

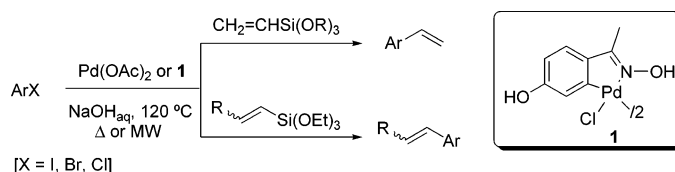
Aqueous Sodium Hydroxide Promoted Cross-Coupling Reactions of Alkenyltrialkoxysilanes under Ligand-Free Conditions[†]

Emilio Alacid and Carmen Nájera*

Departamento de Química Orgánica, Facultad de Ciencias, and Instituto de Síntesis Orgánica (ISO),
Universidad de Alicante, Apdo. 99, 03080-Alicante, Spain

cnajera@ua.es

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Fluoride-free cross-coupling reactions of alkenyltrialkoxysilanes with aryl iodides, bromides, and chlorides are performed on water using sodium hydroxide as activator at 120 °C under normal or microwave heating. This process occurs in the presence of Pd(OAc)₂ or 4-hydroxyacetophenone oxime-derived palladacycle **1** as precatalysts under ligand-free conditions with low Pd loadings (0.01–1 mol %) and using tetra-*n*-butylammonium bromide as additive. Different commercially available vinylalkoxysilanes can be cross-coupled under these reaction conditions to the corresponding styrenes, the best substrates being vinyltrimethoxy- or vinyltriethoxysilane. Alkenyltriethoxysilanes, prepared by Wilkinson-catalyzed hydrosilylation of alkynes with triethoxysilane, are stereospecifically arylated with aryl and vinyl halides under microwave irradiation in moderate to high β/α regioselectivity affording unsymmetrical stilbenes, alkenylbenzenes, and conjugate dienes, respectively. This simple procedure allows the palladium recycling from the aqueous phase during three runs by extractive separation of the products, which contain very low levels of Pd (21–27.5 ppm for an aryl iodide and up to 76 ppm for a bromide).

Introduction

Palladium-catalyzed alkenylation reactions of aryl halides can be performed using two important strategies, namely the Mizoroki–Heck reaction and cross-coupling processes. When following this last strategy, several vinylating reagents can be used, such as alkenylmagnesium, zinc, tin, boron, trifluoroborates, and silicon compounds.¹ The use of organosilicon compounds, initiated by Hiyama and co-workers,² have many advantages in comparison to other organometallic donors.³ Organosilicon compounds present high stability, low toxicity, and high accessibility and are therefore excellent candidates for

industrial processes. However, the lower number of applications of the Hiyama reaction is attributed to the requirement of the corrosive fluoride anion for the activation of organosilanes. The cross-coupling of alkenylsilanes has been performed mainly with aryl iodides under the activation of tetra-*n*-butylammonium fluoride (TBAF). Initially, only vinyltrimethylsilane could be coupled by activation with difluorotrimethylsilicate (TASF) or TBAF.² The C–Si bond has been further activated using alkenylfluorosilanes,⁴ alkenylalkoxysilanes,⁵ and organosilanols,⁶ in the presence of a heteroatom on the silicon, with at least one oxygen function necessary. Denmark and co-workers have recently described the potassium trimethylsilanolate (TMSOK), sodium and potassium hydride, sodium *tert*-butoxide, and cesium carbonate activation of alkenylsilanols and trialkoxysilanes.⁷ Potassium carbonate has been used for the cross-coupling of alkenyl[(2-hydroxymethyl)phenyl]dimethylsilanes.⁸

* To whom correspondence should be addressed. Fax: +34 965903549.

[†] Dedicated to the memory of Professor Yoshihiko Ito.

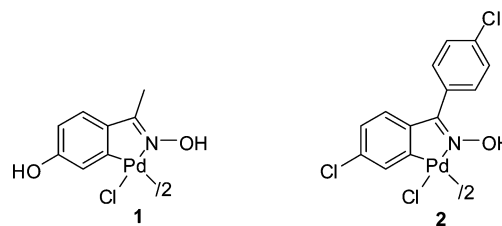
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Only two examples have been described reporting the vinylation of activated aryl bromides and chlorides using vinyltrimethoxysilane and TBAF as activator.⁹ The use of inorganic bases, such as sodium or potassium hydroxide and potassium carbonate as activators for the cross-coupling of arylhalosilanes,¹⁰ silicone,¹¹ and aryltrimethoxysilanes,¹² have been carried out in water as solvent. We have recently described the fluoride-free Hiyama reaction of aryltrialkoxysilanes¹³ and vinyltrialkoxysilanes¹⁴ with aryl bromides and chlorides using sodium hydroxide as activator under thermal and microwave conditions. These processes took place using either Pd(OAc)₂ or phenone oxime-derived palladacycles **1** and **2** as catalysts¹⁵ under low Pd loading and very simple reaction conditions.¹⁶ We report herein a full account about the vinylation of aryl iodides, bromides and chlorides with different vinyltrialkoxysilanes promoted by aqueous sodium hydroxide, using either palladium salts or palladacycle **1** directed to the synthesis of

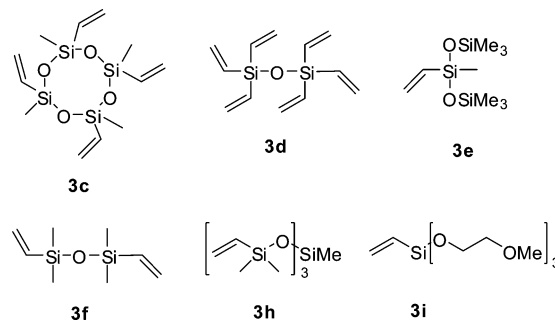
styrenes. The regio- and diastereoselectivity in the arylation and vinylation of alkenyltrialkoxysilanes for the synthesis of stilbenes, alkenylbenzenes, and conjugate dienes has also been studied. Attempts for simple product separation and Pd recycling experiments under these reaction conditions were also considered.



Results and Discussion

Initial studies were performed with 4-bromoacetophenone as an activated aryl bromide with different vinyltrialkoxysilanes and alkaline hydroxides on water as solvent under microwave irradiation at 120 °C during 10 min (Table 1). In the presence of 0.5 mol % of palladium acetate, the cross-coupling with vinyltrimethoxysilane (**3a**) took place in higher yield using sodium rather than potassium hydroxide (Table 1, entries 1 and 2). When 0.5 mol % of other palladium sources, such as palladium dichloride, palladium on carbon, and palladacycles **1** and **2**, were used, only complex **1** gave a quantitative yield (Table 1, entries 3–6). Using complex **1** as precatalyst and the several commercially available vinylalkoxysilanes **3b–i** (Table 1, entries 7–14), only vinyltriethoxysilane (**3b**) and **3i** gave yields similar to those of **3a** (Table 1, compare entry 1 with 7 and 14, respectively). The cross-coupling with vinyltrialkoxysilane **3i** was also performed using palladium acetate as catalyst, giving 4-vinylacetophenone in slightly lower yield than with complex **1** (Table 1, compare entries 14 and 15).

Next, the Pd loading of complex **1**, for the cross-coupling of the best silane **3a**, was decreased to 0.1 mol %, resulting in a lowered yield from 99 to 71%, which could be restored to 99% by addition of 0.5 equiv of tetra-*n*-butylammonium bromide (TBAB) (Table 1, entries 16 and 17). In the case of using 0.1 mol % of palladium diacetate, a 90% yield was obtained in the presence of TBAB (Table 1, entry 18). However, a poor yield was obtained when 0.01 mol % of palladium was employed (Table 1, entry 19).



The scope of the vinylation reaction was studied with aryl iodides under thermal and microwave conditions using both

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TABLE 1. Optimization of the Palladium-Catalyzed Hiyama Reaction of Vinyltrialkoxysilanes and 4-Bromoacetophenone^a

entry	vinylsilane	cat. (mol% Pd)	base	additive	yield ^b (%)
1	CH ₂ =CHSi(OMe) ₃ (3a)	Pd(OAc) ₂ (0.5)	NaOH		97 (90)
2	CH ₂ =CHSi(OMe) ₃ (3a)	Pd(OAc) ₂ (0.5)	KOH		66
3	CH ₂ =CHSi(OMe) ₃ (3a)	PdCl ₂ (0.5)	NaOH		87
4	CH ₂ =CHSi(OMe) ₃ (3a)	Pd/C (0.5)	NaOH		12
5	CH ₂ =CHSi(OMe) ₃ (3a)	1 (0.5)	NaOH		99
6	CH ₂ =CHSi(OMe) ₃ (3a)	2 (0.5)	NaOH		0
7	CH ₂ =CHSi(OEt) ₃ (3b)	1 (0.5)	NaOH		90
8	3c	1 (0.5)	NaOH		21
9	3d	1 (0.5)	NaOH		7
10	3e	1 (0.5)	NaOH		19
11	3f	1 (0.5)	NaOH		27
12	CH ₂ =CHSiMe(OMe) ₂ (3g)	1 (0.5)	NaOH		57 ^c
13	3h	1 (0.5)	NaOH		0 ^d
14	3i	1 (0.5)	NaOH		87
15	3i	Pd(OAc) ₂ (0.5)	NaOH		81 (70)
16	CH ₂ =CHSi(OMe) ₃ (3a)	1 (0.1)	NaOH		71
17	CH ₂ =CHSi(OMe) ₃ (3a)	1 (0.1)	NaOH	TBAB	99
18	CH ₂ =CHSi(OMe) ₃ (3a)	Pd(OAc) ₂ (0.1)	NaOH	TBAB	90
19	CH ₂ =CHSi(OMe) ₃ (3a)	1 (0.01)	NaOH	TBAB	6

^a Reaction conditions: 4-bromoacetophenone (0.5 mmol), silane **3** (1 mmol), catalyst (see column), base (1.25 mmol), TBAB (0.25 mmol, see column), water (1 mL), microwave reactor at 120 °C (40–45 W, 2–5 bar) with air stream cooling. ^b Determined by ¹H NMR using diphenylmethane as internal standard. The yield after flash chromatography is shown in parentheses. ^c A 7% yield of 4,4'-diacetyl biphenyl was also obtained. ^d An 8% yield of 4-methylacetophenone was obtained.

TABLE 2. Palladium-Catalyzed Hiyama Reaction of Vinyltrialkoxysilanes and Aryl Iodides^a

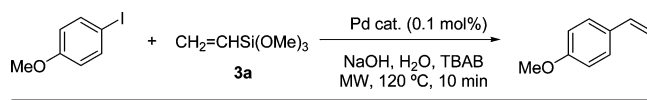
entry	ArI	vinylsilane	cat. (mol% Pd)	additive	heating	time	product	yield ^b (%)
1	4-methoxyiodobenzene	3a	Pd(OAc) ₂ (0.1)		MW	10 min	4-methoxystyrene	90
2		3a	1 (0.1)		MW	10 min		93 (82)
3		3a	Pd(OAc) ₂ (0.1)		Δ	3 h		89
4		3a	1 (0.1)		Δ	3 h		96
5		3a	Pd(OAc) ₂ (0.1)	TBAB	MW	10 min		98
6		3a	1 (0.1)	TBAB	MW	10 min		99
7		3a	Pd(OAc) ₂ (0.01)	TBAB	Δ	4 h		89
8		3a	1 (0.01)	TBAB	Δ	4 h		81
9		3b	1 (0.1)		MW	10 min		93 (84)
10		3i	1 (0.1)		MW	10 min		91
11		3i	1 (0.1)		Δ	3 h		88 (79)
12	1-iodonaphthalene	3a	Pd(OAc) ₂ (0.1)	TBAB	MW	10 min	1-vinylnaphthalene	83
13		3a	1 (0.1)	TBAB	MW	10 min		94
14		3a	Pd(OAc) ₂ (0.1)	TBAB	Δ	3 h		81 (70)
15		3a	1 (0.1)	TBAB	Δ	3 h		84
16		3i	1 (0.5)		MW	10 min		81 (73)
17	4-benzyloxyiodobenzene	3a	Pd(OAc) ₂ (0.5)	TBAB	MW	15 min	4-benzyloxystyrene	94 (60)
18		3a	1 (0.5)	TBAB	MW	15 min		85
19		3a	Pd(OAc) ₂ (0.5)	TBAB	Δ	3 h		89
20		3a	1 (0.5)	TBAB	Δ	3 h		95
21	3,5-dimethoxyiodobenzene	3a	Pd(OAc) ₂ (0.1)	TBAB	MW	15 min	3,5-dimethoxystyrene	83 (79)
22		3a	1 (0.1)	TBAB	MW	15 min		71
23	4-chloriodobenzene	3a	Pd(OAc) ₂ (0.1)		MW	10 min	4-chlorostyrene	89 (84)
24		3a	1 (0.1)		MW	10 min		85
25		3a	Pd(OAc) ₂ (0.1)	TBAB	Δ	3 h		89
26		3a	1 (0.1)	TBAB	Δ	3 h		96

^a Reaction conditions: aryl iodide (0.5 mmol), silane **3** (1 mmol), catalyst (see column), NaOH (1.25 mmol), TBAB (0.25 mmol, see column), water (1 mL), microwave reactor at 120 °C (40–45 W, 2–5 bar) with air stream cooling or conventional heating in a pressure tube at 120 °C bath temperature.

^b Determined by ¹H NMR using diphenylmethane as internal standard. The yield after flash chromatography is shown in parentheses.

catalysts, palladium acetate and palladacycle **1**, in aqueous sodium hydroxide (Table 2). The arylation of vinyltrimethoxysilane (**3a**) with 4-iodoanisole took place in 86–99% yields with a 0.1 mol % palladium loading of both catalysts and under

thermal or microwave heating in the absence or in the presence of TBAB (Table 2, entries 1–6). Alternatively, vinyltriethoxysilane (**3b**) and vinyltris(2-methoxyethoxy)silane (**3i**) gave yields similar to those of **3a** under microwave (Table 2, compare

TABLE 3. Recycling Experiments of the Palladium-Catalyzed Hiyama Reaction of Vinyltrimethoxysilane and 4-Iodoanisole^a


entry	Pd(OAc) ₂		complex 1	
	yield ^b (%)	Pd leaching ^c (ppm)	yield (%)	Pd leaching ^c (ppm)
1	98	27.5	99	22.2
2	99 ^d	22.2	96 ^e	21.7
3	81 ^f	24.8	99 ^g	21.0
4	66 ^h		56 ⁱ	

^a Reaction conditions: 4-iodoanisole (0.5 mmol), **3a** (1 mmol), catalyst (0.1 mol % Pd), NaOH (1.25 mmol), TBAB (0.25 mol), water (1 mL), microwave reactor at 120 °C (40–45 W, 2–5 bar) with air stream cooling.

^b Determined by ¹H NMR using diphenylmethane as internal standard.

^c Determined in the crude product by ICP-OES. ^d A 10% yield of anisole was also obtained. ^e A 1% yield of anisole was also obtained. ^f A 6% yield of anisole was also obtained. ^g A 2% yield of anisole was also obtained.

^h A 20% yield of anisole was also obtained. ⁱ A 5% yield of anisole was also obtained.

entry 2 with 9 and 10) or conventional thermal (Table 2, compare entry 4 with 11) conditions. The palladium loading could be decreased to 0.01 mol % when the palladium nanoparticles stabilizer TBAB was present in the reaction medium (Table 2, entries 7 and 8).

Recycling experiments and leaching analyses were performed for the reaction of vinyltrimethoxysilane (**3a**) and 4-iodoanisole using 0.1 mol % palladium of palladacycle **1** and palladium diacetate as precatalysts under microwave conditions in the first run (Table 3). After finishing each cycle, the reaction was extracted with diethyl ether, and the reagents with the exception of the catalyst were added again to the aqueous phase. During the three first runs, complex **1** gave a much better performance than palladium diacetate, and the reduction of 4-iodoanisole to anisole occurred in a lower ratio using the palladacycle. Unfortunately, the yield during the fourth run decreased for the same reaction time to 66% and 56%. ICP-OES analyses of the obtained crude product indicate relative low levels of Pd in the range of 21.0–27.5 ppm.¹⁷

Parallel studies with palladium acetate and palladacycle **1** were performed for the cross-coupling of aryl bromides and activated aryl chlorides using vinyltrimethoxysilane (**3a**) in aqueous sodium hydroxide under thermal and microwave reaction conditions in the presence of TBAB as additive, affording the corresponding styrenes generally in good to excellent yields (Table 4). Different activated and deactivated aryl bromides resulted vinylated much more efficiently under microwave than under thermal conditions. The palladium loading was increased from 0.1 for 4-bromoacetophenone (Table 4, entries 1–4) to 1 mol % for deactivated bromides (Table 4, entries 5–12). In the case of 2-bromo-6-methoxynaphthalene and β -styryl bromide, the loading was decreased to 0.5 mol % (Table 4, entries 13–20). Starting from the first substrate, 2-methoxy-6-vinylnaphthalene,¹⁸ an intermediate in the synthesis of naproxene,¹⁹ was isolated in 83% yield using complex **1** under microwave irradiation (Table 4, entry 14). For the cross-coupling of **3a** with 3-bromopyridine, the reaction was performed with 1 mol % of Pd using palladacycle **1** under microwave heating (Table 4, entry

21). Activated aryl chlorides, such as 4-chloroacetophenone and benzophenone, only reacted under microwave conditions with 2 mol % of palladium loading to provide the corresponding styrenes in good yields (Table 4, entries 22–25).

For the recycling experiments, the reaction of 4-bromoacetophenone and vinyltrimethoxysilane was performed using both catalysts in the microwave reactor (Table 5). From these studies, it was found that palladacycle gave much better efficiency than palladium diacetate. Thus, complex **1** was active at least during six cycles, whereas palladium diacetate gave good yields only during four cycles. In addition, the reduction of the corresponding bromide to acetophenone was also lower in the case of using the palladacycle. Concerning the leaching of palladium(0) in the final product, this was very low in the two first runs but more than 54 ppm were found in the crude product after the fourth cycle according to ICP-OES analyses.

In all experiments carried out with vinyltrialkoxysilanes **3**, the competition of a Mizoroki–Heck reaction to give the corresponding 2-arylethenyltrialkoxysilanes was never observed. In some experiments, the consecutive Hiyama–Heck reactions to afford symmetrical substituted stilbenes^{16b} occurred, although these byproducts were observed in less than 5%.

This vinylation process was applied to the synthesis of unsymmetrical stilbenes and other alkenes using β -substituted vinyltriethoxysilanes **4**. These compounds were prepared quantitatively by hydrosilylation of phenylacetylene and oct-1-yne with triethoxysilane catalyzed by in situ generated tris(triphenylphosphine)rhodium(I) iodide from Wilkinson's catalyst and NaI²⁰ (Scheme 1). In the case of **4a**²⁰ and using a 1:1 stoichiometry, a 67:33 *E/Z* mixture of diastereomers was obtained after 1 d at 60 °C, whereas 95:5 or 92:8 diastereomeric ratios were observed after 19 h reaction time when 2 equiv of triethoxysilane were used. For the hydrosilylation of oct-1-yne, 2 equiv of triethoxysilane was employed affording the alkenyltriethoxysilane **4b**²¹ as a mixture 84:16 of *E/Z* diastereomers after 16 h at 60 °C.

The cross-coupling of alkenyltriethoxysilanes with different aryl halides was performed under the above-mentioned reaction conditions, in aqueous NaOH, TBAB as additive at 120 °C under microwave heating using palladacycle **1** or Pd(OAc)₂ both as precatalysts (Table 6). In the arylation of styryltriethoxysilane **4a** and octenyltriethoxysilane **4b** with 4-iodoanisole the reaction was rather effective with only 0.1 mol % of Pd in 10 min, but mixtures of β - and α -regioisomers were obtained (Table 6, entries 1–3). The reaction was stereospecific toward the β -regioisomer in the case of styryltriethoxysilane **4a**, whereas a 86:14 mixture of *E/Z* diastereomers of **4b** gave mixtures up to 61:39 of the corresponding *E/Z*-stilbene. However, when 4-bromoanisole was used for the cross-coupling with **4a** instead of 4-iodoanisole, a higher β/α regioselectivity (3.7:1) was obtained (Table 6, compare entry 1 and 4). When a more hindered 1-bromonaphthalene was coupled with **4a**, a higher regioselectivity β/α up to 13:1 was observed and the reaction was again stereospecific for the *E*-stilbene (Table 6, entries

(18) This compound can be also prepared by Mizoroki–Heck reaction of ethylene and 2-bromo-6-methoxynaphthalene at 140 °C and 20 bar: Reetz, M. T.; Lohmer, G.; Schwickardi, R. *Angew. Chem., Int. Ed.* **1998**, 37, 481–483.

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TABLE 4. Palladium-Catalyzed Hiyama Reaction of Vinyltrimethoxysilane and Aryl Bromides and Chlorides^a

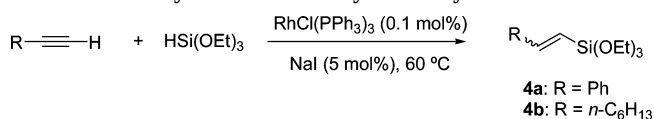
$\text{ArX} + \text{CH}_2=\text{CHSi}(\text{OMe})_3 \xrightarrow[\text{NaOH, H}_2\text{O, } \Delta \text{ or MW, 120 } ^\circ\text{C}]{\text{Pd cat.}} \text{Ar}-\text{CH}=\text{CH}_2$ 3a (X = Br, Cl)						
entry	ArX	cat. (mol% Pd)	heating	t	product	yield ^b (%)
1	4-bromoacetophenone	Pd(OAc) ₂ (0.1)	MW	10 min	4-vinylacetophenone	90
2		1 (0.1)	MW	10 min		99
3		Pd(OAc) ₂ (0.5)	Δ	20 h		95 (82)
4		1 (0.5)	Δ	20 h		93 (89)
5	4-bromoanisole	Pd(OAc) ₂ (1)	MW	20 min	4-methoxystyrene	97
6		1 (1)	MW	20 min		94
7	1-bromonaphthalene	Pd(OAc) ₂ (1)	MW	20 min	1-vinylnaphthalene	90
8		1 (1)	MW	20 min		92
9		Pd(OAc) ₂ (1)	Δ	1 d		96
10		1 (1)	Δ	1 d		98 (90)
11	4-bromochlorobenzene	Pd(OAc) ₂ (1)	MW	15 min	4-chlorostyrene	83
12		1 (1)	MW	15 min		71
13	2-bromo-6-methoxynaphthalene	Pd(OAc) ₂ (0.5)	MW	10 min	2-methoxy-6-vinylnaphthalene	80
14		1 (0.5)	MW	10 min		91 (83)
15		Pd(OAc) ₂ (0.5) ^c	Δ	1 d		64
16		1 (0.5) ^c	Δ	1 d		89
17	(<i>E</i>)-2-phenylvinyl bromide	Pd(OAc) ₂ (0.5)	MW	15 min	(<i>E</i>)-1-phenylbuta-1,3-diene	75
18		1 (0.5)	MW	15 min		90 (81)
19		Pd(OAc) ₂ (0.5)	Δ	1 d		95
20		1 (0.5)	Δ	1 d		72 (41)
21	3-bromopyridine	1 (1)	MW	15 min	3-vinylpyridine	97 (88)
22	4-chloroacetophenone	Pd(OAc) ₂ (2)	MW	25 min	4-chlorostyrene	60
23		1 (2)	MW	25 min		71 (60)
24	4-chlorobenzophenone	Pd(OAc) ₂ (2)	MW	25 min	4-vinylbenzophenone	70 (61)
25		1 (2)	MW	25 min		65 (54)

^a Reaction conditions: aryl halide (0.5 mmol), **3a** (1 mmol), catalyst (see column), NaOH (1.25 mmol), TBAB (0.25 mmol), water (1 mL), microwave reactor at 120 °C (40–45 W, 2–5 bar) with air stream cooling or conventional heating in a pressure tube at 120 °C bath temperature. ^b Determined by ¹H NMR using diphenylmethane as internal standard. The yield after flash chromatography is shown in parentheses. ^c 2 mmol of TBAB.

TABLE 5. Recycling Experiments of the Palladium-Catalyzed Hiyama Reaction of Vinyltrimethoxysilane and 4-Bromoacetophenone^a

$\text{MeCO}-\text{C}_6\text{H}_4-\text{Br} + \text{CH}_2=\text{CHSi}(\text{OMe})_3 \xrightarrow[\text{NaOH, H}_2\text{O, TBAB, MW, 120 } ^\circ\text{C, 15 min}]{\text{Pd cat. (0.5 mol\%)}} \text{MeCO}-\text{C}_6\text{H}_4-\text{CH}=\text{CH}_2$				
entry	Pd(OAc) ₂		complex 1	
	yield ^b (%)	Pd leaching ^c (ppm)	yield ^b (%)	Pd leaching ^c (ppm)
1	99	3.6	99	3.6
2	99 ^d	3.6	99	3.6
3	90 ^e		99	
4	99 ^f	76.4	99 ^g	54.5
5	50 ^h	192	95 ⁱ	90.5
6			99 ^j	
7			42 ^k	219

^a Reaction conditions: 4-bromoacetophenone (0.5 mmol), **3a** (2 mmol), catalyst (0.5 mol % Pd), NaOH (1.25 mmol), TBAB (0.25 mmol), water (1 mL), microwave reactor at 120 °C (40–45 W, 2–5 bar) with air stream cooling. ^b Determined by GC using decane (1 mL) as internal standard. ^c Determined in the crude product by ICP-OES. ^d A 3% yield of acetophenone was also obtained. ^e A 7% yield of acetophenone was also obtained. ^f A 16% yield of acetophenone was also obtained. ^g A 5% yield of acetophenone was also obtained. ^h A 21% yield of acetophenone was also obtained. ⁱ A 4% yield of acetophenone was also obtained. ^j A 8% yield of acetophenone was also obtained. ^k A 11% yield of acetophenone was also obtained.

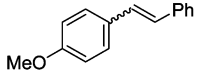
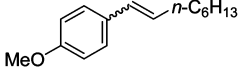
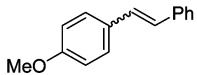
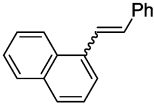
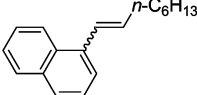
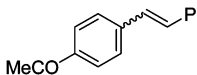
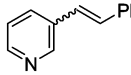
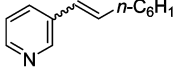
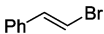
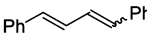
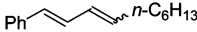
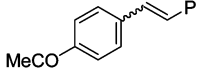
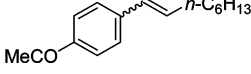
SCHEME 1. Synthesis of Alkenyltrialkoxysilanes **4**

5–7). The same bromide and **4b** gave a better 2:1: β/α ratio of the corresponding 1-naphthyl-1-ene, the *E*-diastereomer being obtained stereospecifically (Table 6, entry 8). The more activated 4-bromoacetophenone was coupled with 0.1 mol % loading of Pd giving the corresponding products with good β/α regioselectivity, 8:1 and 3:1 for **4a** and **4b**, respectively, and

high stereospecificity for the *E*-isomer (Table 6, entries 9 and 10). Similarly, when 3-bromopyridine was coupled with **4a** and **4b**, the corresponding products were obtained regioselectively as a 1:0 and 8:1 β/α ratio, and with the same *E*:*Z* ratio for the *E*-isomer than the starting alkenyltriethoxysilane (Table 6, entries 11 and 12).

In the cross-coupling of alkenyltrialkoxysilanes **4a** and **4b** with (*E*)-styryl bromide, a 0.5 mol % loading of Pd was employed to afford the corresponding conjugated dienes in good yields with a 1:0 and 2.5:1 β/α ratio, respectively (Table 6, entries 13–15). 1,4-Diphenylbuta-1,3-diene was obtained stereospecifically, whereas the *E*/*Z* diastereomer ratio for 1-phe-

TABLE 6. Palladium-Catalyzed Hiyama Reaction of Alkenyltrialkoxysilanes **4** and Aryl Halides^a

$\text{ArX} + \text{RCH=CHSi(OEt)}_3 \xrightarrow[\text{NaOH, TBAB, H}_2\text{O, MW, 120 }^\circ\text{C}]{\text{Pd cat.}}$ $\text{Ar-CH=CH-R} \quad \text{or} \quad \text{Ar-C(R)=CH}_2$ 4a : R = Ph 4b : R = <i>n</i> -C ₆ H ₁₃								
entry	ArX	4 (<i>E</i> : <i>Z</i>)	cat. (mol% Pd)	t (min)	β:α ratio ^b	product	<i>E</i> : <i>Z</i> ^b	yield (%) ^c
1	4-iodoanisole	4a (95:5)	1 (0.1)	10	1.3:1		96:4	91 (80 ^d)
2		4b (86:14)	Pd(OAc) ₂ (0.5)	10	1:2		61:39	86
3			1 (0.1)	10	1:2.4		64:36	85 (75)
4	4-bromoanisole	4a (92:8)	1 (0.1)	20	3.7:1		98:2	96
5	1-bromonaphthalene	4a (95:5)	1 (1)	20	6.7:1		93:7	85
6		4a (67:33)	Pd(OAc) ₂ (1)	20	12:1		66:34	84
7		4a (67:33)	1 (1)	20	13:1		66:34	93 (81 ^e)
8		4b (86:14)	1 (1)	20	2:1		91:9	99 (76 ^d)
9	4-bromoacetophenone	4a (95:5)	1 (0.1)	20	9:1		92:8	90 (82 ^e)
10		4a (67:33)	1 (0.1)	20	1:0		57:43	85
11		4b (86:14)	1 (0.1)	20	3:1		80:20	99 (89)
12	3-bromopyridine	4a (95:5)	1 (1)	20	1:0		94:6	99 (91 ^e)
13		4b (86:14)	1 (1)	20	8:1		88:12	99 (84 ^e)
14		4a (67:33)	1 (0.5)	20	1:0		67:33	93 (81 ^f)
15		4a (67:33)	Pd(OAc) ₂ (0.5)	20	1:0		67:33	84
16		4b (86:14)	1 (0.5)	20	2.5:1		55:45	99 (83 ^f)
17	4-chloroacetophenone	4a (95:5)	1 (2)	30	8.5:1		91:9	76 (68 ^e)
18		4b (86:14)	1 (2)	30	3:1		75:25	70 (60)

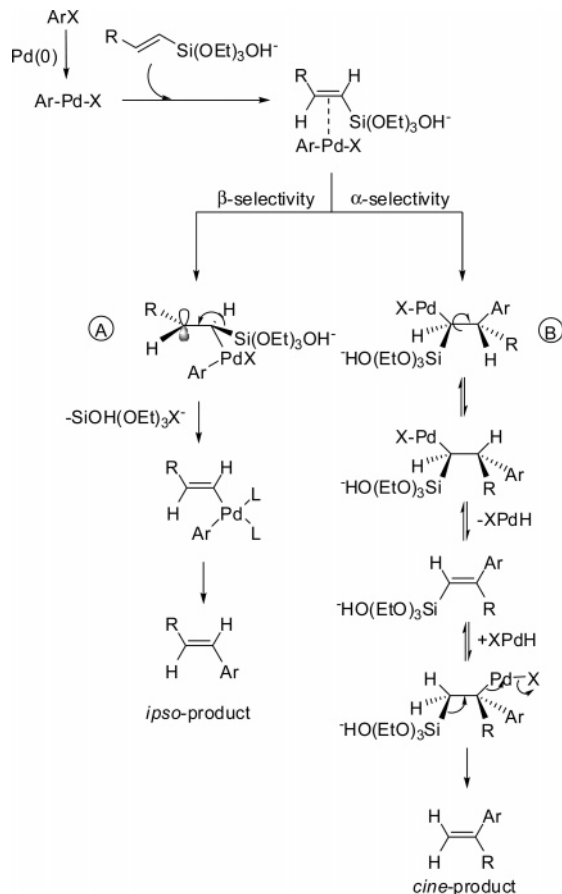
^a Reaction conditions: aryl halide (0.5 mmol), vinyltrimethoxysilane (1 mmol), catalyst (see column), NaOH (1.25 mmol), TBAB (0.25 mmol), water (1 mL), microwave reactor at 120 °C (40–45 W, 2–5 bar) with air stream cooling or conventional heating in a pressure tube at 120 °C bath temperature.

^b Determined by ¹H NMR. ^c Determined by ¹H NMR using diphenylmethane as internal standard. The yield after flash chromatography is given in parentheses. ^d 3:1 (β/α) ratio. ^e Yield of the pure β product. ^f 4:1 (β/α) ratio.

nyldeca-1,3-diene was 55:45 instead of the 96:14 in the starting alkenyltriethoxysilane **4b**. In general, the arylation with these bromides took place with high conversions, especially when palladacycle **1** was used as precatalyst, and in many cases, the

pure β-product was isolated exclusively after flash chromatography. However, the activated 4-chloroacetophenone needed 2 mol % loading of Pd and 30 min irradiation time to provide the corresponding alkenes in 70–76% conversion (Table 6,

SCHEME 2. Mechanism for the Arylation of Alkenyltriethoxysilanes 4



entries 16 and 17). The regio- and diastereoselectivity observed was similar when 4-bromoacetophenone was used as arylating reagent (Table 6, compare entries 16 and 17 with 9 and 10).

The formation of α,α -disubstituted alkenes was observed by Hiyama in the TBAF-promoted arylation of 1-fluoro(dimethyl)silyl-1-alkenes^{2b,3a} and can be explained by a competitive mechanism to the conventional transmetalation followed by reductive elimination to afford the ipso products (β selectivity). This alternative mechanism proceeds through a carbopalladation, which takes place by 1,3-migration of the aryl group from Pd to the β -carbon. This migration should be favored by aryl groups with electron-donating substituents. Then, a dehydropalladation-hydropalladation sequence followed by β -elimination of Pd and Si affords the cine product (α -selectivity). In our case, this competitive mechanism was preferentially observed for an aryl iodide than a bromide because iodides are more reactive than bromides in carbopalladation reactions. The same bias was observed for the alkenyltriethoxysilane **4b**, which gave higher α -arylation ratios than the styryltriethoxysilane **4a** because the β -cationic silicate A is more reactive, less stabilized, when R is an alkyl than an aryl group and suffers the 1,3-migration to give B faster than elimination of the silicate species (Scheme 2).

Conclusions

The reaction conditions found for the Hiyama reaction between aryl halides and alkenyltrialkoxysilanes, aqueous sodium hydroxide, and TBAB as additive under conventional

or microwave heating are appropriate for preparation of styrenes of unsymmetrical stilbenes. Ligandless $Pd(OAc)_2$ or 4-hydroxyacetophenone oxime-derived palladacycles, which are efficient sources of Pd nanoparticles, act as precatalysts under low Pd loading. In addition, these conditions allow the separation of the products by extractive workup and the recovery of Pd in the aqueous basic layer. Among all vinylsilanes, vinyltriethoxy- and trimethoxysilane gave the best results for the synthesis of styrenes. In the case of alkenyltriethoxysilanes, the reaction was, in general, stereospecific. Concerning the regioselectivity, a competitive α -arylation was observed in higher proportions with aryl iodides than bromides or chlorides and for octenyltriethoxysilane than for styryltriethoxysilane.

Experimental Section

General Procedure for the Coupling of Aromatic and Vinyl Halides with Vinyltrialkoxysilanes (2-Methoxy-6-vinylnaphthalene, for Example). A pressure glass vessel (10 mL) sealed with a septum was charged with aromatic halide (0.5 mmol), alkenyltrialkoxysilane (1 mmol), tetra-*n*-butylammonium bromide (0.25 mmol, 81 mg, see Tables 1–6), Pd salts, or palladacycle (0.01–2 mol % Pd, see Tables 1–6) and water (1 mL). Then, an aqueous solution 50% NaOH (1.25 mmol, 0.05 mL) was added dropwise while vigorous stirring of a white-off solid that appeared in the mixture was carried out. After that, general conditions were established for the microwave heating: 40 W, 4–6 bar, 120 °C and air stream cooling during 10–20 min. When the reaction was performed under conventional heating, a 10 mL pressure tube was used and the reaction mixture was heated during the time shown in Tables 1–6. After the reaction mixture was cooled at room temperature, it was extracted in diethyl ether (5×10 mL), and the combined organic layers were washed successively with aqueous 2 M NaOH (2×25 mL), 2 M HCl (1×30 mL), and water or brine (2×20 mL). The organic layer was dried over $MgSO_4$, and the solvent was removed under vacuum (15 mmHg). The reaction yield was calculated by 1H NMR using diphenylmethane as internal standard, and the residue was purified by flash chromatography on silica gel with diethyl ether/hexane. For recycling experiments, the product was extracted in situ with diethyl ether (6×10 mL). The conversion of the reaction was calculated by GC using decane as internal standard taking the aromatic halide as reference. The aqueous layer was dried under vacuum, and new reagents, except for catalyst, were added again.

2-Methoxy-6-vinylnaphthalene:¹⁸ white solid; mp 91–93 °C; R_f 0.60 (hexane/diethyl ether 10/1); IR (KBr) $\nu = 3054, 2838, 1633, 1597, 1482, 1258$ cm^{-1} ; 1H NMR ($CDCl_3$, 300 MHz) δ 7.72–7.68 (m, 3H), 7.62 (d, 1H, $J = 8.5$ Hz), 7.14 (d, 2H, $J = 8.1$ Hz), 6.89 (dd, 1H, $J = 17.6$ and 10.9 Hz), 5.85 (d, 1H, $J = 17.6$ Hz), 5.29 (d, 1H, $J = 10.9$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 157.7, 136.9, 134.2, 132.9, 129.5, 128.8, 126.9, 126.1, 123.7, 118.9, 113.0, 105.7, 55.2; MS m/z 184 (M^+ , 100), 169 (17), 141 (50), 115 (19).

Preparation of Alkenyltrialkoxysilanes via Hydrosilylation of Alkynes.²⁰ To a screw-capped glass tube were added $RhCl(PPh_3)_3$ (20 mg, 0.002 mmol), NaI (150 mg, 1 mmol), alkyne (20 mmol), and triethoxysilane (3.740 mL, 20.4 mmol), under stirring at room temperature. The resulting mixture was heated at 55–60 °C until completion of the reaction was confirmed by 1H NMR (16–24 h). Purification was carried out by distillation in a Kugelrohr apparatus to afford the corresponding alkenyltrialkoxysilane **4**.

Styryltriethoxysilane (4a):²⁰ colorless oil; bp 180 °C (30 Torr); IR (film) ν 2874, 1612, 1575, 1107, 1078 cm^{-1} ; 1H NMR ($CDCl_3$, 300 MHz) δ 7.58, 7.48 (2d, 1H, $J = 7.2$ Hz), 7.48–7.45 (m, 2H), 7.39–7.26 (m, 3H), 6.21, 5.61 (2d, 1H, $J = 19.3, 15.3$ Hz), 3.92, 3.79 (2q, 6H, $J = 6.87$ Hz), 1.29, 1.17 (2t, 9H, $J = 7.0$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 151.2, 149.2, 138.5, 137.7, 128.8, 128.3, 128.1, 126.8, 120.2, 117.7, 58.6, 58.4, 18.3, 18.1; MS m/z 266 (M^+ , 11), 251 (50), 222 (100), 193 (43), 176 (58), 149 (56), 147 (63).

1-Octenyltriethoxysilane (4b):²¹ brown oil; bp 85 °C (30 Torr); IR (film) ν 2955, 2920, 2872, 1618, 1467, 1458, 1235, 1015, 979 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 6.53, 6.43 (2 m, 1H), 5.41, 5.29 (2d, 1H, J = 18.4, 13.0 Hz), 3.86–3.79 (m, 6H), 2.28, 2.16 (m, 2H), 1.41–1.21 (m, 17H), 0.88 (2t, 3H, J = 5.1 Hz); ^{13}C NMR (CDCl_3 , 75 MHz) δ 155.2, 154.2, 118.9, 118.4, 59.2, 58.3, 36.7, 34.1, 31.8, 31.7, 28.9, 28.4, 28.3, 22.8, 22.7, 18.3, 18.2, 14.1.

The following compounds are commercially available: 4-methoxystyrene, 1-vinylnaphthalene, 4-chlorostyrene, 3-vinylpyridine, 4-vinylacetophenone, (*E*)-4-methoxystilbene, 1-(4-methoxyphenyl)-1-phenylethylene, (*E*)- and (*Z*)-1-styrylnaphthalene, (*E*)-4-styrylacetophenone, (*E*)-3-styrylpyridine, (*E*)-1-phenylbuta-1,3-diene, and (1*E*,3*E*)-1,4-diphenylbuta-1,3-diene.

The following compounds have been described: 3,5-dimethoxystyrene,^{15g} 4-benzyloxystyrene,²² 4-vinylbenzophenone,¹⁴ (1*Z*,3*E*)-1,4-diphenylbuta-1,3-diene,²³ (*E*)-1-(1-naphthyl)oct-1-ene,^{8b} (*E*)-1-

(4-acetylphenyl)oct-1-ene,^{8b} (*E*)-1-(4-methoxyphenyl)oct-1-ene,^{8b} (*E*)-1-(3-pyridyl)oct-1-ene,^{8b} and (1*E*,3*E*)-1-phenyldeca-1,3-diene.^{8b}

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Supporting Information Available: General experimental details, physical and spectral data, as well as the ^1H NMR and ^{13}C NMR spectra of known compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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