

Solvent-Less and Fluoride-Free Hiyama Reaction of Arylsiloxanes with Aryl Bromides and Chlorides Promoted by Sodium Hydroxide: A Useful Protocol for Palladium Recycling and Product Isolation

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Abstract: Palladium salts and oxime-derived palladacycles catalyze the cross-coupling reaction of arylsiloxanes with aryl bromides and chlorides in low catalyst loading (0.001–0.1 mol % of Pd) under fluoride-free conditions to provide biaryls and heterobiaryls. For some deactivated aryl bromides and for aryl chlorides, the corresponding cross-couplings need TBAB as additive. Concentrated aqueous sodium hydroxide (50%) promoted this Hiyama reaction in

practically the absence of solvents under air in good yields. The process can be performed at 120 °C either under heating in a pressure tube or under microwave irradiation. This protocol allows palladium recycling and facilitates the final isolation of the products simply by ether extraction.

Keywords: arylsiloxanes; biaryls; cross-coupling; microwave heating; palladacycles

Introduction

Aryl-aryl cross-coupling reactions catalyzed by transition metals constitute fundamental transformations in organic chemistry. Several reactions, such as the Kumada, Negishi, Stille, Suzuki and Hiyama couplings can be used for this carbon-carbon bond forming process.^[1] This strategy gives rise to biaryls and heterobiaryls, moieties widely present in numerous classes of organic compounds, such as natural products, pharmaceuticals, agrochemicals and ligands for asymmetric synthesis and in new materials, such as liquid crystals.^[2] The palladium-catalyzed cross-coupling of organosilicon compounds with organic halides has become the best alternative to the use of tin reagents from an environmental point of view. In addition, silicon compounds are more stable than organomagnesium and organozinc reagents. Organosilanes are becoming popular for industrial purposes, whereas organoboron compounds are difficult to purify and some are unstable, losing boron readily to give homocoupling products.

Several types of silicon reagents have been used, such as arylhalosilanes,^[3] aryl(halo)silacyclobutanes,^[4] aryl(trialkyl)silanes,^[5] aryl(dimethyl)silanol,^[6] arylbis(catechol) silicates,^[7] and aryl(trialkoxy)silanes.^[8] Among these types of organosilanes, alkoxy silanes are very sta-

ble and accessible compounds, being inexpensive and commercially available. In general, all the couplings with organosilicon compounds are promoted by fluoride anion, usually TBAF, by formation of the corresponding hypervalent fluorosilicate. Recently, it has been found that arylhalosilanes,^[9] silicone,^[10] and aryltrimethoxysilane^[11] can be coupled with aryl halides using inorganic bases, such as KOH, NaOH, and K₂CO₃ in water as solvent under fluoride-free conditions. However, under these reaction conditions high catalyst loadings are usually required and in our hands the *in situ* polymerization of alkoxy silanes complicates the isolation of the final product.

The oxime-derived palladacycles **1** and **2** have shown high catalytic activity in carbon-carbon bond forming reactions either in organic or in aqueous solvents.^[12–14] The 4-hydroxyacetophenone oxime-derived palladacycle (**1**) has shown a good catalytic activity in aqueous media for Heck^[12] and Suzuki^[12] reactions in aqueous media. The 4,4'-dichlorobenzophenone oxime-derived palladacycle (**2**) shows an excellent catalytic activity in Heck, Suzuki, Rossi, Sonogashira, Glaser, and sila-Sonogashira reactions and also for the acylation of alkynes in organic solvents. The catalytic activity of **1** and **2** is based on the slow generation of palladium nanoparticles which are the real catalyst, these complexes acting as a

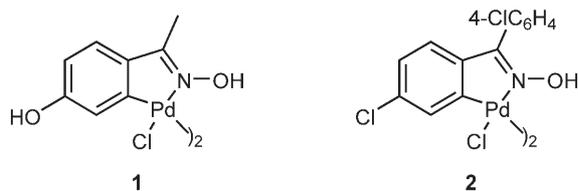


Figure 1. Oxime-derived palladacycles **1** and **2**.

source of very active Pd(0).^[15] We report the development of a simple and practical protocol which allows the cross-coupling of aryltrimethoxysilanes with aryl bromides and chlorides promoted by concentrated NaOH using a very low loading of palladacycles and ligand-free Pd salts as catalysts under solvent-less and fluoride-free conditions. This procedure allows not only an easy isolation of the final product but also the reuse of the catalyst.

Results and Discussion

Initial studies were performed with the deactivated aryl bromide, 4-methoxybromobenzene (**3a**, 1 mmol) and phenyltrimethoxysilane (**4a**, 1.5 mmol) in water (2 mL) with NaOH (2.5 mmol) under microwave heating.^[16] In the presence of palladacycle **1** or Pd(OAc)₂ (0.1 mol % Pd) as catalysts, 4-methoxybiphenyl (**5aa**) was obtained in 55 or 40% yield, respectively (120 °C, 80 W, 10 min irradiation time).^[17] The same reaction was performed under conventional heating during 4 h, affording product **5aa** in similar yields. However, under

these reaction conditions the isolation of the product was rather troublesome due to the formation of emulsions complicating the extractive work-up. Therefore the reaction was performed without solvent, just with 2.5 equivs. of 50% NaOH in a pressure tube at 120 °C (Table 1). Under these reaction conditions the efficiency of Pd(OAc)₂, PdCl₂, Pd on carbon, and palladacycles **1** and **2** with a loading of 0.1 mol % of Pd was evaluated (Table 1, entries 1–5). The two former salts were efficient catalysts for the cross-coupling reaction, whereas in the case of Pd/C only the homocoupling products of 4-bromoanisole and anisole were obtained even with 0.5 mol % of Pd. Palladacycle **2** gave the highest yield (95%) of compound **5aa**, which was isolated by adding ether to the reaction mixture. The polar phase could be reused several times for new coupling reactions as described below. This coupling was also performed under an argon atmosphere giving product **5aa** in similar yield after 3 h reaction time (Table 1, compare entries 5 and 6). The loading of palladacycle **2** could be reduced until 0.005 mol % to provide product **5aa** in 91% yield in the same reaction time with an estimated TOF of 3033 h⁻¹. The same process was carried out under microwave irradiation to afford product **5aa** in 86% yield in 10 min with an estimated TOF up to 51600 h⁻¹ (Table 1, entries 7 and 8). Some inorganic bases including KOH and K₂CO₃, which were active for the Suzuki couplings,^[12c, d] were investigated and only KOH gave similar results than NaOH (Table 1, entries 9 and 10). In addition, other siloxanes, such as phenyltriethoxysilane (**4b**) and silicone (**4c**) could alternatively be used, although in the case of silicone only moderate yield of product **5aa** was obtained (Table 1, entries 11 and 12). The formation

Table 1. Hiyama coupling of arylsiloxanes with 4-bromoanisole: reaction conditions study.^[a]

Entry	Arylsiloxane	Cat. [mol% Pd]	Base	<i>t</i>	Yield [%] ^[b]	TON	TOF [h ⁻¹] ^[c]
1	PhSi(OMe) ₃	Pd(OAc) ₂ (0.1)	50% NaOH	3 h	57	570	190
2	PhSi(OMe) ₃	PdCl ₂ (0.1)	50% NaOH	3 h	57	570	190
3	PhSi(OMe) ₃	Pd/C (0.5)	50% NaOH	3 h	– ^[d]	–	–
4	PhSi(OMe) ₃	1 (0.1)	50% NaOH	3 h	78	780	260
5	PhSi(OMe) ₃	2 (0.1)	50% NaOH	3 h	95	950	316
6	PhSi(OMe) ₃	2 (0.1)	50% NaOH	3 h ^[e]	96	960	320
7	PhSi(OMe) ₃	2 (0.01)	50% NaOH	3 h	91 (83)	9100	3033
8	PhSi(OMe) ₃	2 (0.01)	50% NaOH	10 min ^[f]	86	8600	51600
9	PhSi(OMe) ₃	2 (0.1)	50% KOH	3 h	72	720	260
10	PhSi(OMe) ₃	2 (0.1)	K ₂ CO ₃	3 h	–	–	–
11	PhSi(OEt) ₃	2 (0.1)	50% NaOH	3 h	93	930	310
12	Ph(MeSiO) _n	2 (0.1)	50% NaOH	3 h	61	610	203

^[a] Reaction conditions: 4-bromoanisole (1 mmol), siloxane (1.5 mmol), cat. (see column), and base (2.5 mmol) were heated in a pressure tube at 120 °C.

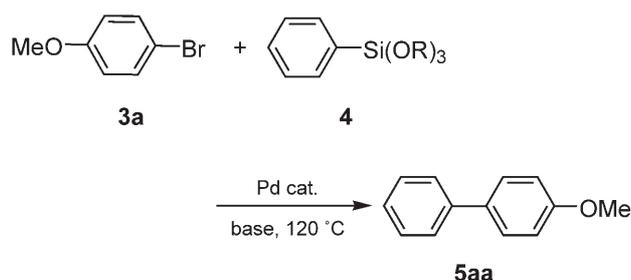
^[b] Of compound **5aa**, determined by ¹H NMR using *N,N*-diphenylformamide as internal standard. In parenthesis isolated yield after flash chromatography.

^[c] Estimated values.

^[d] 42% of the homocoupled product 4,4'-dimethoxybiphenyl was obtained.

^[e] Under argon.

^[f] Under microwave heating at 120 °C (80 W).



Scheme 1.

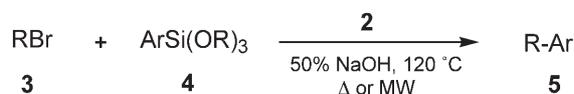
of Pd black in the reaction mixture was observed in all these experiments. A 3% leaching of palladium in the crude product **5aa** was found by ICP-OES analysis in the case of the cross-coupling catalyzed by palladacycle **2** (Table 1, entry 5).

The optimized reaction conditions were chosen for the Hiyama cross-coupling reactions of different aryl and vinyl bromides **3** with aryltrimethoxysilanes **4**. Thus, heating these reagents and palladacycle **2** at 120 °C in the presence of 2.5 equivs. of 50% aqueous NaOH afforded products **5** which were isolated by extraction with ether (Scheme 2 and Table 2). The coupling of activated 4-bromoacetophenone (**3b**) with phenyltrimethoxysilane (**4a**) was carried out similarly as with 4-bromoanisole, either under heating in a pressure tube during 1 h or under microwave irradiation during 10 min (Table 2, entries 1–4). This coupling could also be performed with a lower loading of Pd (0.001 mol %) to give 4-acetylbiphenyl (**5ba**) in quantitative yield in 4 h with a TON of 99000 and a TOF of 24750 h⁻¹ (Table 2, entry 5). 4-Tolyltriethoxysilane (**4d**) was coupled with 4-bromoacetophenone with 0.1 mol % Pd in 3 h to provide biphenyl **5bd** in good yield (Table 2, entry 6). Deactivated 3- and 4-bromophenols, (**3c**) and (**3d**), were arylated with phenyltrimethoxysilane (**4a**) using 0.1 mol % of Pd to give biaryls **5ca** and **5da**, respectively in good yields (Table 2, entries 7 and 8). The anti-inflammatory 4-biphenylacetic acid (**5ea**)^[18] was obtained in 84% yield by reaction of *p*-bromophenylacetic acid (**3e**) with phenyltrimethoxysilane (**4a**) (Table 2, entry 9). 3-Bromopyridine (**3f**) was coupled in 2.5 to 3 h with different siloxanes **4a**, **4d**, and **4e** to afford the corresponding 3-arylpyridines **5fa**, **5fd**,^[20] **5fe**, respectively, in high yields (Table 2, entries 10–14). The presence of tetra-*n*-butylammonium bromide (TBAB)^[19] was important only for the coupling of 3-bromopyridine (**3f**) with (4-methoxyphenyl)triethoxysilane (**4e**) under conventional thermal conditions (Table 2, entries 13 and 14). For the arylation of deacti-

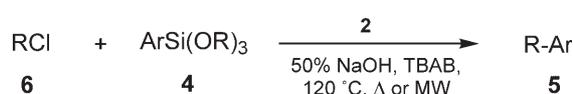
vated aryl bromides, such as 2-bromotoluene (**3g**) and 2-bromothiophene (**3h**), the presence of TBAB improved the conversions and the reaction rates either under heating or under microwave irradiation using 0.1 mol % of Pd to afford products **5ga** and **5ha** in good yields (Table 2, entries 15–18). Under similar reaction conditions (*E*)-styryl bromide gave stereospecifically (*E*)-stilbene in good yields (Table 2, entries 19 and 20).

The stability of complex **2** during the Hiyama cross-coupling reaction and the reusing of the active catalytic species was studied in the arylations of phenyltrimethoxysilane with 4-bromoanisole and 4-bromoacetophenone using palladacycle **2** (0.05 mol %) at 120 °C during 3 h and 1 h, respectively (Table 3). After extraction of the corresponding products, fresh reagents were added to the residue and the catalytic cycle was run for 3 h and 1 h, respectively, and in general good conversions were obtained during 5 consecutive catalytic cycles.

Cross-couplings of different chloroarenes **6** with siloxanes **4** to give biphenyls **5** were performed with catalyst **2** in the presence of TBAB (0.5 equivs.) and aqueous 50% NaOH as base (Scheme 3 and Table 4). Initial studies about the loading of Pd for the coupling between phenyltrimethoxysilane (**4a**) and 4-chloroanisole (**6a**) showed that higher yields could be obtained with 1 mol % of Pd under thermal conditions (Table 4, entries 1 and 2). However, under microwave irradiation with 0.1 mol % of Pd high conversions were observed (Table 4, entries 3 and 4). The use of PdCl₂ as catalyst gave lower yield than with palladacycle **2** (Table 4, compare entries 4 and 5). Good yields were obtained with activated 4-chloroacetophenone (**6b**) and siloxanes **4a** and **4d** either under thermal or microwave conditions (Table 4, entries 6–8). Heterocyclic chlorides, such as 3-chloropyridine (**6f**), were coupled with different siloxanes, such as phenyltrimethoxysilane (**4a**), (4-methoxyphenyl)triethoxysilane (**4e**) and (4-trifluorophenyl)triethoxysilane (**4f**) to afford products **5fa**, **5fe**, and **5ff**,^[21] respectively, in good yields under both reaction conditions (Table 4, entries 9–15). The presence of 0.5 equivs. of TBAB as additive was crucial in order to obtain good yields, because when the reaction of 3-chloropyridine (**6f**) and phenyltrimethoxysilane (**4a**) was performed in the absence of TBAB only a 16% yield of product **5fa** was obtained (Table 4, compare entries 9 and 10). In the coupling between **4a** and other chloroarenes, such as 4-chloroquinoline (**6j**), 4-(trifluoromethyl)chlorobenzene (**6k**), and 3-chloroaniline (**6l**), products **5ja**, **5ka**, and **5la** were obtained in good yields although the

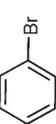
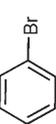
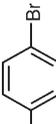
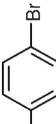
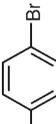
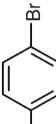
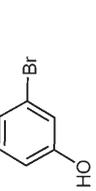
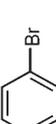
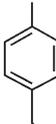


Scheme 2.



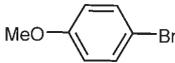
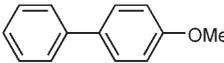
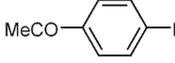
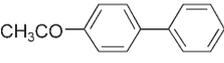
Scheme 3.

Table 2. Hiyama coupling of aryl and vinyl bromides with arylsiloxanes catalyzed by palladacycle **2**.^[a]

Entry	ArBr	Siloxane (No.)	Mol % Pd	Additive	<i>t</i>	Product No.	Yield [%] ^[b]	TON	TOF [h ⁻¹]
1		PhSi(OMe) ₃ (4a)	0.01	–	3 h	5aa	91 (83)	9100	3033
2		PhSi(OMe) ₃ (4a)	0.01	–	10 min ^[c]	5aa	86 ^[d]	8600	51600
3		PhSi(OMe) ₃ (4a)	0.01	–	1 h	5ba	84	8400	8400
4		PhSi(OMe) ₃ (4a)	0.01	–	10 min ^[c]	5ba	98	9800	58800
5		4-MeC ₄ H ₄ Si(OEt) ₃ (4d)	0.001 ^[e]	–	4 h	5ba	99 ^[d]	99000	24750
6		4-MeC ₄ H ₄ Si(OEt) ₃ (4d)	0.1	–	3 h	5bd	72 (88) ^[d]	880	293
7		PhSi(OMe) ₃ (4a)	0.1	–	5 h	5ca	72 (85) ^[d]	850	170
8		PhSi(OMe) ₃ (4a)	0.1	–	3 h	5da	90	900	300
9		PhSi(OMe) ₃ (4a)	0.1	–	1.5 h	5ea	84 ^[f]	840	560
10		PhSi(OMe) ₃ (4a)	0.1	–	2.5 h	5fa	85	850	340
11		4-MeC ₄ H ₄ Si(OEt) ₃ (4d)	0.5	TBAB ^[g]	3 h	5fd	96 (100) ^[d]	500	167
12		4-MeOC ₄ H ₄ Si(OEt) ₃ (4e)	0.1	–	3 h	5fe	100 ^[d]	1000	334
13		4-MeOC ₄ H ₄ Si(OEt) ₃ (4e)	0.1	TBAB ^[g]	3 h	5fe	100 ^[d]	1000	334
14		4-MeOC ₄ H ₄ Si(OEt) ₃ (4e)	0.1	–	10 min ^[c]	5fe	100 ^[d]	1000	6000
15		PhSi(OMe) ₃ (4a)	0.2	TBAB ^[g]	14 h	5ga	78 (91) ^[d]	455	32
16		PhSi(OMe) ₃ (4a)	0.1	–	10 min ^[c]	5ga	90	900	5400
17		PhSi(OMe) ₃ (4a)	0.1	TBAB ^[h]	5 h	5ha	86	860	172
19		PhSi(OMe) ₃ (4a)	0.1	TBAB ^[h]	10 min ^[c]	5ha	99	990	5940
19		PhSi(OMe) ₃ (4a)	0.1	TBAB ^[h]	3 h	5ia	87 ^[d]	870	290
20		PhSi(OMe) ₃ (4a)	0.1	TBAB ^[h]	10 min ^[c]	5ia	81 (95) ^[d]	950	5700

^[a] Reaction conditions: aryl bromide (1 mmol), aryltrimethoxysilane (1.5 mmol), aryltrimethoxysilane (2.5 mmol), aqueous 50% NaOH, 120 °C in a pressure tube.^[b] Yield after flash chromatography.^[c] Under microwave irradiation at 120 °C (80 W).^[d] Determined by ¹H NMR using diphenylmethane as internal standard.^[e] The reaction was performed on a 3-mmol scale:standard.^[f] After recrystallization.^[g] 1 equiv.^[h] 0.5 equivs.

Table 3. Recycling experiments for the Hiyama reaction of aryl bromides with phenyltrimethoxysilane catalyzed by palladacycle **2**.^[a]

Run	ArBr	Siloxane (equivs.)	Mol % Pd	Additive	<i>t</i>	Product		Yield [%] ^[b]
						No	Chemical Structure	
1		PhSi(OMe) ₃ (2)	0.2	TBAB ^[c]	3 h	5aa		98
2					3 h	5aa		94
3					3 h	5aa		73
4					3 h	5aa		70
5					3 h	5aa		70
1		PhSi(OMe) ₃ (1.5)	0.1	TBAB ^[d]	1 h	5ba		90
2				TBAB ^[d]	1 h	5ba		90
3				TBAB ^[d]	1 h	5ba		96
4				TBAB ^[d]	1 h	5ba		83
5				TBAB ^[d]	1 h	5ba		82

^[a] Reaction conditions: aryl bromide (1 mmol), phenyltrimethoxysilane (see column), **2** (see column), aqueous 50% NaOH (2.5 mmol), 120 °C in a pressure tube.

^[b] Yield determined by ¹H NMR, by using diphenylmethane as internal standard.

^[c] 2.5 equivs.

^[d] 0.5 equivs.

amount of TBAB was increased to 1 equiv. with a loading of Pd between 1–1.5 mol % (Table 4, entries 16–19, 21 and 22). The use of silicone (**4c**) instead of **4a** for the arylation of **6k** provided product **5ka** in lower yield than phenyltrimethoxysilane (Table 4, compare entries 18 and 20). 2-Chlorobenzaldehyde diethyl acetal (**6m**) could be arylated with **4a** at the *ortho*-position to afford 2-phenylbenzaldehyde (**5ma**) in good yield after acidic hydrolysis (Table 4, entry 23).

For the reuse of the catalyst the coupling of 3-chloropyridine (**6f**) and phenyltrimethoxysilane (**4a**) to provide 3-phenylpyridine (**5fa**) was chosen as a model reaction (Table 5). Under thermal conditions three runs of 20 h were performed, the yield being lowered only to 73% after the third experiment (Table 5, entries 1–3). Similar results were observed under microwave heating during 15 min, the yield decreasing to 52% after the third run (Table 5, entries 4–6).

Conclusion

In conclusion, we have developed a straightforward procedure for the cross-coupling reaction between siloxanes and aryl bromides and chlorides using a very low loading of catalyst under solvent-less and fluoride-free conditions, only promoted by concentrated NaOH. Pd(OAc)₂, PdCl₂ or oxime-derived palladacycles can be used as catalyst, the 4,4'-dichlorobenzophenone oxime-derived palladacycle **2** being the catalyst of choice. These process can be performed at 120 °C either under normal heating in a pressure tube or under microwave

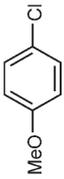
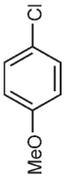
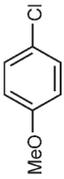
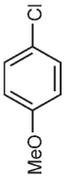
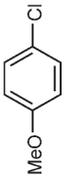
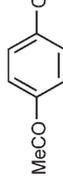
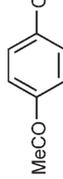
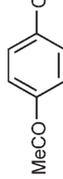
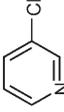
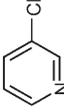
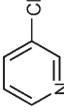
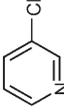
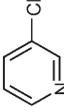
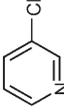
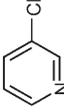
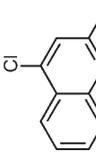
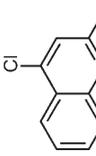
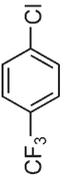
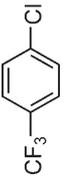
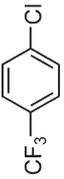
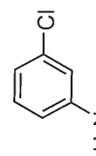
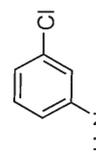
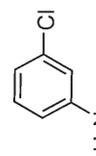
irradiation in only 10 to 15 min. In general, aryl chlorides needed the presence of 0.5 to 1 equiv. of TBAB as additive for good conversions and higher Pd loadings than aryl bromides. No differences have been found in the reactivity of different siloxanes, although silicone was the less reactive. These reaction conditions allow the easy extractive recovery of the final product, and the solid residue showing catalytic activity can be reused several times. So far this phosphine-free protocol can be considered as the most simple and efficient method described to perform these type of couplings.

Experimental Section

General

The reagents and solvents were obtained from commercial sources and were generally used without further purification. Flash chromatography was performed on silica gel 60 (0.040–0.063 mm, Merck). Thin layer chromatography was performed on Polygram[®] SIL G/UV₂₅₄ plates. Melting points were determined on a Reichert Thermovar apparatus. Gas chromatographic analyses were performed on a HP-6890 instrument equipped with a WCOT HP-1 fused silica capillary column. IR data were collected on a Nicolet Impact-400D-FT spectrophotometer in cm⁻¹. ¹H NMR spectra were recorded on Bruker AC-300 (300 MHz) and when specified on Bruker Advance-DRX-500 (500 MHz) spectrometers. Chemical shifts are reported in ppm using tetramethylsilane (TMS, 0.00 ppm) as internal standard. ¹³C NMR spectra were recorded at 75 MHz with CDCl₃ as the internal reference. EI-MS were measured on a Mass Selective Detector G2579A from Agilent Technolo-

Table 4. Miyama coupling of aryl chlorides with arylsiloxanes catalyzed by palladacycle **2**.^[a]

Entry	ArCl	Siloxane (No.)	Mol % Pd	TBAB (equivs.)	<i>t</i>	Product No.	Yield [%] ^[b]
1		PhSi(OMe) ₃ (4a)	0.1	0.5	15 h	5aa	55
2		PhSi(OMe) ₃ (4a)	1	0.5	15 h	5aa	83
3		PhSi(OMe) ₃ (4a)	1	0.5	10 min ^[c]	5aa	93 ^[d]
4		PhSi(OMe) ₃ (4a)	0.1	0.5	10 min ^[c]	5aa	92 ^[d]
5		PhSi(OMe) ₃ (4a)	0.1 ^[e]	0.5	10 min ^[c]	5aa	63 ^[d]
6		PhSi(OMe) ₃ (4a)	0.1	0.5	15 h	5ba	78
7		4-MeC ₄ H ₃ Si(OEt) ₃ (4d)	1	0.5	15 h	5ba	91 ^[d]
8		4-MeC ₄ H ₃ Si(OEt) ₃ (4d)	1	0.5	15 min ^[c]	5ba	97 ^[d]
9		PhSi(OMe) ₃ (4a)	0.1	0.5	15 h	5fa	73 (90) ^[d]
10		PhSi(OMe) ₃ (4a)	0.1	–	14 h	5fa	16 ^[d]
11		PhSi(OMe) ₃ (4a)	1	0.5	10 min ^[c]	5fa	92 (96) ^[d]
12		4-MeOC ₄ H ₄ Si(OEt) ₃ (4e)	1	0.5	15 h	5fe	91 ^[d]
13		4-MeOC ₄ H ₄ Si(OEt) ₃ (4e)	1	0.5	10 min ^[c]	5fe	99 ^[d]
14		4-CF ₃ C ₄ H ₄ Si(OEt) ₃ (4f)	1	0.5	15 h	5ff	84
15		4-CF ₃ C ₄ H ₄ Si(OEt) ₃ (4f)	1	0.5	10 min ^[c]	5ff	98
16		PhSi(OMe) ₃ (4a)	1	1	24 h	5ja	85
17		PhSi(OMe) ₃ (4a)	1	1	15 min ^[c]	5ja	96 ^[d]
18		PhSi(OMe) ₃ (4a)	1	1	24 h	5ka	86 ^[d]
19		PhSi(OMe) ₃ (4a)	1	1	15 min ^[c]	5ka	86 (90) ^[d]
20		(PhMeSiO) _n (4c)	1	1	24 h	5ka	45 ^[d]
21		PhSi(OMe) ₃ (4a)	1.5	1	24 h	5la	54 ^[d]
22		PhSi(OMe) ₃ (4a)	1.5	1	15 min ^[c]	5la	84 (92) ^[d]
23		PhSi(OMe) ₃ (4a)	1	0.5	15 h	5na	81 (96) ^[d]

^[a] Reaction conditions: aryl chloride (1 mmol), aryltrimethoxysilane (1.5 mmol), **2** (see column), aqueous 50% NaOH (2.5 mmol), 120 °C in a pressure tube.^[b] Yield after flash chromatography.^[c] Under microwave irradiation at 120 °C (80 W).^[d] Determined by ¹H NMR using diphenylmethane as internal standard.^[e] PdCl₂ was used as catalyst.

Table 5. Recycling experiments for the Hiyama reaction of 3-chloropyridine with phenyltrimethoxysilane catalyzed by palladacycle **2**.^[a]

Entry	Run	Reaction conditions	T	Yield [%] ^[b]
1	1	Thermal	20 h	85
2	2	Thermal	20 h	94
3	3	Thermal	20 h	73
4	1	Microwave	15 min	99
5	2	Microwave	15 min	85
6	3	Microwave	15 min	52

^[a] Reaction conditions: aryl chloride (1 mmol), phenyltrimethoxysilane (2 mmol), **2** (0.5 mol %), aqueous 50% NaOH (2.5 mmol), TBAB (0.25 mmol), 120 °C in a pressure tube or under microwave irradiation at 120 °C and 80 W.

^[b] Yield determined by ¹H NMR, by using diphenylmethane as internal standard.

^[c] 2.5 equivs.

^[d] 0.5 equivs.

gies 5973N in *m/z* (rel. intensity in % of base peak). ICP-OES analyses were performed with a Perkin Elmer Optima 4300. The catalysts were weighed in an electronic microscale (Sartorius, XM1000P) with a precision of 1 µg. Microwave reactions were performed with a CEM Discover Synthesis Unit in glass vessels (10 mL) sealed with a septum under magnetic stirring.

Typical Experimental Procedure for Hiyama Coupling of Aromatic and Heteroaromatic Bromides and Chlorides with Arylsiloxanes under Thermal Conditions

A mixture of aryl halide (1 mmol), siloxane (1.5 mmol), TBAB (0.5 to 1 mmol, see Tables 2–5) and Pd salts or palladacycles **1** or **2** (see Tables 1–5) in a 15-mL Ace tube was stirred during 5 min. Then an aqueous 50% NaOH solution (0.1 mL, 2.5 mmol) was added and the reaction was heated at 120 °C during the time indicated in Tables 1–5. After the reaction was completed or stopped, the reaction mixture was poured into ether (5 mL). The resulting suspension was filtered off and the solid was washed with ether (8 × 5 mL). The ethereal filtrates were dried and evaporated (15 mm Hg). The residue was purified by recrystallization or by flash chromatography on silica gel to give pure products **5**. All compounds **5** are commercially available.

Typical Experimental Procedure for Hiyama Coupling of Aromatic and Heteroaromatic Bromides and Chlorides with Arylsiloxanes under Microwave Irradiation

A glass tube (10 mL) was charged with the aryl halide (0.5 mmol), siloxane (0.75 mmol), TBAB (0.25 to 0.5 mmol, see Tables 2–5), aqueous 50% NaOH (0.05 mL, 1.25 mmol) and palladacycle **2** (see Tables), sealed with a septum and heated at 120 °C (80 W, 10 bar) during 10–15 min with air stream cooling. The reaction mixture was cooled at room temperature followed by extractive work up as above.

Typical Experimental Work-Up for Hiyama Coupling of Aromatic and Heteroaromatic Bromides and Chlorides with Arylsiloxanes. Recycling Experiments

When the reaction under thermal or MW conditions was finished, the mixture was cooled to room temperature and AcOEt was added (3 × 10 mL). The organic solution was dried and evaporated as described above to give the corresponding crude product **5**. The solid residue was dried under vacuum and the new reagents (except the catalysts) were added again (see Tables 3 and 5).

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