

Selected Paper

Cationic Palladium Complex-Catalyzed Hydrosilylative Cross-Coupling of Alkynes with Alkenes. 1,4-Addition of Trichlorosilane to Form 4-Silyl-1-butene Framework

Takamitsu Shimamoto, Motoharu Chimori, Hiroaki Sogawa, Yūki Harada, Masaharu Aoki, and Keiji Yamamoto*

Department of Materials Science and Environmental Engineering, Tokyo University of Science, Yamaguchi, 1-1-1 Daigaku-Dori, Sanyo-Onoda, Yamaguchi 756-0884

Received March 8, 2007; E-mail: kyamamoto_ji@yahoo.co.jp

A new hydrosilylative cross-coupling reaction of a variety of alkynes with several alkenes, which is catalyzed by a cationic palladium complex **A** (1 mol %) without or with added PPh_3 ligand, was studied systematically. The reaction using $HSiCl_3$ as an addend afforded more or less two types of products consisting of four possible derivatives, $R^1CH{=}CR^2{-}CHR^3{-}CHR^4{-}SiCl_3$, which always contained 4-trichlorosilyl-1-butene frameworks, in acceptable combined yields. The coupling pattern was dependent both on the precatalyst **A** in the absence or presence of PPh_3 [also $P(C_6F_5)_3$] and on the combination of the alkyne and alkene counterpart employed. A possible catalytic cycle that involves an initial hydropalladation of an alkyne, followed by a facile and specific carbopalladation of an alkene, is proposed. At the same time, the lack of regioselectivity in the latter step is noted. The effect of the added phosphine ligand on the coupling pattern is briefly discussed.

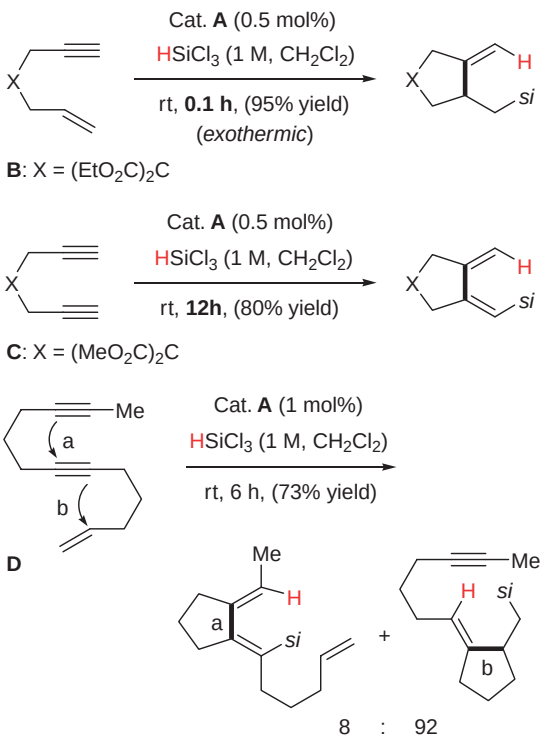
Ample research activities in the transition metal complex-catalyzed hydrosilylation of alkenes and alkynes are still focused on achieving either chemo-, regio-, or stereoselective hydrosilylation as well as to obtain an insight into mechanisms of the reaction. Catalytic hydrosilylation is a versatile synthetic method for obtaining organosilicon compounds. The value of this hydrosilylation has been further augmented by protocols for converting the silyl group in the products to other functional groups.[1]

Among a variety of catalysts so far studied, late transition metal complexes, especially those of groups 8–10, have been found to play a key role in providing effective catalyst precursors. The catalytic reaction is generally thought to proceed by either hydrometalation (Chalk–Harrod mechanism) or silylmetalation (so-called modified Chalk–Harrod mechanism) as one of the key steps in the catalytic cycles that depend on both transition metals and hydrosilanes employed.[2]

We have been studying the palladium complex-catalyzed hydrosilylation of alkynes, which involves primarily non-conventional reaction categories other than 1,2-addition of a hydrosilane to the substrate.[3] Specifically, dimerization–hydrosilylation of 1-alkynes is catalyzed by a bulky palladium(II) complex as a precatalyst,[4] and the cyclization–hydrosilylation of 1,6-alkadiynes or 1,6-alkenynes[5,6] as well as the competitive, yet intriguing, cyclization–hydrosilylation of 1-alkene-6,11-diynes[7] have been realized using a cationic palladium(II) complex. A key mechanistic feature of these transformations appears to involve catalytic cycles driven by a hydridopalladium species, for which simple hydrosilylation is suppressed.

Although there are a variety of examples of the late transition metal (Rh,[8] Ni,[9] Pd,[10] and Pt[11]) complex-catalyzed cyclization–hydrosilylation of α,ω-alkadiynes,[8a,e,g,9a,11b] alkenynes,[8c,g] and alkadienes,[8f,10a–d] it is worthy to note that trialkylsilanes must be used as addends in these cases, and $HSiMe_nCl_{3-n}$ ($n = 0$–2) but none of trialkylsilanes are applicable for our studies (Scheme 1; vide infra).[5,12]

The unique findings have originated from the fact that, when



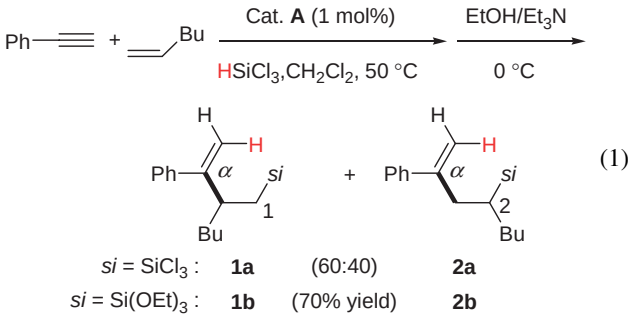
Scheme 1. Facile cyclization of 1,6-enynes.

Published on the web September 13, 2007; doi:10.1246/bcsj.80.1814

$HSiCl_3$ is an addend, a palladium complex, $[Pd(\eta^3\text{-}C_3H_5)(cod)]^+[PF_6]^-$ (**A**) (cod = 1,5-cyclooctadiene) can catalyze the cyclization–hydrosilylation of a 1-hepten-6-yne (**B**) evidently much faster than that of the corresponding 1,6-heptadiyne (**C**), as indicated in Scheme 1.[6] An intramolecular competitive cyclization of endiyne **D** reinforces this fact.[7] As such, it seems possible to develop a reaction between an alkyne with an alkene, i.e., an intermolecular version of cyclization–hydrosilylation of α,ω-alkenynes as mentioned above. Herein, we report that the cationic palladium complex **A** catalyzes a selective cross-coupling of alkynes with alkenes, which occurs under hydrosilylation conditions.[13]

Results and Discussion

With the above findings in hand, we carried out a reaction of a mixture of phenylacetylene (1.0 mmol) and 1-hexene (1, 3, or 5 equiv) with $HSiCl_3$ (1 M, CH_2Cl_2, 1 mL) (1 M = 1 mol dm^{-3} in the presence of the catalyst $[Pd(\eta^3\text{-}C_3H_5)(cod)]^+[PF_6]^-$ (**A**) (0.01 mmol, 1 mol %), under an argon atmosphere at 50 °C for 1–4 h in a 5 mL screw-capped test tube. The reaction mixture immediately turned clear dark-brown in color and then pale brown, and a black precipitate, which is indicative of a final stage of the reaction, formed. The mixture was either subjected directly to a bulb-to-bulb distillation, in vacuo, to isolate reaction products containing a moisture-sensitive trichlorosilyl group or treated immediately with excess dry ethanol and triethylamine in CH_2Cl_2 at 0 °C for 2 h to isolate the corresponding triethoxy derivative of the hydrosilylative cross-coupling products. In the latter case, two major products were obtained in 70% combined yield after a usual work up, as indicated in Eq. 1. It was also found that use of excess 1-hexene (3 equiv) resulted in a better yield of the cross-coupling products, whereas product ratios of **1a** (α-1)[14] to **2a** (α-2)[14] (ca. 60:40) did not change (see, Experimental).



(1)

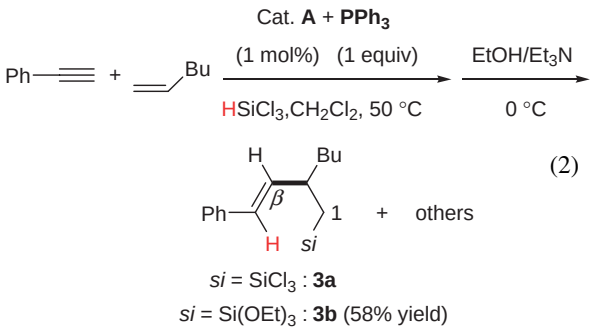
Since we have already confirmed that the initial step of cyclization–hydrosilylation of substrate **D** (Scheme 1) must take place at the alkyne site (path b rather than path a), the result obtained here may be understood as follows: hydropalladation initially occurs with phenylacetylene at an α-position regioselectively,[14] forming an alkenylpalladium intermediate. Then, clean insertion of 1-hexene, rather than the second phenylacetylene molecule,[4] into the resulting alkenylpalladium intermediate (carbopalladation) proceeds with a lack of regioselectivity. As a result, both a terminally silylated product (designated as 1)[14] and an internally silylated one (designated as 2)[14] are formed, the former being predominant (vide infra). There was found little dimerization–hydrosilylation product of phenylacetylene.[15]

Table 1. Effect of Phosphorus Ligand on the Reaction (Eq. 2)[a)]

Entry	Ligand (L)	L/Pd	Yield/%[b)]	Composition (**1b** + **2b**):**3b**
1	PPh_3	1	58	3:97
2[c)]	PPh_3	2	50	4:96
3	$P(p\text{-Tol})_3$	1	26	10:90
4	$P(tm\text{-}tp)_3$[d)]	1	42	53:47
5	$P(C_6F_5)_3$	1	55	85[e)]:15
6	$(ArO)_3P$[f)]	1	49	7:93
7	$(PhO)_3P$	1	34	9:91
8	$(EtO)_3P$	1	21	29:71
9	$C_6H_{11}O_3P$[g)]	1	46	23:77
10	$C_6H_{11}O_3P$[g)]	2	52	12:88

a) 1-Hexene (3 equiv) to phenylacetylene was used. b) Isolated as triethoxysilyl derivatives. c) 1-Hexene (5 equiv) was used. d) A bowl-shaped phosphine (Ref. 16). e) **1b**:**2b** = 82:18. f) Ar = 2,4-Di-*t*-butylphenyl. g) Trimethylolpropane phosphite.

However, once triphenylphosphine (1 equiv) was added to the precatalyst **A**, the same reaction as above exhibited a quite different reaction pattern after 3 h, as shown in Eq. 2. The initial hydropalladation appears to attach the palladium center to the β-position of phenylacetylene exclusively, resulting in coupling product **3a** (β-1),[14] which was isolated as triethoxysilyl derivative **3b** in 58% isolated yield.

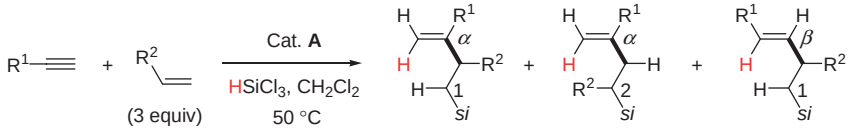


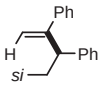
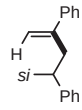
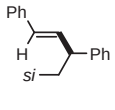
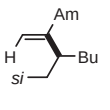
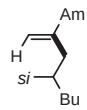
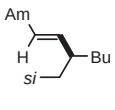
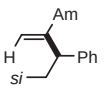
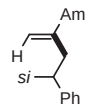
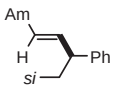
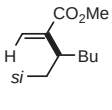
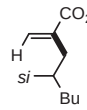
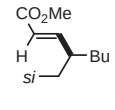
(2)

Being interested in the reversed regioselectivity giving **3b** (β-1), we investigated the effects of other phosphorus ligands for the precatalyst **A** on the regiocontrol of this reaction. All results obtained are listed in Table 1. Several features may be seen from Table 1. In the case of PPh_3, the molar ratios of phosphine ligand (L) to **A** (L/Pd = 1 or 2) had the little effect on the product composition (**1b** + **2b**):**3b** (Entries 1 and 2), whereas $P(p\text{-tolyl})_3$ and much bulkier, so-called bowl-shaped, $P(tm\text{-}tp)_3$[16] (L/Pd = 1) gave rise to lower and even inverted regiocontrol, respectively (Entries 3 and 4). Use of $P(C_6F_5)_3$ (L/Pd = 1) gave a mixture of **1b** and **2b** as major cross-coupling products (up to 85%) along with minor **3b** (15%) (Entry 5). In addition, the ratio of **1b** (α-1) to **2b** (α-2) was 82:18, which was better than that without added PPh_3 (60:40) (cf. Eq. 1). The increased yield and regiocontrol using $P(C_6F_5)_3$ as a ligand must arise from its strong electronegative influence.[17]

On the other hand, both triaryl phosphites and trialkyl phosphites generally scarcely affected the product composition. Thus, $(PhO)_3P$ as well as bulky tris(2,4-di-*t*-butylphenyl) phos-

Table 2. Hydrosilylative Cross-Coupling of 1-Alkynes with 1-Alkenes Catalyzed by Complex A



Entry	R^1	R^2	Time/h	Yield/%[a]	Composition[b] (α-1 + α-2):β-1		
1[c]	C_6H_5	C_4H_9	1.5	70	91 (60:40)		9
					1a	**2a**	**3a**
2	C_6H_5	C_6H_5	3	71	93 (78:22)		7
							
					4a	**5a**	**6a**
3	C_5H_{11}	C_4H_9	3	56	89 (66:34)		11
							
					7a	**8a**	**9a**
4	C_5H_{11}	C_6H_5	2.5	52	73 (81:19)		27
							
					10a	**11a**	**12a**
5	CO_2Me	C_4H_9	4	40	~100 (88:12)[d]		—
							
					13a	**14a**	**15a**

a) Combined yield as triethoxysilyl derivatives (**b** series). b) Glc analysis of trichlorosilyl derivatives (**a** series). c) See, Eq. 1. d) Minor product estimated to be α-2.

phite gave a similar level of regiocontrol as ordinary triarylphosphines (Entries 6 and 7), whereas two trialkyl phosphites examined did not (Entries 8 and 9). However, the sterically least-demanding trimethylolpropane phosphite (L/Pd = 2; Entry 10) gave results similar to $(PhO)_3P$. After all, the effect of PPh_3 added to precatalyst **A** on the reversal of regiocontrol from α- to β-position in the hydropalladation of phenylacetylene is steric in origin. Significance of the observed reversal in the regioselectivity will also be mentioned later.

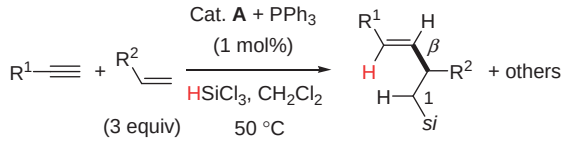
Although the critical nature of a cationic palladium(II)-catalyzed hydrosilylation is not clear yet, the scope and limitations with regard of the present hydrosilylative cross-coupling between alkynes and alkenes were examined: phenylacetylene, 1-heptyne, or methyl propiolate, respectively, was used as a typical 1-alkyne, while 1-hexene or styrene was used as a 1-alkene counterpart.

Hydrosilylative cross-coupling, which was catalyzed by complex **A** alone, was carried out, and the results are listed in Table 2. As is seen in Table 2, although the combined yields were not optimal and moderate, the general trend in the product composition, ((α-1 + α-2) and β-1),[14] for phenylacetylene with 1-hexene (Entry 1: cf. Eq. 1) and that with styrene (Entry 2: **4a** + **5a** and **6a**) did not substantially change. Also, the product composition for 1-heptyne with 1-hexene (Entry 3: **7a** + **8a** and **9a**) and with styrene (Entry 4: **10a** + **11a** and **12a**) exhibited only a trivial change. Thus, as for a specific insertion step of 1-alkenes to the alkenylpalladium intermediate, styrene may undergo insertion a little more selectively, giving a terminal (α-1) product, than 1-hexene (**4a** vs. **1a**, and **10a** vs. **7a**). However, the reaction of methyl propiolate with 1-hexene was exceptional, and coupling products **13a** and **14a** were obtained exclusively. This was the highest regioselectivity for **13a** (α-1) (Entry 5) exhibited so far. It is worthy to note that the isolated methyl 2-{1-[(triethoxysilyl)-methyl]pentyl}propenoate (**13b**) is an immediate precursor, by means of the Tamao–Fleming oxidation of alkenylsilanes, to 3-butyl-2-methylenebutanolide,[18a] which may be a useful building block (See, Experimental).

With the same combination of 1-alkynes and 1-alkenes as shown in Table 2, the hydrosilylative cross-coupling was also conducted using the cationic complex **A** with added PPh_3 (1 equiv) as catalyst, and the results are listed in Table 3. As can be seen, there was a preference for β-1 over α-1[14] (Entries 1, 2 (**3a**, **6a**), and 3, 4 (**9a**, **12a**)), and the combined yields were

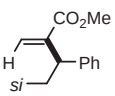
moderate yet acceptable. However, a similar coupling of methyl propiolate with 1-hexene exhibited, despite the presence of PPh_3, mixed regioselectivity to afford both **13a** (α-1) and **15a** (β-1) in a ratio 57:43 (Entry 5). Furthermore, use of an equimolar amount of $P(C_6F_5)_3$ (L/Pd = 1) was found to enhance the ratio of **13a**:**15a** (75:25) (Entry 6). The same and rather confusing trend as described here has also been found in the case of phenylacetylene (Table 1, Entry 5).[17] Consequently, it is of interest to point out, in terms of the observed coupling pattern, that methyl propiolate and phenylacetylene behave quite similarly under the catalytic conditions examined. Finally, the cross-coupling of methyl propiolate with styrene under the same conditions as in Entry 6 took place in an exclusive α regioselective manner, and the product ratio of **16a** (α-1):**17a** (α-2) was 81:19 (Entry 7). Again, isolated **16a** is a possible precursor to 2-methylene-3-phenylbutanolide[18b] by undergoing the Tamao oxidation.

Table 3. Hydrosilylative Cross-Coupling of 1-Alkynes with 1-Alkenes Catalyzed by Cat. A + PPh_3 (1 equiv)

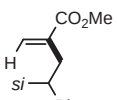


Entry	R^1	R^2	Time/h	Yield/%[a]	Composition[b] β-1	Composition[b] α-1[c]
1[d]	C_6H_5	C_4H_9	3	58	**3a** 91	**1a** 9
2	C_6H_5	C_6H_5	0.5	61	**6a** 93	**4a** 7
3[e]	C_5H_{11}	C_4H_9	4	55	**9a** 92	**7a** 8
4	C_5H_{11}	C_6H_5	0.5	64	**12a** 96	**10a** 4
5	CO_2Me	C_4H_9	4	51	**15a** 43	**13a** 57
6[f]	CO_2Me	C_4H_9	3	38	**15a** 25	**13a** 75
7[f]	CO_2Me	C_6H_5	2	40	—	**16a 17a** 81:19

a) Combined yield as triethoxysilyl derivatives (**b** series). b) Glc analysis of trichlorosilyl derivatives (**a** series). c) Hard to characterize α-2 except Entry 5. d) See, Eq. 2. e) In case of added $P(C_6F_5)_3$ **9a**:**7a** = 78:22 (see, Ref. 17). f) $P(C_6F_5)_3$ was employed instead of PPh_3.



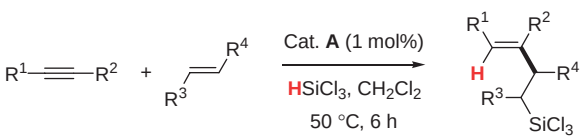
16a



17a

Certain internal alkynes or alkenes as coupling components can also be used in hydrosilylative cross-coupling catalyzed by cationic complex **A**, without or with PPh_3 under the conditions given in Eq. 1 or Eq. 2. In Table 4, selected examples, which circumvent potentially complex coupling pattern, giving mostly two products with moderate combined yields, are listed. The reaction of phenylacetylene with (*E*)-3-hexene gave regioisomeric 3-ethyl-2-phenyl-4-trichlorosilyl-1-hexene (**18a**) and (*E*)-3-ethyl-1-phenyl-4-trichlorosilyl-1-hexene (**19a**) in a ratio of 80:20 with 50% combined isolated yield as triethoxysilyl derivatives **18b** and **19b** (Entry 1). It is of interest that the observed isomer ratio was significantly lowered than that of (**1a** + **2a**):**3a** = 91:9 using 1-hexene as a coupling partner (see, Table 2, Entry 1). The fact that the two isomer ratios above differ significantly may be explained in terms of a reversible hydropalladation of phenylacetylene, which occurs prior to the successive carbopalladation with (*E*)-3-hexene and 1-hexane, respectively.[19] In the coupling reaction of 3-hexyne with allylbenzene, (*E*)-2-benzyl-3-ethyl-1-trichlorosilyl-3-hexene (**20a**) and (*E*)-4-ethyl-7-phenyl-6-trichlorosilyl-3-heptene (**21a**) were found in a ratio of 80:20, being isolated as triethoxysilyl derivatives (**20b** and **21b**) in 40% combined yield (Entry 2). The hydrosilylative reaction of ethyl 2-butynoate with 1-hexene catalyzed by complex **A** with added PPh_3 (1 equiv) gave ethyl (*Z*)-2-[1-(trichlorosilyl)methyl]pentyl-2-butenoate (**22a**) and ethyl (*E*)-3-methyl-4-(trichlorosilyl)-methyl-2-octenoate (**23a**) in a ratio of 60:40 and in 64% combined yield as triethoxysilyl derivatives (Entry 3). It was found, in this particular case, that both compounds were con-

Table 4. Palladium-Catalyzed Hydrosilylative Cross-Coupling Using Internal Alkynes or Alkenes



Entry	Alkyne	Alkene	Products	R^1	R^2	R^3	R^4	Yield/%[a]	Ratio[b]
1	Phenylacetylene	(*E*)-3-Hexene	**18a**	H	Ph	Et	Et	50	**18a**:**19a**
			19a	Ph	H	Et	Et		80:20
2	3-Hexyne	Allylbenzene	**20a**	Et	Et	H	Bn[c]	40	**20a**:**21a**
			21a	Et	Et	Bn[c]	H		80:20
3[d]	Ethyl 2-butynoate	1-Hexene	**22a**[e]	Me	E[f]	H	Bu	64	**22a**:**23a**
			23a[e]	E[f]	Me	H	Bu		60:40
4[d]	Phenylacetylene	2-Methyl-1-pentene[g]	**24a**	Ph	H	H	Me, Pr[h]	58[i]	—

a) Combined yield as triethoxysilyl derivatives (**b** series). b) Determined by GLC peak ratios. c) Benzyl. d) Triphenylphosphine (1 equiv) added. e) A regioisomer of hexene component as a contaminant. f) Ethoxycarbonyl. g) 2-Methyl-1-hexene also gave coupling product **24′a** (see, text and Experimental). h) Diastereomeric isomer not observed. i) Dimerization/hydrosilylation of phenylacetylene slightly observed.

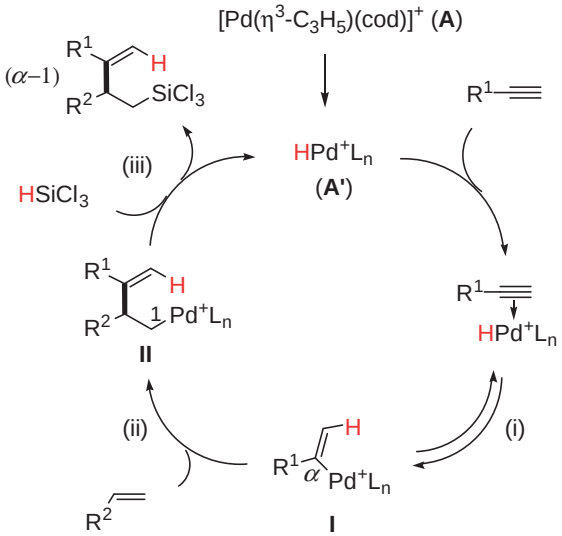
taminated by a significant amount of regioisomers probably from reversed insertion of 1-hexene component. However, the major reaction pattern was basically akin to that of methyl propiolate with 1-hexene (see, Table 3, Entry 5). Finally, the coupling reaction of phenylacetylene with 2-methyl-1-pentene, a typical 1,1-disubstituted alkene, under exactly the same conditions as in Entry 3 was examined, and (*E*)-3-methyl-1-phenyl-3-(trichlorosilyl)methyl-1-hexene (**24a**) (β-1)[14] was exclusively obtained in 58% yield (Entry 4). This reaction is characterized as a quaternary carbon bond-forming coupling reaction. Also, 2-methyl-1-hexene reacted to afford (*E*)-3-methyl-1-phenyl-3-(trichlorosilyl)methyl-1-heptene (**24′a**) as a sole product in 38% yield as a triethoxy derivative **24b′**. However, the coupling reaction of 3-hexyne with (*E*)-3-hexene was found to be very sluggish, and the starting material was recovered unchanged.

Throughout the hydrosilylative cross-coupling reactions presented here (Tables 1–4), various amounts of simple hydrosilylation product from alkenes, but not from alkynes, were usually obtained. In the case of allylbenzene, a large amount of hydrosilylation products were obtained at the expense of diminished cross-coupling with 3-hexyne (Table 4, Entry 2).

Finally, although palladium complex **A**-catalyzed hydrosilylative cross-coupling of alkynes with alkenes is new, it is obvious that, besides the regioselectivity at the alkyne site, less than satisfactory regiocontrol for the incoming 1-alkene partners was observed.

Catalytic Process. On the basis of the above observations, the coupling reaction has two salient features. Firstly, the use of both catalyst precursor $[Pd(\eta^3\text{-}C_3H_5)(cod)]^+[PF_6]^-$ (**A**) and $HSiCl_3$ as a hydrosilylating addend is essential for the cross-coupling of alkynes with alkenes to proceed. Although another non-coordinating counter anion $[BF_4]^-$ worked equally well, use of other chlorinated hydrosilanes, $HSiMe_nCl_{3-n}$ ($n = 1$ or 2), gave rise to hydrosilylation of alkenes employed. An attempted stoichiometric reaction of complex **A** with $HSiCl_3$ (1 M, CH_2Cl_2) in CD_2Cl_2 showed that propene and $SiCl_4$,[20] both of which were detected by ^1H and ^{29}Si NMR (see, Experimental),[21] were evolved. However, no hydridopalladium species was detected. It appears most probable that the $HSiCl_3$ solution we have prepared is inevitably contaminated with HCl, and that the presence of $HSiCl_3$, HCl, and complex **A** would have resulted in giving propene, $SiCl_4$ and a hydridopalladium species, $[HPd^+L_n]$ (**A′**) (L = ligand, substrate, or solvent),[22] which may play a key role in the catalytic process, as discussed below. Secondly, the coupling pattern of the hydrosilylative reactions between alkynes and alkenes was dramatically affected by using either catalyst precursor **A** or that modified with added PPh_3 (e.g., Eq. 1 vs. Eq. 2). Thus, a simple 1-alkyne undergoes hydropalladation, if reversible, with the catalyst **A′** containing PPh_3, a β-substituted intermediate, i.e., a distal alkenylpalladium intermediate, whereas reversed hydropalladation proceeds with the catalyst **A′** without PPh_3 to form preferentially an α-substituted, proximal alkenylpalladium one. These facts can be understood by a substantial change in effective steric bulk of the active catalyst **A′**.

Given **A′** plays a role in the reaction, as discussed above, a possible catalytic process for the reaction is depicted in Scheme 2. The initial step must be activation of an alkyne substrate by coordinating selectively to **A′**. The catalytic cycle may be explained in terms of elementary steps (i)–(iii) in Scheme 2. (i) Initial hydropalladation of the alkyne takes place, either in an α-directing or in a β-directing manner, to form an alkenylpalladium (**I**) (depicted α only for clarity). (ii) The latter, in turn, undergoes a rapid and specific alkene insertion, the direction of which is not regioselective without added PPh_3. (iii) The resulting homoallylic organopalladium (**II**) (depicted α-1 only) terminates one catalytic cycle by undergoing $HSiCl_3$ σ-metathesis, if any, to substitute the palladium center with a trichlorosilyl group, giving rise to coupling product(s), and, at the same time, regenerating **A′** as an active catalyst.



Scheme 2. Proposed catalytic cycle.

The reason why the step (ii) proceeds so selectively, if not regioselectively, may be explained as follows. Cationic alkenylpalladium **I** has a few ligands, exhibiting substantial electrophilicity that promotes a facile electrophilic addition to alkenes (carbopalladation).[23] It is emphasized that, even though alkenes were utilized in three-fold equivalents to alkynes, the observation of an exclusive alkene insertion to the alkenylpalladium **I** in step (ii), rather than a successive alkyne insertion,[4] is unprecedented.

In conclusion, we conceptually studied a new hydrosilylative cross-coupling reaction of a variety of alkynes with several alkenes, which is catalyzed by a cationic palladium complex **A** (1 mol %) in the absence or presence of an added PPh_3 ligand. The reaction, using $HSiCl_3$ as an addend, afforded more or less two types of coupling products consisting of four possible derivatives, $R^1CH{=}CR^2{-}CHR^3{-}CHR^4{-}SiCl_3$, that always contain 4-trichlorosilyl-1-butene frameworks, in acceptable combined yields.

Experimental

General. NMR spectra were recorded on a JEOL JNM FX 270 spectrometer (270 MHz for ^1H and 67.8 MHz for ^{13}C) in $CDCl_3$ or Bruker Avance 500 spectrometer (99.35 MHz for ^{29}Si) in CD_2Cl_2. Chemical shifts of the protons and the carbons are reported in δ and referenced to tetramethylsilane as an internal standard. IR spectra were recorded on a JEOL JIR-WINSPEC

50 spectrophotometer using a liquid film, absorptions being given in wavenumbers (cm^{-1}). GLC analyses were conducted on a Shimadzu GC-14B (equipped with programmed heating) chromatograph connected with a C-R6A chromatopack recorder. Preparative column chromatography employing silica gel (hexane–ethyl acetate) was performed according to the method of Still.[24] Elemental analyses for the representative cross-coupling products in this study were performed by the Kyoto University Microanalysis Center.

All moisture-sensitive manipulations were carried out under an argon atmosphere. All reactions were conducted in a 5 mL screw-capped testing tube containing a stirring bar. Dichloromethane was used after distillation over diphosphorus pentaoxide. Absolute ethanol and triethylamine distilled over calcium hydride were used for ethoxylation of trichlorosilyl derivatives. Hexane was distilled over sodium wire. Commercial trichlorosilane in an ampoule (25 mL) was always used as an 1 M CH_2Cl_2 solution, which was stored under argon in a 100-mL Schlenk tube. $[Pd(\eta^3\text{-}C_3H_5)(cod)]^+[PF_6]^-$ (**A**) was synthesized according to the literature procedure.[25] Triphenylphosphine was purified by recrystallization from ethanol. All alkenes and alkynes were purchased from Aldrich, Wako Chemicals, or Tokyo Chemical Ind. and used after distillation under reduced pressure. As for the reactions, yields have not been optimized.

Catalytic Hydrosilylative Cross-Coupling of Alkynes with Alkenes.[26] **Typical Procedure for Eq. 1: 2-Phenyl-3-(trichlorosilyl)methyl-1-heptene** (**1a**: α-1) and 2-phenyl-4-trichlorosilyl-1-octene (**2a**: α-2): A mixture of phenylacetylene (1 mmol), 1-hexene (3 mmol), and the catalyst **A** (1×10^{-2} mmol, 1 mol %) dissolved in dry CH_2Cl_2 (1 mL) was placed in a 5-mL screw-capped test tube under an argon atmosphere. To this solution was added $HSiCl_3$ (1 M, CH_2Cl_2, 1 mL), and the mixture was heated at 50 °C in a thermostated oil bath for 4 h. Color change of the reaction mixture was diagnostic of the end-point of reaction. GLC analysis of the reaction mixture ($3\,mm^{\phi} \times 3$ m column packed with SE-30 grease on Celite (10%) under programmed heating at a rate 10 °C min^{-1} from 100 °C (for 2 min) to 280 °C) revealed clearly that the reaction was complete, and that the peak area ratio of the cross-coupling products containing a trichlorosilyl group (T_R = 17.0 (**1a**) and 17.2 (**2a**) min) was estimated to be 60:40. A small amount of hydrosilylation products from 1-hexene, which were usually neglected, were also obtained. The products were directly subjected to bulb-to-bulb distillation under reduced pressure to give the regioisomeric products consisting of **1a** and **2a** (0.223 g, 70% combined yield). Little change in the ratio **1a** to **2a** except combined yields was observed by using 1 or 5 equiv of 1-hexene to phenylacetylene. They were separated by preparative GLC for the spectral identification. Spectral data for **1a**: ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 0.85 (t, J = 7.1 Hz, 3H), 1.2–1.4 (m, 6H), 1.67 (dd, J = 15.5, 7.3 Hz, 1H), 1.79 (dd, J = 15.5, 6.9 Hz, 1H), 3.03 (quint, J = 6.9 Hz, 1H), 5.12 (s, 1H), 5.29 (d, J = 0.7 Hz, 1H), 7.3–7.4 (aromatic H, 5H). ^{13}C NMR (67.8 MHz): δ 14.0, 22.6, 28.7, 29.8, 31.4, 39.1, 113.6, 126.9, 127.5, 128.3, 141.9, 151.8. Spectral data for **2a**: ^{1}H NMR: δ 0.85 (t, J = 7.1 Hz, 3H), 1.19 (quint, J = 7.1 Hz, 1H), 1.45–1.65 (m, 6H), 2.55 (ddd, J = 14.5, 10.2, 0.7 Hz, 1H), 3.09 (ddd, J = 14.5, 4.3, 0.7 Hz, 1H), 5.17 (d, J = 0.7 Hz, 1H), 5.36 (q, J = 0.7 Hz, 1H), 7.3–7.4 (aromatic H, 5H). ^{13}C NMR: δ 13.8, 22.8, 27.4, 29.9, 34.1, 35.8, 115.4, 126.5, 127.8, 128.5, 139.7, 145.8. The corresponding triethoxysilyl compounds **1b** and **2b** were derived from **1a** and **2a** for analytical purpose. The distilled sample obtained above was treated with an excess EtOH and Et_3N dissolved in CH_2Cl_2 in an ice-cooled bath for 1 h. Salt Et_3N/HCl formed was removed by repeated trituration with cold hexane and filtration through a short celite plug, and the filtrates were concentrated using a coolnit evaporator. The residual oil was purified by a bulb-to-bulb distillation under a reduced pressure to give products. If necessary, they were purified by a preparative GLC. Spectral data for **1b**: ^{1}H NMR: δ 0.83_4 (t, J = 7.1 Hz, 3H), 0.86 (dd, J = 15.2, 8.2 Hz, 1H), 0.95 (dd, J = 15.2, 6.4 Hz, 1H), 1.20 (t, J = 6.9 Hz, 9H), 1.3–1,4 (m, 6H), 2.81 (quint, J = 6.8 Hz, 1H), 3.79 (q, J = 6.9 Hz, 6H), 5.06 (d, J = 1.0 Hz, 1H), 5.18 (d, J = 1.3 Hz, 1H), 7.2–7.4 (m, aromatic, 5H). **2b**: ^{1}H NMR: δ 0.82_6 (t, J = 7.1 Hz, 3H), 1.22 (t, J = 6.9 Hz, 9H), 1.43–1.53 (m, 6H), 2.35 (ddd, J = 14.5, 10.7, 0.7 Hz, 1H), 2.93 (ddd, J = 14.5, 4.0, 0.8 Hz, 1H), 3.84 (q, J = 6.9 Hz, 6H), 5.06 (d, J = 1.0 Hz, 1H), 5.27 (q, J = 1.3 Hz, 1H), 7.2–7.4 (m, aromatic, 5H). Anal. Found: C, 68.25; H, 9.51%. Calcd for $C_{20}H_{34}O_3Si$ (**1b**): C, 68.52; H, 9.78%.

The procedure was applied for all other cross-coupling reactions catalyzed by the precursor **A** in the absence of PPh_3: see, Table 2.

Typical Procedure for Eq. 2, and Table 1: (*E*)-1-Phenyl-3-(triethoxysilyl)methyl-1-heptene (**3b**: β-1): A catalyst system consisting of the palladium complex **A** and PPh_3 (or other phosphorus ligand given in Table 1; 1 or 2 equiv) was employed, and the reaction of phenylacetylene (1 mmol) and 1-hexene (3 mmol) with $HSiCl_3$ (1 M, CH_2Cl_2, 1 mL) was conducted at 50 °C for 4 h, in exactly the same manner as for Eq. 1. The products of trichlorosilyl derivatives were detected by GLC analysis (T_R = 16.7 min (**3a**)), and isolated as triethoxy derivatives. In the case of Eq. 2, the distilled product **3a** was substantially a single one (0.203 g, 58% yield). Spectral data for **3a**: ^{1}H NMR: δ 0.89 (t, J = 6.6 Hz, 1H), 1.23–1.37 (m, 6H), 1.58 (dd, J = 15.2, 8.9 Hz, 1H), 1.68 (dd, J = 15.2, 5.3 Hz, 1H), 2.63 (qt, J = 8.9, 5.3 Hz, 1H), 5.95 (dd, J = 15.5, 9.2 Hz, 1H), 6.43 (d, J = 15.5 Hz, 1H), 7.2–7.4 (m, aromatic, 5H). **3b**: ^{1}H NMR: δ 0.80 (dd, J = 15.2, 7.4 Hz, 1H), 0.87 (t, J = 6.9 Hz, 3H), 0.89 (dd, J = 15.2, 6.6 Hz, 1H), 1.20 (t, J = 6.9 Hz, 9H), 1.17–1.45 (m, 6H), 2.31–2.45 (m, 1H), 3.80 (q, J = 6.9 Hz, 6H), 6.06 (dd, J = 15.7, 8.9 Hz, 1H), 6.33 (dd, J = 15.7, 0.3 Hz, 1H), 7.1–7.4 (m, aromatic, 5H). ^{13}C NMR: δ 14.1, 17.5, 18.3, 22.7, 29.6, 37.6, 38.1, 58.3, 126.0, 126.6, 128.2, 128.4, 137.0, 138.0. Anal. Found: C, 68.56; H, 9.77%. Calcd for $C_{20}H_{34}O_3Si$ (**3b**): C, 68.52; H, 9.78%.

Spectral and Certain Analytical Data for All Products Listed in Tables 2 and 3. Table 2, Entry 1: Phenylacetylene/1-Hexene, Same as for Eq. 1: Table 2, Entry 2: Phenylacetylene/Styrene: 2,3-Diphenyl-4-trichlorosilyl-1-butene (**4a**: α-1): ^{1}H NMR: δ 2.04 (dd, J = 15.2, 8.9 Hz, 1H), 2.15 (dd, J = 15.2, 6.6 Hz, 1H), 4.27 (ddd, J = 8.9, 6.6, 1.0 Hz, 1H), 5.27 (d, J = 1.0 Hz, 1H), 5.42 (s, 1H), 7.2–7.4 (aromatic H, 10H). ^{13}C NMR: δ 30.8, 45.1, 113.9, 126.9 (×2), 127.1, 127.5, 128.1 (×2), 128.2 (×2), 128.6 (×2), 141.4, 141.7, 151.3.

2,3-Diphenyl-4-triethoxysilyl-1-butene (**4b**): ^{1}H NMR: δ 1.12 (t, J = 6.9 Hz, 9H), 1.24 (dd, J = 15.2, 9.2 Hz, 1H), 1.35 (dd, J = 15.2, 5.9 Hz, 1H), 3.63 (q, J = 6.9 Hz, 6H), 4.09 (dd, J = 8.7, 6.4 Hz, 1H), 5.27 (t, J = 1.2 Hz, 1H), 5.33 (s, 1H), 7.1–7.3 (aromatic H, 10H). Anal. Found: C, 71.31; H, 8.23%. Calcd for $C_{22}H_{30}O_3Si$: C, 71.31; H, 8.16%.

2,4-Diphenyl-4-trichlorosilyl-1-butene (**5a**: α-2): ^{1}H NMR: δ 2.85 (dd, J = 11.5, 3.6 Hz, 1H), 3.06 (dd, J = 13.9, 11.5 Hz, 1H), 3.42 (dd, J = 13.9, 3.6 Hz, 1H), 4.94 (s, 1H), 5.13 (s, 1H), 7.2–7.4 (m, aromatic, 10 H). ^{13}C NMR: δ 34.8, 41.0, 115.6, 126.4 (×2), 127.3, 127.3, 128.5 (×4), 129.1 (×2), 135.5, 139.9, 144.9.

2,4-Diphenyl-4-triethoxysilyl-1-butene (**5b**): ^{1}H NMR: δ 1.14 (t, $J = 6.9$ Hz, 9H), 2.31 (dd, $J = 11.4$, 3.5 Hz, 1H), 2.86 (dd, $J = 15.3$, 11.4 Hz, 1H), 3.22 (dd, $J = 15.3$, 3.5 Hz, 1H), 3.70 (q, $J = 6.9$ Hz, 6H), 4.79 (d, $J = 0.7$ Hz, 1H), 5.05 (d, $J = 1.0$ Hz, 1H), 7.2–7.4 (m, aromatic, 10H).

(*E*)-1,3-Diphenyl-4-trichlorosilyl-1-butene (**6a**: β-1): ^{1}H NMR: δ 2.03 (dd, $J = 15.2$, 7.3 Hz, 1H), 2.07 (dd, $J = 15.2$, 7.9 Hz, 1H), 3.93 (q, $J = 7.7$ Hz, 1H), 6.32 (dd, $J = 15.8$, 7.9 Hz, 1H), 6.49 (d, $J = 15.8$ Hz, 1H), 7.2–7.4 (aromatic H, 10H).

(*E*)-1,3-Diphenyl-4-triethoxysilyl-1-butene (**6b**): ^{1}H NMR: δ 1.14_8 (t, $J = 6.9$ Hz, 9H), 1.24 (dd, $J = 15.2$, 7.3 Hz, 2H), 1.28 (dd, $J = 15.2$, 7.9 Hz, 1H), 3.60 (q, $J = 6.9$ Hz, 1H), 3.70 (q, $J = 6.9$ Hz, 6H), 6.37 (d, $J = 15.8$ Hz, 1H), 6.41 (dd, $J = 15.8$, 5.6 Hz, 1H), 7.15–7.35 (aromatic H, 10H). ^{13}C NMR: δ 18.2 (×3), 43.5 (×2), 58.3 (×3), 126.2 (×2), 126.9, 127.5 (×2), 128.3, 128.4 (×4), 135.9, 137.7, 146.0.

(*E*)-1,4-Diphenyl-4-triethoxysilyl-1-butene (**6′b**: β-2) was separated by column chromatography (Silica gel, hexane–ethyl acetate 2%) from a mixture with **6b**: ^{1}H NMR: δ 1.15_3 (t, $J = 6.9$ Hz), 2.32 (dd, $J = 10.1$, 5.4 Hz), 2.76 (centered m), 3.70 (q, $J = 6.9$ Hz), 6.14 (dt, $J = 15.8$, 6.8 Hz), 6.32 (d, $J = 15.5$ Hz), 7.15–7.35 (aromatic H). ^{13}C NMR δ 18.2 (×3), 33.7, 34.1, 58.8 (×3), 126.0 (×2), 126.7, 126.9, 127.9 (×2), 128.3 (×2), 128.7 (×2), 130.2, 130.4, 137.9, 141.4.

Table 2, Entry 3 and Table 3, Entry 3: 1-Heptyne/1-Hexene: 2-Pentyl-3-(trichlorosilyl)methyl-1-heptene (**7a**: α-1): ^{1}H NMR: δ 0.88 (t, $J = 7.4$ Hz, 3H), 0.89 (t, $J = 7.4$ Hz, 3H), 1.2–1.6 (m, 12H), 1.43 (dd, $J = 14.2$, 6.3 Hz, 1H), 2.00 (t, $J = 7.4$ Hz, 2H), 2.12 (dd, $J = 14.2$, 9.6 Hz, 1H), 2.49 (quint, $J = 7.1$ Hz, 1H), 4.82 (s), 4.86 (s).

2-Pentyl-3-(triethoxysilyl)methyl-1-heptene (**7b**): ^{1}H NMR: δ 0.81 (dd, $J = 14.4$, 7.6 Hz, 1H), 0.87 (t, $J = 7.3$ Hz, 6H), 0.88 (dd, $J = 14.4$, 7.4 Hz, 1H), 1.15–1.30 (br m, 12H), 1.22 (t, $J = 6.9$ Hz, 9H), 1.95 (quint, $J = 7.9$ Hz, 2H), 2.06 (m, 1H), 3.83 (q, $J = 6.9$ Hz, 6H), 4.69 (br s, 1H), 4.74 (s, 1H). ^{13}C NMR: δ 14.1, 18.3, 20.2, 22.6, 23.2, 22.7, 27.4, 28.4, 31.0, 35.1, 35.7, 41.1, 58.5, 109.8, 149.1.

2-Pentyl-4-trichlorosilyl-1-octene (**8a**: α-2): Diagnostic signals were hardly separated.

2-Pentyl-4-triethoxysilyl-1-octene (**8b**): ^{1}H NMR: δ 0.87 (t, $J = 7.3$ Hz, 3H), 0.89 (t, $J = 6.9$ Hz, 3H), 0.98 (m, 1H), 1.10–1.50 (m, 12H), 1.22 (t, $J = 6.9$ Hz, 9H), 1.99 (dd, $J = 14.2$, 7.3 Hz, 1H), 2.10 (t, $J = 7.3$ Hz, 2H), 2.30 (dd, $J = 14.2$, 3.3 Hz, 1H), 3.82 (q, $J = 6.9$ Hz, 6H), 4.69 (s, 1H), 4.72 (s, 1H). ^{13}C NMR: δ 14.1, 16.7, 18.3, 22.8, 23.2, 27.5, 28.4, 29.7, 31.7, 32.1, 35.1, 35.5, 58.3, 107.7, 154.3.

(*E*)-5-(Trichlorosilyl)methyl-6-dodecene (**9a**: β-1): ^{1}H NMR: δ 0.88 (t, $J = 6.9$ Hz, 6H), 1.2–1.4 (m, 12H), 1.45 (dd, $J = 15.2$, 9.2 Hz, 1H), 1.55 (dd, $J = 15.2$, 5.3 Hz, 1H), 1.98 (q, $J = 6.9$ Hz, 2H), 2.32–2.44 (m, 1H), 5.15 (dd, $J = 15.2$, 8.9 Hz, 1H), 5.46 (dd, $J = 15.2$, 6.9 Hz, 1H).

(*E*)-5-(Triethoxysilyl)methyl-6-dodecene (**9b**): ^{1}H NMR: δ 0.69 (dd, $J = 15.2$, 7.3 Hz, 1H), 0.73 (dd, $J = 15.2$, 6.6 Hz, 1H), 0.87 (t, $J = 6.9$ Hz, 3H), 0.88 (t, $J = 6.6$ Hz, 3H), 1.15–1.30 (m, 12H), 1.22 (t, $J = 6.9$ Hz, 9H), 1.96 (q, $J = 6.9$ Hz, 2H), 2.16 (m, 1H), 3.80 (q, $J = 6.9$ Hz, 6H), 5.23 (ddt, $J = 15.2$, 8.6, 0.7 Hz, 1H), 5.34 (dt, $J = 15.2$, 6.4 Hz, 1H) ^{13}C NMR: δ 14.1 (×2), 17.6, 18.3, 22.6, 22.7, 29.3, 29.7, 31.4, 32.5, 37.5, 37.7, 58.2, 128.8, 136.3. Anal. Found: C, 66.51, H, 11.79%. Calcd for $C_{19}H_{40}O_3Si$: C, 66.22, H, 11.70%.

Table 2, Entry 4 and Table 3, Entry 4: 1-Heptyne/Styrene: 2-[1-Phenyl-2-(trichlorosilyl)ethyl]-1-heptene (**10a**: α-1): ^{1}H NMR: δ 0.86 (t, $J = 6.9$ Hz, 3H), 1.2–1.6 (m, 6H), 1.94 (dd, $J = 15.2$, 8.6 Hz, 1H), 2.06 (dd, $J = 15.2$, 6.6 Hz, 1H), 2.27 (t, $J = 6.9$ Hz, 2H), 4.09 (q, $J = 6.8$ Hz, 1H), 6.35 (t, $J = 1$ Hz, 0.8H), 6.39 (t, $J = 1$ Hz, 0.8H), 7.20–7.30 (m, aromatic, 5H). **2-[1-Phenyl-2-(triethoxysilyl)ethyl]-1-heptene** (**10b**): ^{1}H NMR: δ 0.87 (t, $J = 6.8$ Hz, 3H), 1.09–1.23 (m, 6H), 1.22 (t, $J = 6.9$ Hz, 9H), 1.30 (dd, $J = 15.2$, 7.0 Hz, 1H), 1.40 (dd, $J = 15.2$, 7.3 Hz, 1H), 2.08 (t, $J = 6.9$ Hz, 2H), 3.80 (q, $J = 6.9$ Hz, 6H), 3.99 (q, $J = 6.9$ Hz, 1H), 6.18 (s, 1H), 6.22 (s, 1H), 7.13–7.29 (m, aromatic, 5H). ^{13}C NMR: δ 14.1, 18.2, 22.3, 22.5, 30.1, 31.7, 37.5, 41.3, 58.2, 125.8, 127.0, 128.1, 130.9, 146.4, 151.6.

2-[2-Phenyl-2-(trichlorosilyl)ethyl]-1-heptene (**11a**: α-2) could only be assigned as a minor component in a mixture with **10a**: ^{1}H NMR: δ 0.55 (d, $J = 2$ Hz, 0.2H), 5.58 (d, $J = 2$ Hz, 0.2H), diagnostic vinylidene protons. **(*E*)-2-Phenyl-1-trichlorosilyl-3-nonene** (**12a**: β-1): ^{1}H NMR: δ 0.87 (t, $J = 6.8$ Hz, 3H), 1.20–1.40 (m, 6H), 1.89 (dd, $J = 15.2$, 6.9 Hz, 1H), 1.95 (dd, $J = 15.2$, 8.4 Hz, 1H), 1.99 (m, 2H), 3.65–3.74 (m, 1H), 5.56 (dd, $J = 14.2$, 6.2 Hz, 1H), 5.57 (dd, $J = 14.2$, 6.2 Hz, 1H), 7.20–7.30 (m, aromatic, 5H). ^{13}C NMR: δ 14.0, 22.5, 28.8, 31.4, 31.7, 32.3, 43.5, 126.7, 127.1, 128.7, 131.6, 132.6, 144.3. **(*E*)-2-Phenyl-1-triethoxysilyl-3-nonene** (**12b**): ^{1}H NMR: δ 0.86 (t, $J = 6.9$ Hz, 3H), 1.10–1.30 (m, 6H), 1.15 (t, $J = 6.9$ Hz, 9H), 1.30 (dd, $J = 15.2$, 7.1 Hz, 1H), 1.40 (dd, $J = 15.2$, 7.3 Hz, 1H), 1.96 (q, $J = 6.9$ Hz, 2H), 3.69 (q, $J = 6.9$ Hz, 6H), 3.51 (q, $J = 7.6$ Hz, 1H), 5.41 (dtd, $J = 14.2$, 6.6, 1.0 Hz, 1H), 5.60 (ddt, $J = 14.2$, 7.3, 1.3 Hz, 1H), 7.15–7.28 (m, aromatic, 5H). ^{13}C NMR: δ 14.1, 18.2, 22.5, 29.1, 31.5, 32.4, 32.5, 43.1, 58.2, 125.8, 127.4, 128.2, 129.1, 135.5, 146.9.

Table 2, Entry 5 and Table 3, Entries 5 and 6: Methyl Propiolate/1-Hexene: Methyl 2-{1-[(trichlorosilyl)methyl]pentyl}-propenoate (**13a**: α-1): ^{1}H NMR: δ 0.89 (t, $J = 7.0$ Hz, 3H), 1.15–1.35 (m, 6H), 1.55 (dd, $J = 15.5$, 8.1 Hz, 1H), 1.62 (dd, $J = 15.5$, 6.1 Hz, 1H), 2.62 (m, 1H), 3.76 (s, 3H), 5.64 (br s, 1H), 6.27 (d, $J = 1.0$ Hz, 1H).

Methyl 2-{1-[(triethoxysilyl)methyl]pentyl}propenoate (**13b**): ^{1}H NMR: δ 0.86 (t, $J = 6.9$ Hz, 3H), 0.91 (d, $J = 7.6$ Hz, 2H), 1.21 (t, $J = 6.9$ Hz, 9H), 1.2–1.3 (m, 6H), 2.78 (quint, $J = 7.2$ Hz, 1H), 3.74 (s, 3H), 3.79 (q, $J = 6.9$ Hz, 6H), 5.54 (brs, 1H), 6.17 (d, $J = 1$ Hz, 1H). Diastereotopic hydrogens (2H) are not resolved. ^{13}C NMR: δ 14.1, 16.7, 18.2, 22.7, 29.4, 36.2, 36.3, 51.6, 58.3, 124.0, 145.4, 167.7. IR (neat): 2973.7, 2927.5, 2885.0, 2734.6, 1724.1, 1627.7, 1437.7, 1390.4, 1274.7, 1201.5, 958.5 cm^{-1}. Anal. Found C, 57.90; H, 9.49%. Calcd for $C_{16}H_{32}O_5Si$: C, 57.79; H, 9.70%.

Methyl 2-[2-(trichlorosilyl)hexyl]propenoate (**14a**: α-2): Spectral data of **14a** were obtained only for reference. **Methyl 2-[2-(triethoxysilyl)hexyl]propenoate** (**14b**): ^{13}C NMR: δ 14.1, 16.7, 18.3, 22.8, 29.3, 35.8, 36.5, 51.7, 58.5, 125.5, 140.1, 167.8.

Methyl (*E*)-4-(trichlorosilyl)methyl-2-octenoate (**15a**: β-1): ^{1}H NMR: δ 0.87 (t, $J = 7.0$ Hz, 3H), 1.27 (centered m, 6H), 1.70 (dd, $J = 15.5$, 6.3 Hz, 1H), 1.91 (dd, $J = 15.5$, 8.9 Hz, 1H), 2.90 (tt, $J = 8.7$, 5.9 Hz, 1H), 3.77 (s, 3H), 5.86 (dd, $J = 15.5$, 0.7 Hz, 1H), 6.75 (dd, $J = 15.5$, 9.2 Hz, 1H).

Methyl (*E*)-4-(triethoxysilyl)methyl-2-octenoate (**15b**): ^{1}H NMR: δ 0.73 (dd, $J = 15.2$, 6.9 Hz, 1H), 0.80 (dd, $J = 15.2$, 6.9 Hz, 1H), 0.87 (t, $J = 6.9$ Hz, 3H), 1.21 (t, $J = 6.9$ Hz, 9H), 1.2–1.3 (m, 6H), 2.4 (m, 1H), 3.72 (s, 3H), 3.80 (q, $J = 6.9$ Hz, 6H), 5.78 (dd, $J = 15.5$, 1.0 Hz, 1H), 6.83 (dd, $J = 15.5$, 8.9 Hz, 1H). ^{13}C NMR: δ 14.0, 16.5, 18.2, 22.6, 29.4, 36.4, 37.4, 51.4, 58.4, 119.3, 155.1, 167.4. IR (neat): 2973.7, 2927.5, 2885.0, 1726.0, 1654.6, 1435.8, 1269.9, 1104.0, 1081.9, 959.4 cm^{-1}.

Anal. Found C, 57.74; H, 9.40%. Calcd for $C_{16}H_{32}O_5Si$: C, 57.79; H, 9.70%.

Table 3, Entry 7: Methyl Propiolate/Styrene: Methyl 2-[(1-phenyl-2-triethoxysilyl)ethyl]propenoate (**16b**: α-1): ^{1}H NMR: δ 1.13 (t, $J = 6.9$ Hz, 9H), 1.20 (dd, $J = 15.2$, 8.9 Hz, 0.85H), 1.28 (dd, $J = 15.2$, 6.6 Hz, 0.85H), 3.64 (q, $J = 6.9$ Hz, 6H), 3.65 (s, 3H), 4.14 (t, $J = 7.9$ Hz, 0.85H), 5.76 (br s, 0.85H), 6.27 (s, 0.85H). 7.10–7.25 (m, aromatic, 5H). ^{13}C NMR: δ 17.2, 18.1, 41.2, 51.7, 58.2, 125.1, 126.3, 128.0, 128.1, 145.4, 153.6, 167.3.

Methyl 2-[(2-phenyl-2-triethoxysilyl)ethyl]propenoate (**17b**: α-2) could only be detected as a minor component in a mixture with **16b**: ^{1}H NMR: δ 2.51 (dd, $J = 15.5$, 3.6 Hz, 0.15H), 2.96 (dd, $J = 15.5$, 3.3 Hz, 0.15H) (diastereotopic hydrogens), 3.70 (t, $J = 3.5$ Hz, 0.15H) (a benzylic hydrogen), 5.26 (d, $J = 1.3$ Hz, 0.15H), 5.95 (d, $J = 1.3$ Hz, 0.15H) (vinylidene hydrogens).

Spectral Data for Products Listed in Table 4. Table 4, Entry 1: Phenylacetylene/(*E*)-3-Hexene: 3-Ethyl-2-phenyl-4-trichlorosilyl-1-hexene (**18a**: α): ^{1}H NMR: δ 0.95 (t, $J = 7.6$ Hz, 3H), 1.02 (t, $J = 7.1$ Hz, 3H), 1.33 (ddd, $J = 9.2$, 4.3, 2.6 Hz, 1H), 3.17 (dt, $J = 10.6$, 2.5 Hz, 1H), 5.07 (s, 1H), 5.45 (s, 1H) 7.20–7.40 (m, aromatic, 5H). Diastereotopic methylene hydrogens (4H) could not be resolved. ^{13}C NMR: δ 12.5, 14.5, 17.5, 22.2, 39.5, 44.8, 114.4, 126.7 (×2), 127.6, 128.5 (×2), 142.5, 148.0 (a *threo* isomer would be formed).

(*E*)-3-Ethyl-1-phenyl-4-trichlorosilyl-1-hexene (**19a**: β): ^{1}H NMR: δ 0.91 (t, $J = 7.4$ Hz, 3H), 1.09 (t, $J = 7.4$ Hz, 3H), 2.54 (ddt, $J = 9.6$, 7.6, 4.6 Hz, 1H), 6.10 (dd, $J = 15.5$, 9.6 Hz, 1H), 6.43 (d, $J = 15.5$ Hz, 1H), 7.20–7.35 (m, aromatic, 5H). Diastereotopic hydrogens (5H) hardly be assigned. ^{13}C NMR: δ 12.3, 13.5, 19.8, 26.2, 41.7, 44.8, 126.3 (×2), 127.0, 127.6 (×2), 131.5, 132.0, 137.2.

Table 4, Entry 2: 3-Hexyne/Allylbenzene: (*E*)-2-Benzyl-3-ethyl-1-trichlorosilyl-3-hexene (**20a**): ^{1}H NMR: δ 0.93 (t, $J = 7.6$ Hz, 3H), 0.97 (t, $J = 7.6$ Hz, 3H), 1.52 (dd, $J = 15.5$, 5.1 Hz, 1H), 1.61 (dd, $J = 15.5$, 9.1 Hz, 1H), 1.92 (q, $J = 7.6$ Hz, 2H), 1.98 (quint, $J = 7.3$ Hz, 2H), 2.6 (m, 1H), 5.20 (t, $J = 7.1$ Hz, 1H), 7.1–7.3 (m, aromatic, 5H). Benzylic protons were hardly assigned.

(*E*)-4-Ethyl-7-phenyl-6-trichlorosilyl-3-heptene (**21a**): ^{1}H NMR: δ 0.83 (t, $J = 7.6$ Hz, 3H), 0.94 (t, $J = 7.6$ Hz, 3H), 1.77 (m, 1H), 1.91 (q, $J = 7.3$ Hz, 2H), 1.98 (quint, $J = 7.3$ Hz, 2H), 2.15 (dd, $J = 14.2$, 8.9 Hz, 1H), 2.46 (dd, $J = 14.2$, 6.1 Hz, 1H), 2.73 (dd, $J = 14.2$, 7.6 Hz, 1H), 2.99 (dd, $J = 14.2$, 6.1 Hz, 1H), 5.22 (t, $J = 7.1$ Hz, 1H), 7.1–7.3 (m, aromatic 5H).

Table 4, Entry 3: Ethyl 2-Butynoate/1-Hexene: Ethyl (*Z*)-2-[1-(triethoxysilyl)methyl]pentyl-2-butenoate (**22b**: α-1): ^{1}H NMR: δ 0.86 (t, $J = 6.9$ Hz, 3H), 0.9–1.3 (m, 6H), 1.21 (t, $J = 6.9$ Hz, 9H), 1.30 (t, $J = 7.3$ Hz, 3H), 1.58 (d, $J = 7.2$ Hz, 2H), 1.89 (d, $J = 7.3$ Hz, 3H), 2.57 (quint, $J = 7.2$ Hz, 1H), 3.79 (q, $J = 6.9$ Hz, 6H), 4.21 (q, $J = 7.3$ Hz, 2H), 5.87 (q, $J = 7.3$ Hz, 1H). Diastereotopic hydrogens (2H) are not resolved. ^{13}C NMR: δ 14.1, 14.3, 15.5, 16.7, 18.2, 22.7, 29.6, 36.2, 38.9, 58.2, 59.8, 133.0, 138.1, 168.6. **Ethyl (*E*)-3-methyl-4-(triethoxysilyl)methyl-2-octenoate** (**23b**: β-1): ^{1}H NMR: δ 0.86 (t, $J = 6.9$ Hz, 3H), 1.0–1.6 (m, 6H), 1.13 (d, $J = 7.6$ Hz, 2H), 1.21 (t, $J = 6.9$ Hz, 9H), 1.28 (t, $J = 7.3$ Hz, 3H), 2.07 (s, 3H), 2.34 (m, 1H), 3.79 (q, $J = 6.9$ Hz, 6H), 4.15 (q, $J = 7.3$ Hz, 2H), 5.69 (s, 1H). Diastereotopic hydrogens (2H) are not resolved. ^{13}C NMR: δ 14.0, 14.4, 18.2, 18.3, 20.5, 23.0, 28.4, 30.9, 40.9, 58.5, 59.4, 116.5, 160.0, 166.8. Both compounds were found to be contaminated by a significant amount (in a ratio ca. 5:1 by GLC analysis) of respective regioisomers resulting from reversed insertion of 1-hexene component (presumably, α-2 and β-2), spectral data of the latter two being obtained only for diagnostic signals.

Table 4, Entry 4: Phenylacetylene/2-Methyl-1-pentene: (*E*)-3-Methyl-1-phenyl-3-(trichlorosilyl)methyl-1-hexene (**24a**: β-1): ^{1}H NMR: δ 0.90 (t, $J = 7.3$ Hz, 3H), 1.22–1.32 (m, 2H), 1.35 (s, 3H), 1.51–1.57 (m, 2H), 1.77 (d, $J = 15.3$ Hz, 1H), 1.79 (d, $J = 15.3$ Hz, 1H), 6.20 (d, $J = 16.4$ Hz, 1H), 6.33 (br d, $J = 16.4$ Hz, 1H). ^{13}C NMR: δ 14.5, 17.6, 25.5, 38.0, 39.0, 46.6, 126.2, 127.2, 127.5, 128.6, 131.9, 138.0.

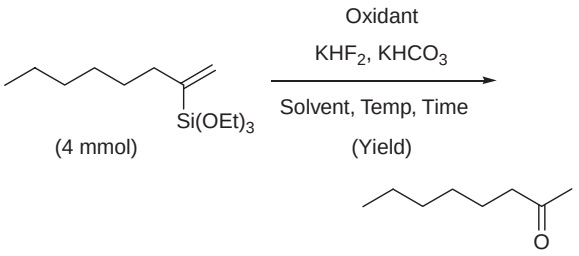
(*E*)-3-Methyl-1-phenyl-3-(triethoxysilyl)methyl-1-hexene (**24b**): ^{1}H NMR: δ 0.87 (t, $J = 7.3$ Hz, 3H), 0.90 (br s, 2H), 1.19 (t, $J = 6.9$ Hz, 9H), 1.20 (s, 3H), 1.24–1.33 (m, 2H), 1.38–1.51 (m, 2H), 3.80 (q, $J = 6.9$ Hz, 6H), 6.24 (d, $J = 16.5$ Hz, 1H), 6.30 (d, $J = 16.5$ Hz, 1H), 7.17 (t, $J = 7.3$ Hz, 1H), 7.28 (t, $J = 7.3$ Hz, 2H), 7.36 (d, $J = 7.3$ Hz, 2H). ^{13}C NMR: δ 14.8, 17.9, 18.2 (×3), 24.3, 26.1, 37.7, 46.1, 58.2 (×3), 125.2, 126.0 (×2), 126.5, 128.4 (×2), 138.3, 141.5. ^{13}C NMR: δ 14.1, 23.2, 25.4, 26.6, 38.0, 38.9, 44.0, 126.2, 127.2, 127.5, 128.6, 132.0, 138.0.

Table 4, Entry 4, Footnote g: Phenylacetylene/2-Methyl-1-hexene: (*E*)-3-Methyl-1-phenyl-3-(trichlorosilyl)methyl-1-heptene (**24′a**: β-1): ^{1}H NMR: δ 0.89 (t, $J = 6.9$ Hz, 3H), 1.22–1.31 (m, 4H), 1.35 (s, 3H), 1.53–1.58 (m, 2H), 1.77 (d, $J = 15.2$ Hz, 1H), 1.79 (d, $J = 15.2$ Hz, 1H), 6.22 (d, $J = 16.3$ Hz, 1H), 6.33 (d, $J = 16.3$ Hz, 1H), 7.20–7.45 (m, aromatic, 5H).

(*E*)-3-Methyl-1-phenyl-3-(triethoxysilyl)methyl-1-heptene (**24′b**): ^{1}H NMR: δ 0.87 (t, $J = 6.9$ Hz, 3H), 0.90 (br s, 2H), 1.15–1.31 (m, 4H), 1.19 (t, $J = 6.9$ Hz, 9H), 1.20 (s, 3H), 1.40–1.53 (m, 2H), 3.80 (q, $J = 6.9$ Hz, 6H), 6.24 (d, $J = 16.2$ Hz, 1H), 6.30 (d, $J = 16.2$ Hz, 1H), 7.20–7.45 (m, aromatic, 5H). ^{13}C NMR: δ 14.2, 18.3, 18.8, 23.4, 24.4, 26.1, 26.9, 37.6, 43.5, 58.2, 125.3, 126.0, 128.4, 138.0, 141.5. Anal. Found: C, 69.43; H, 10.05%. Calcd for $C_{21}H_{36}O_3Si$: C, 69.18; H, 9.95%.

Tamao Oxidation of Methyl 2-{1-[(Triethoxysilyl)methyl]-pentyl}propenoate (13b). Preparation of 2-Triethoxysilyl-1-octene (25): In a 100-mL three-necked round-bottomed flask, under an argon atmosphere, was placed a solution of 1-octyne (5.50 g, 50 mmol) and $HSi(OEt)_3$ (8.25 g, 50 mmol) dissolved in CH_2Cl_2 (50 mL). To this solution, cooled in an ice-water bath, was added $[Ru(cp^*)(NCMe)_3]^+[PF_6]^-$ (cp^* = pentamethylcyclopentadienyl)[27] (252.2 mg, 0.5 mmol; 1 mol %), and the mixture was stirred magnetically at room temperature for 2 h. The solvent was removed by evaporation, and the residue was distilled in vacuo to give crude products (11.2 g, 82% crude yield), GLC analysis of which revealed **25** and (*E*)-1-triethoxysilyl-1-octene[28] in a ratio of 90:10. Redistillation gave a purer sample (8.9 g, 65%), the isomer ratio being unchanged. **2-Triethoxysilyl-1-octene** (**25**): ^{1}H NMR: δ 0.88 (t, $J = 6.6$ Hz, 3H), 1.23 (t, $J = 6.9$ Hz, 9H), 1.23–1.32 (m, 6H), 1.38–1.50 (m, 2H), 2.14 (tt, $J = 7.8$, 1.5 Hz, 1.8H), 3.82 (q, $J = 6.9$ Hz, 6H), 5.63 (dt, $J = 3.3$, 1.0 Hz, 0.9H), 5.72 (dt, $J = 3.3$, 1.6 Hz, 0.9H). Diagnostic signals for **(*E*)-1-triethoxysilyl-1-octene**: 2.28 (qd, $J = 7.3$, 1.0 Hz, 0.2H), 5.29 (dt, $J = 14.2$, 1.3 Hz, 0.1H), 6.52 (dt, $J = 14.2$, 7.6 Hz, 0.1H). ^{13}C NMR: δ 14.1, 18.2, 22.6, 28.6, 29.1, 31.7, 36.0, 58.4, 129.0, 143.8.

Tamao Oxidation of 25: According to the literature procedure,[29] the following conditions were examined (see, Scheme 3) as a controlling experiment using **25**, affording 2-octanone in moderate yields: ^{1}H NMR: δ 0.88 (t, $J = 6.9$ Hz, 3H), 1.24–1.34 (m, 6H), 1.56 (br quint, $J = 7.3$ Hz, 2H), 2.14 (s, 3H), 2.42 (t, $J = 7.4$ Hz, 2H). a) Ac_2O–H_2O_2 (12 equiv)/KHF_2 (3 equiv)/no $KHCO_3$/DMF/rt, 7 h: Yield of 2-octanone 45%. b) H_2O_2 (6 equiv)/KHF_2 (3 equiv)/no $KHCO_3$/MeOH–THF/60 °C, 7 h:



Scheme 3. Oxidative cleavage of alkenylsilane.

49%. c) H_2O_2 (6 equiv)/KHF_2 (1 equiv)/$KHCO_3$ (1 equiv)/MeOH–THF/reflux, 6 h: 57%.

Thus, conditions a) and c) were adopted for the oxidation of **13b**.

Tamao Oxidation of 13b: d) In a similar manner as in a), 30% H_2O_2 (0.41 g, 12 mmol) and Ac_2O (1.23 g, 12 mmol) were added to a mixture of **13b** (0.67 g, 2.0 mmol) and KHF_2 (0.47 g, 6.0 mmol) dissolved in DMF (10 mL), and the whole mixture was stirred at room temperature for 14 h. The mixture was treated with a 10% $NaHSO_3$ solution (20 mL) and then extracted thoroughly with ether. After a usual work-up, the residual organic layer was purified by column chromatography to afford a colorless oil. Spectral data of this product indicate **methyl 2-[1-(hydroxymethyl)pentyl]propenoate** (0.09 g, 24%): ^{1}H NMR: δ 0.88 (t, $J = 6.9$ Hz, 3H), 1.20–1.34 (m, 4H), 1.50 (brq, $J = 7.2$ Hz, 2H), 1.74 (t, $J = 5.9$ Hz, OH); disappeared by added D_2O), 2.76 (dq, $J = 8.2$, 5.6 Hz, 1H), 3.67 (t, $J = 5.9$ Hz, 2H), 3.72 (s, 3H), 5.62 (d, $J = 1.0$ Hz, 1H), 6.30 (d, $J = 1.0$ Hz, 1H). IR: 3429, 2955, 2932, 2872, 2860, 1721 cm^{-1}. Acetylation of this unexpected γ-hydroxy carboxylic ester did form **methyl 2-[1-(acetoxymethyl)-pentyl]propenoate**: ^{1}H NMR: δ 0.88 (t, $J = 6.9$ Hz, 3H), 1.27 (centered m, 4H), 1.53 (br q, 2H), 2.02 (s, 3H), 2.92 (quint, $J = 6.9$ Hz, 1H), 3.77 (s, 3H), 4.10 (dd, $J = 10.9$, 7.3 Hz, 1H), 4.15 (dd, $J = 10.9$, 6.3 Hz, 1H), 5.59 (br s, 1H), 6.30 (s, 1H). ^{13}C NMR: δ 13.9, 20.9, 22.6, 29.2, 30.3, 40.2, 51.9, 66.5, 126.0, 140.6, 167.3, 171.0. IR: 2956, 2933, 2873, 2861, 1742, 1722, 1240 cm^{-1}. e) In a similar manner as in c), 30% H_2O_2 (0.41 g, 12 mmol) was added to a mixture of **13b** (1.13 g, 3.4 mmol), KHF_2 (0.32 g, 4.1 mmol), and $KHCO_3$ (0.51 g, 5.1 mmol) dissolved in MeOH (25 mL) and THF (25 mL), and the whole mixture was stirred at room temperature for 12 h. The mixture was treated with a saturated $Na_2S_2O_3$ solution (20 mL) and then extracted thoroughly with ether. After a usual work-up, the residual organic layer was purified by column chromatography to afford colorless oil, **3-butyl-2-methylene-butanolide**[18a] (0.12 g, 25% yield): ^{1}H NMR: δ 0.92 (t, $J = 7.2$ Hz, 3H), 1.20–1.50 (m, 6H), 2.98–3.10 (m, 1H), 3.98 (dd, $J = 8.9$, 5.9 Hz, 1H), 4.02 (dd, $J = 9.8$, 5.9 Hz, 1H), 5.59 (d, $J = 2.6$ Hz, 1H), 6.27 (d, $J = 2.6$ Hz, 1H).

Stoichiometric Reaction of [Pd(η^3-C_3H_5)(cod)]$^+$[PF_6]$^-$ (A) with $HSiCl_3$.[21] In a 5 mm$^\phi$ × 180 mm NMR tube, which has a joint to connect with the vacuum line (0.27 Pa), were placed under nitrogen a cationic palladium complex **A** (20.0 mg, 5×10^{-2} mmol) and CD_2Cl_2 (0.70 mL), and the resulting solution was subjected twice to freeze-thawing. To this solidified solution was added a chilled $HSiCl_3$ stock solution (50 µL, 1 M CH_2Cl_2, 5×10^{-2} mmol), and the mixture was immediately subjected once to freeze-thawing. The tube was sealed under vacuum. The ^{1}H NMR measurement of this sample at probe temperature (25 °C) was conducted at given time intervals to detect the evolution of free propene, while the mixture solution began soon to darken and became eventually turbid. The signal of CH_2Cl_2 (δ 5.33) was utilized as an internal standard for the extent of propene evolution, which ceased completely in 5 h. ^{29}Si NMR of this final sample exhibited a signal at δ −18.5 characteristic of $SiCl_4$.[1c]

This work was partly supported by a Grant-in-Aid from the Japan Society of Promotion of Sciences (No. 15550099), to which the authors' thanks are due. We thank Professors Y. Tsuji (Kyoto University) and K. Goto (The University of Tokyo) for their generous gift of a bowl-shaped phosphine, P(tm-tp)$_3$. We also thank UBE Scientific Analysis Laboratory, Inc. for ^{29}Si NMR measurements.

Supporting Information

The chemical names (9CI) and CAS Registry Numbers for the cross-coupling products, which have appeared in our preliminary communication (see, Ref. 13). This material is available free of charge on the Web at http://www.csj.jp/journals/bcsj/.

References

1 For reviews, see: a) I. Ojima, *The Hydrosilylation Reaction* in *The Chemistry of Organic Silicon Compounds*, ed. by S. Patai, Z. Rappoport, Wiley Interscience, New York, **1989**, Vol. 2, pp. 1479–1526. b) B. Marciniec, J. Gulinski, W. Urbaniak, Z. W. Kornetka, in *Comprehensive Handbook on Hydrosilylation*, ed. by B. Marciniec, Pergamon Press, Oxford, **1992**. c) M. A. Brook, *Silicon in Organic, Organometallic, and Polymer Chemistry*, John Wiley & Sons, New York, **2000**. d) K. Yamamoto, T. Hayashi, *Hydrosilylation of Olefins* in *Transition Metals for Organic Synthesis*, ed. by M. Beller, C. Bolm, Wiley-VCH, New York, **1998**, Vol. 2, pp. 120–131. e) K. Yamamoto, T. Hayashi, *Hydrosilylation of Olefins* in *Transition Metals for Organic Synthesis*, 2nd ed., ed. by M. Beller, C. Bolm, Wiley-VCH, New York, **2004**, Vol. 2, pp. 167–181.

2 a) A. J. Chalk, J. F. Harrod, *J. Am. Chem. Soc.* **1965**, *87*, 16. b) M. A. Schroeder, M. S. Wrighton, *J. Organomet. Chem.* **1977**, *128*, 345. c) S. Sakaki, M. Ogawa, Y. Musashi, T. Arai, *J. Am. Chem. Soc.* **1994**, *116*, 7258. d) S. Sakaki, N. Mizoe, M. Sugimoto, *Organometallics* **1998**, *17*, 2510; For a relevant review, see: J. Y. Corey, J. Braddock-Wilking, *Chem. Rev.* **1999**, *99*, 175.

3 For a review on addition of metalloid hydrides to alkynes, see: B. M. Trost, Z. T. Ball, *Synthesis* **2005**, 853.

4 Y. Kawanami, K. Yamamoto, *Synlett* **1995**, 1232.

5 a) Y. Kawanami, K. Yamamoto, 43rd Symposium on Organometallic Chemistry, Osaka: Japan, **1996**, Abstr., No. PB114. b) T. Uno, S. Wakayanagi, Y. Sonoda, K. Yamamoto, *Synlett* **2003**, 1997.

6 S. Wakayanagi, T. Shimamoto, M. Chimori, K. Yamamoto, *Chem. Lett.* **2005**, *34*, 160.

7 T. Shimamoto, T. Hirano, H. Nishimoto, K. Yamamoto, *Chem. Lett.* **2006**, *35*, 846.

8 a) I. Ojima, R. J. Donovan, W. R. Shay, *J. Am. Chem. Soc.* **1992**, *114*, 6580. b) I. Ojima, A. T. Vu, J. V. McCullagh, A. Kinoshita, *J. Am. Chem. Soc.* **1999**, *121*, 3230. c) I. Ojima, A. T. Vu, S.-Y. Lee, J. V. McCullagh, A. C. Moralee, M. Fujiwara, T. H. Hoang, *J. Am. Chem. Soc.* **2002**, *124*, 9164. d) T. Muraoka, I. Matsuda, K. Itoh, *Tetrahedron Lett.* **1998**, *39*, 7325. e) T. Muraoka, I. Matsuda, K. Itoh, *Organometallics* **2002**, *21*, 3650. f) C. Liu, R. A. Widenhoefer, *Organometallics* **2002**, *21*, 5666. g) H. Chakrapani, C. Liu, R. A. Widenhoefer, *Org. Lett.* **2003**, *5*, 157.

9 a) K. Tamao, K. Kobayashi, Y. Ito, *J. Am. Chem. Soc.*

1989, *111*, 6478. b) K. Tamao, K. Kobayashi, Y. Ito, *Synlett* **1992**, 539. c) For a related Ni^0-catalyzed dimerization of 1-alkynes, see: M. F. Lappert, T. A. Nile, S. Takahashi, *J. Organomet. Chem.* **1974**, *72*, 425.

10 a) R. A. Widenhoefer, M. A. DeCarli, *J. Am. Chem. Soc.* **1998**, *120*, 3805. b) R. A. Widenhoefer, A. Vadehra, *Tetrahedron Lett.* **1999**, *40*, 8499. c) R. A. Widenhoefer, C. N. Stengone, *J. Org. Chem.* **1999**, *64*, 8681. d) N. S. Perch, R. A. Widenhoefer, *J. Am. Chem. Soc.* **1999**, *121*, 6960. e) C. N. Stengone, R. A. Widenhoefer, *Tetrahedron Lett.* **1999**, *40*, 1451. f) N. S. Perch, P. Kisanga, R. A. Widenhoefer, *Organometallics* **2000**, *19*, 2541. g) X. Wang, H. Chakrapani, C. N. Stengone, R. A. Widenhoefer, *J. Org. Chem.* **2001**, *66*, 1755. h) X. Wang, S. Z. Stankovich, R. A. Widenhoefer, *Organometallics* **2002**, *21*, 901.

11 a) J. W. Madine, X. Wang, R. A. Widenhoefer, *Org. Lett.* **2001**, *3*, 385. b) X. Wang, H. Chakrapani, J. A. Madine, M. A. Keyerleber, R. A. Widenhoefer, *J. Org. Chem.* **2002**, *67*, 2778.

12 For a discussion about the mechanistic crossover, see: a) Y. Maruyama, K. Yamamura, T. Sagawa, H. Katayama, F. Ozawa, *Organometallics* **2000**, *19*, 1308. b) F. Ozawa, *J. Organomet. Chem.* **2000**, *611*, 332.

13 For a preliminary report, see: T. Shimamoto, M. Chimori, H. Sogawa, K. Yamamoto, *J. Am. Chem. Soc.* **2005**, *127*, 16410.

14 In the chemical formula, the designations α or β and 1 or 2 refer to the carbopalladation that occur at α or β position of the 1-alkyne employed, and C–Si bond occurring at terminal or internal carbon of the 1-alkene counterpart, respectively.

15 Immediate reaction products consist of α's (> 90%), a little β isomer (<5%) and others on the basis of GLC analysis, the latter two being hardly isolated at this stage.

16 A bowl-shaped phosphine, $P(tm\text{-}tp)_3$ = tris{2,2″,6,6″-tetramethyl-*m*-terphenyl-5′-yl}-phosphine: a) K. Goto, Y. Ohzu, H. Sato, T. Kawashima, *Phosphorus, Sulfur Silicon Relat. Elem.* **2002**, *177*, 2179. b) O. Niyomura, T. Iwasawa, N. Sawada, M. Tokunaga, Y. Obora, Y. Tsuji, *Organometallics* **2005**, *24*, 3468. An intriguing nature of a Rh complex that contains $P(tm\text{-}tp)_3$ in the hydrosilylation of ketones is discussed by Tsuji et al.

17 In this regard, it should be mentioned that, in the hydrosilylative cross-coupling of 1-heptyne with 1-hexene (3 equiv) in the presence of catalyst **A**, $P(C_6F_5)_3$ caused very rapid conversion at room temperature, giving rise to products (55% yield) in **7a** (α-1):**9a** (β-1) = 22:78 (see, Table 3, Entry 3, footnote e). Thus, the fact that phenylacetylene, (**1b** (α-1) + **2b** (α-2)):**3b** (β-1) = 85:15 (Table 1, Entry 5), and 1-heptyne show contrasting regioselectivities well reinforces that $P(C_6F_5)_3$ as a ligand exhibits a reversed electronic effect on the hydropalladation step for these two alkynes.

18 a) 3-Butyl-2-methylenebutanolide = 4-Butyl-3-methylene-4,5-dihydro-2(3*H*)furanone: E. Roeder, H. Krauss, *Ann. Chim.* **1992**, 177. b) 2-Methylene-3-phenylbutanolide: H. Nishiyama, H. Yokoyama, S. Narimatsu, K. Itoh, *Tetrahedron Lett.* **1982**, *23*, 1267.

19 Reversivility of the hydropalladation in the Pd-catalyzed alkadiynes has not been established. However, reversible silylpalladation in the case of alkadienes under similar reaction conditions are discussed. See: X. Wang, H. Chakrapani, C. N. Stengone, R. A. Widenhoefer, *J. Org. Chem.* **2001**, *66*, 1755.

20 With regard to this discussion, Hayashi et al. have observed that the reaction of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ with $HSiEt_3$ in the presence of a diphosphine generates a Pd^0L_2 species together with $ClSiEt_3$ and propene. The reaction with $HSiCl_3$ and PPh_3 should also produce a Pd^0 species. See: Y. Uozumi, H. Tsuji, T. Hayashi, *J. Org. Chem.* **1998**, *63*, 6137; Hydrosilylation of 1,5- and 1,3-cyclooctadiene has long been known to be catalyzed easily by various types of Pt catalysts: K. Yamamoto, M. Kumada, *J. Organometal. Chem.* **1968**, *13*, 131.

21 Stoichiometric reactions of π-allylic palladium(II) complexes containing phosphorus ligand or *N*-heterocyclic carbene ligand with $HSiCl_3$ will be discussed elsewhere: N. Takaoka, B.S. Thesis, Tokyo University of Science, Yamaguchi, **2004**.

22 K. K. Hii, *Hydridopalladium Complexes* in *Handbook of Organopalladium Chemistry for Organic Synthesis*, ed. by E. Negishi, Wiley Interscience, New York, **2002**, Vol. 1, pp. 81–90.

23 A cationic arylpalladium species is known to undergo a facile alkene insertion in the Mizoroki–Heck reaction: F. Ozawa, T. Hayashi, *J. Am. Chem. Soc.* **1991**, *113*, 1417; For a relevant review, see: T. Nishikata, N. Miyaura, *Shokubai* **2005**, *47*, 619.

24 W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923.

25 D. A. White, *Inorg. Synth.* **1972**, *13*, 61.

26 Throughout this section, all chemical names for the products of hydrosilylative cross-coupling of alkynes with alkenes are given on the basis of common 4-organosilyl-1-butene frameworks, $R^1CH{=}CR^2{-}CHR^3{-}CHR^4{-}SiX_3$ (X = Cl or OEt) and not consonant with those by CAS (9CI).

27 B. M. Trost, Z. T. Ball, *J. Am. Chem. Soc.* **2001**, *123*, 12726, and references cited therein.

28 M. R. Chaulagain, G. M. Mahandru, J. Montgomery, *Tetrahedron* **2006**, *62*, 7560.

29 K. Tamao, N. Ishida, T. Tanaka, M. Kumada, *Organometallics* **1983**, *2*, 1694.