a) T. Hiyama, T. Kusumoto, in: M. Trost, I. Flemming (Eds.), Comprehensive Organic Synthesis, vol. 8, Pergamon Press, Oxford, 1991, p. 763;
(b) J.A. Reichl, D.H. Berry, Adv. Organomet. Chem. 43 (1998) 197.
[2] B. Marciniec, Comprehensive Handbook on Hydrosilylation, Pergamon Press, Oxford, 1992.
[3] (a) I. Ojima, Z. Li, J. Zhu, in: S. Roppoport, Y. Apeloig (Eds.), The Chemistry of Organic Silicon Compounds, Wiley, New York, 1998;
(b) E. Langkopf, D. Schinzer, Chem. Rev. 95 (1995) 1375;
(c) E.W. Colvin, in: Silicon Reagents in Organic Synthesis, Academic Press, London, 1988.
[4] (a) R. Takeuchi, N. Tanouchi, J. Chem. Soc. Perkin Trans. 1 (1994) 2909;
(b) R. Takeuchi, S. Nitta, D. Watanabe, J. Org. Chem. 60 (1995) 3045.
[5] (a) A. Mori, E. Takahashi, H. Kajiro, K. Hirabayashi, Y. Nishihara, T. Hiyama, Chem. Lett. (1998) 443;
(b) A. Mori, E. Takahashi, H. Kajiro, Y. Nishihara, T. Hiyama, Polyhedron 19 (2000) 567;
(c) A. Mori, E. Takahisa, H. Kajiro, Y. Nishihara, T. Hiyama, Macromolecules 33 (2000) 1115.
[6] Y. Maruyama, K. Yamamura, I. Nakayama, K. Yoshiuchi, F. Ozawa, J. Am. Chem. Soc. 120 (1998) 1421.
[7] (a) Y. Maruyama, K. Yamamura, T. Sagawa, H. Katayama, F. Ozawa, Organometallics 19 (2000) 1308;
(b) Y. Maruyama, K. Yamamura, F. Ozawa, Chem. Lett. (1998) 905.
[8] (a) I. Ojima, N. Clos, R.J. Donovan, P. Ingellina, Organometallics 9 (1990) 3127;
(b) R.S. Tanke, R.H. Crabtree, J. Am. Chem. Soc. 112 (1990) 7984;
(c) C.-H. Jun, R.H. Crabtree, J. Organomet. Chem. 447 (1993) 177 and references cited therein.
[9] M.A. Esteruelas, J. Herrero, L.A. Oro, Organometallics 12 (1993) 2377.
[10] S.M. Maddock, C.E.F. Rickard, W.R. Roper, L.J. Wright, Organometallics 15 (1996) 1793.
[11] Y. Na, S. Chang, Org. Lett. 2 (2000) 1887.
[12] (a) M.R. Torres, A. Vegas, A. Santos, J. Organomet. Chem. 309 (1986) 169;
(b) M.R. Torres, A. Vegas, A. Santos, J. Ros, J. Organomet. Chem. 326 (1987) 413;
(c) H. Werner, M.A. Esteruelas, H. Otto, Organometallics 5 (1986) 2295.
[13] An excess amount of alkyne is known to improve the stereoselectivity by suppressing isomerization of (*Z*)-alkenylsilane to thermodynamically more stable (*E*)-isomer [8a].
[14] Since no details of reaction conditions have been reported [9], we are uncertain the reported reaction to be checked precisely.
[15] The formation of styrene from **6b** and $HSiMe_2Ph$ may proceed via process (v) which involves prior dissociation of phosphine ligand (Scheme 2), while the detail of reaction could not be confirmed owing to the extremely low reactivity of **6b**.
[16] Note that the present discussion never excludes the direct formation path of **5b** from **4b** and hydrosilane [9].
[17] (a) Y. Hatanaka, T. Hiyama, Synlett (1991) 845;
(b) K. Tamao, K. Kobayashi, Y. Ito, Tetrahedron Lett. 30 (1989) 6051;
(c) T. Hiyama, in: F. Diedrich, P.J. Stang (Eds.), Metal-Catalyzed Cross-Coupling Reactions, Wiely-VHC, Weinheim, 1998, p. 421.
[18] J.J. Levinson, S.D. Robinson, J. Chem. Soc. Sect. A (1970) 2947.
[19] M.A. Esteruelas, H. Werner, J. Organomet. Chem. 303 (1986) 221.
[20] C.S. Yi, D.W. Lee, Y. Chen, Organometallics 18 (1999) 2043.
[21] D. Huang, W.E. Streib, J.C. Bollinger, K.G. Caulton, R.F. Winter, T. Scheiring, J. Am. Chem. Soc. 121 (1999) 8087.
[22] K. Tamao, A. Kawachi, Adv. Organomet. Chem. 38 (1995) 1.