Improved Synthesis of Aryltriethoxysilanes via Palladium(0)-Catalyzed Silylation of Aryl Iodides and Bromides with Triethoxysilane†

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The scope of the palladium-catalyzed silylation of aryl halides with triethoxysilane has been expanded to include aryl bromides. A more general Pd(0) catalyst/ligand system has been developed that activates bromides and iodides: palladium(0) dibenzylideneacetone (Pd(dba)$_2$) is activated with 2-(di-*tert*-butylphosphino)biphenyl (Buchwald's ligand) (1:2 mol ratio of Pd/phosphine). Electron-rich para- and meta-substituted aryl halides (including unprotected aniline and phenol derivatives) undergo silylation to form the corresponding aryltriethoxysilane in fair to excellent yield; however, ortho-substituted aryl halides failed to be silylated.

Introduction

Stille (organostannane) and Suzuki (organoborane) coupling methodologies are widely employed for the synthesis of unsymmetrical biaryl derivatives and substituted alkenes due to the generally excellent yields and high stereoselectivities.[1–3] Nonetheless, organosilicon reagents have played an increasingly important role in Pd(0)-catalyzed cross coupling with organohalides and organo(pseudo)halides because they avoid the reagent toxicity and limited functional group compatibility associated with the tin and boron counterparts.[4–13] Previous studies from our group[4–8] as well as Hiyama,[9] Ito,[10] Denmark,[11] and others[12] have shown that a variety of silicon derivatives undergo fluoride-mediated, Pd(0)-catalyzed aryl group transfer reactions.[13]

Our laboratory has focused specifically on aryltrialkoxysilanes as surrogates for Stille or Suzuki reagents, respectively (Scheme 1).[4,6–8] Recently, we reported the synthesis of unsymmetrically substituted biaryls via phenylation of aryl iodides,[4,7] bromides, and chlorides[6,7]

Scheme 1
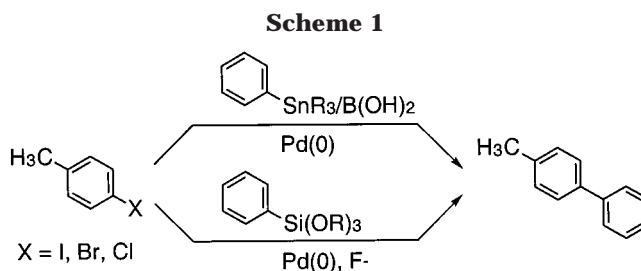
with phenyltrimethoxysilane. Having demonstrated the efficient phenylation, we undertook a study of the transfer of substituted aryl groups to ascertain the scope and limitations of the methodology. This study necessitated the synthesis of ortho-, meta-, and para-substituted electron-rich and electron-deficient arylsiloxanes.

Existing methods for the synthesis of arylsiloxanes fall into two categories: (1) treatment of an aryl Grignard or lithium reagent with a silicon electrophile (Scheme 2) and (2) silylation of an aryl iodide by triethoxysilane (HSi(OEt)$_3$) in the presence of a Pd catalyst as reported by Masuda (Scheme 3).[14] Both methods, as presently constituted, have their limitations. The metalloid reaction is limited by the generally inferior yields of siloxane as

† Dedicated to Professor Richard W. Franck on the occasion of his 65th birthday.

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Scheme 2

Scheme 3
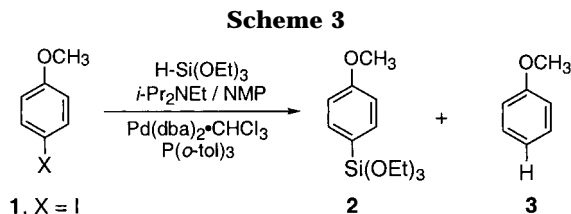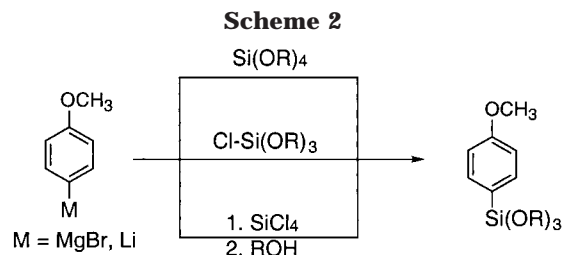
well as the problems associated with the synthesis of arylmetalloids having electrophilic functional groups (i.e., esters, ketones, etc.).[15]

The Pd-mediated silylation protocol of Masuda is limited to electron-rich iodoarenes.[14] Masuda reported that electron-rich, para-substituted aryl iodides gave excellent yields of arylsiloxane. In contrast to aryl iodides, aryl bromides were reported to provide low yields of arylsiloxane under identical conditions. In addition, the silylation of ortho- or meta-substituted aryl iodides/bromides was not reported. Accordingly, the goals of this study were (1) to extend the silylation reaction to aryl bromides and (2) to evaluate the Masuda methodology for the synthesis of ortho- and meta-substituted arylsiloxanes.

Results and Discussion

Toward our goal of synthesizing a variety of highly functionalized siloxane derivatives for use in aryl-coupling reactions, it was necessary to determine whether

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Table 1. Silylation of 4-Bromoanisole
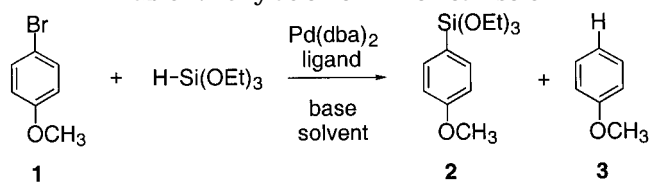
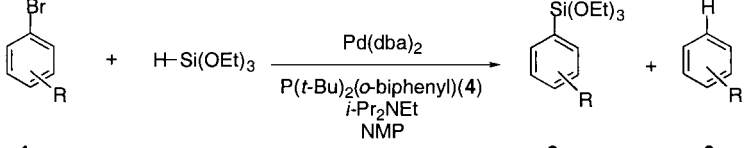| entry	conditions[a]			yield[b,c] (%)	
	ligand	base	solvent	**2**	**3**
1	P(*o*-tol)$_3$	*i*-Pr$_2$NEt	NMP	21	79
2	P(*o*-tol)$_3$	*i*-Pr$_2$NEt	DMF	15	70
3	none	*i*-Pr$_2$NEt	DMF	14	86
4	PPh$_3$	*i*-Pr$_2$NEt	DMF	0	5
5	P(*t*-Bu)$_2$(*o*-biphenyl)	*i*-Pr$_2$NEt	NMP	75	25
6	P(*t*-Bu)$_2$(*o*-biphenyl)	*i*-Pr$_2$NEt	DMF	36	64
7	P(*t*-Bu)$_3$	*i*-Pr$_2$NEt	NMP	59	41
8	P(*t*-Bu)$_3$	*i*-Pr$_2$NEt	DMF	45	55
9	P(*t*-Bu)$_2$(*o*-biphenyl)	*i*-Pr$_2$NEt	THF	6	54
10	P(*t*-Bu)$_2$(*o*-biphenyl)	*i*-Pr$_2$NEt	CH$_3$CN	6	93
11	P(*t*-Bu)$_2$(*o*-biphenyl)	*i*-Pr$_2$NEt	toluene	3	19
12	P(*t*-Bu)$_2$(*o*-biphenyl)	none	NMP	0	4
13	P(*t*-Bu)$_2$(*o*-biphenyl)	Et$_3$N	NMP	55	45
14	P(*t*-Bu)$_2$(*o*-biphenyl)	pyridine	NMP	0	5
15	P(*t*-Bu)$_2$(*o*-biphenyl)	2,6-lutidine	NMP	32	26
16	P(*t*-Bu)$_2$(*o*-biphenyl)	DBU	NMP	0	57
17	P(*t*-Bu)$_2$(*o*-biphenyl)	KOAc	NMP	22	78
18	P(*t*-Bu)$_2$(*o*-biphenyl)	CsCO$_3$	NMP	3	97

[a] Reactions of 4-bromoanisole (**1**) (1.0 mmol) with HSi(OEt)$_3$ (1.5 mmol) were performed at room temperature for 12h in 4 mL of solvent by using Pd(dba)$_2$ (5 mol %), phosphine (10 mol %), and base (3 mmol). [b] GC yields are based on amount of 4-bromoanisole. [c] Remaining percentage was unreacted starting material.
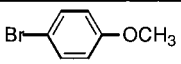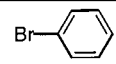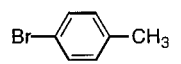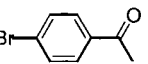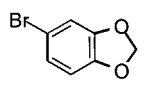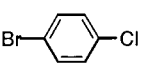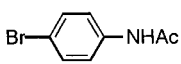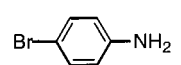
Masuda conditions could be modified and the scope extended to encompass silylation of aryl bromide derivatives. Our study focused primarily on aryl bromides; initial experiments demonstrated that aryl chloride and triflate derivatives were unreactive toward silylation under a variety of reaction conditions. Standard optimization approaches involving change of solvent, reaction temperature, catalyst, base, and catalyst/ligand ratio failed to provide improved yields of siloxane from the corresponding aryl bromide. As reported by Masuda, the silylation reaction of br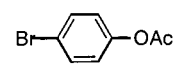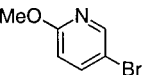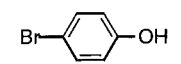omoarenes under these conditions afforded the reduced arene rather than the desired siloxane derivative (see Scheme 3).[14]

Previous studies in our laboratory[6] had shown that incorporation of Buchwald's phosphine into Pd-catalyzed reactions resulted in dramatically improved yields of adducts.[16] The use of Buchwald's and related phosphine derivatives in the silylation reaction was investigated, and the results are summarized in Table 1. Entries 1 and 2 are the results obtained employing the standard conditions reported by Masuda and show that the silylation provided a low yield of the desired arylsiloxane. The major product was the reduced arene. Substitution of Buchwald's ligand (**4**) as the phosphine resulted in a marked improvement in the yield of siloxane obtained (Table 1, entry 5). Similarly, inclusion of tributylphosphine (Table 1, entries 7 and 8), as reported by Fu,[17] had a less significant effect and showed an appreciable difference in yield depending on the solvent. Subsequent

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Table 2. Silylation of Aryl Bromides

entry	aryl bromide (**1**)	% yield (**2**)[a,b]	entry	aryl bromide (**1**)	% yield (**2**)[a,b]
1	Br—⟨⟩—OCH₃	68	8	Br—⟨⟩	(5)
2	Br—⟨⟩—CH₃	43	9	Br—⟨⟩—C(O)CH₃	0
3	Br—⟨benzodioxole⟩	44	10	Br—⟨⟩—Cl	0
4	Br—⟨⟩—NHAc	33	11	2-bromopyridine	0
5	Br—⟨⟩—NH₂	38[c,d]	12	3-bromopyridine	0
6	Br—⟨⟩—OAc	30	13	MeO-pyridine-Br	57
7	Br—⟨⟩—OH	28[c,d]	14	2-bromothiophene	43

[a] Reactions of aryl bromide **1** (1.0 equiv) with HSi(OEt)₃ (1.5 equiv) were performed at 60 °C for 12 h in NMP by using 3 mol % Pd(dba)₂, (*t*-Bu)₂P(*o*-biphenyl) (**4**) (6 mol %), and *i*-Pr₂NEt (3 equiv). [b] Yields shown in parentheses are GC yields; all other yields are isolated yields of purified (>95%) product. [c] Reaction performed at room temperature. [d] Reaction stopped at 2 h.

studies were performed with the Buchwald ligand because of its inherent ease of handling, thus avoiding the air-sensitive nature of tributylphosphine. A variety of other ligands was investigated including mono- and bidentate phosphines (dppp, dppf, etc.), Buchwald's 2-(dicyclohexylphosphino)biphenyl, and triphenylarsine; however, these ligands failed to provide siloxane in acceptable yields. Similarly, additives such as tetraalkylammonium iodides, copper iodide, silver(I) salts, thallium acetate, or the inclusion of molecular sieves failed to improve the reaction outcome.

The solvent and the nature of the base had a marked effect on the reaction. In contrast to the Masuda conditions (Table 1, entries 1 and 2), NMP is the unrivalled solvent choice for the reaction in question as illustrated in entries 5 and 6 (Table 1). Solvents that either are less polar than NMP or can coordinate with the catalyst resulted in dramatically reduced yields of the siloxane (Table 1, entries 9−11). An amine base was required for silylation. In the absence of base, slow reduction of the starting material was observed (Table 1, entry 12). Triethylamine (Table 1, entry 13) gave more reduced material when compared to diisopropylethylamine, possibly due to its ability to coordinate as a ligand. Pyridine (Table 1, entry 14) and 2,6-lutidine (Table 1, entry 15)

slowed the reaction dramatically and resulted in reduction preferentially. Replacement of the amine base by weak alkali bases such as KOAc (Table 1, entry 17) and CsCO₃ (Table 1, entry 18) was ineffective.

To demonstrate the scope of the modified silylation reaction, a variety of substituted aryl bromides was examined (Table 2). The best yields of siloxane were obtained for electron-rich aryl bromides (Table 2, entries 1−7) although the yields obtained are generally modest. This trend was not unexpected on the basis of the report from Masuda with iodides.[14] Silylation of bromobenzene or electron-poor aryl bromides was unsuccessful (Table 2, entries 8−10), exclusively resulting in dehalogenation of the starting material. Mixed results were obtained for heteroaromatic systems (Table 2, entries 11−14). For example, 5-triethoxysilyl-2-methoxypyridine (Table 2, entry 13) and 2-(triethoxysilyl)thiophene (Table 2, entry 14) were prepared from the corresponding bromides in moderate yields. This is in contrast to attempted silylation of 2- and 3-bromopyridine (Table 2, entries 11 and 12, respectively), which gave solely the reduced product. A tentative explanation for these results is that the presence of the strongly electron-donating 2-methoxy substituent on the pyridine (Table 2, entry 13) leads to selective silylation, as is observed in the benzene derivatives.

Given that the yield of silylated arene was dependent upon the electron-rich character of the arene system, it

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Table 3. Silylation of Aryl Bromides: Effect of Substituent Position

entry	aryl bromide (**1**)	% yield (**2**)[a,b]	entry	aryl bromide (**1**)	% yield (**2**)[a,b]
1	Br——OCH$_3$	68	4	Br——CH$_3$	43
2	OCH$_3$ / Br	25	5	CH$_3$ / Br	10
3	H$_3$CO / Br	0	6	H$_3$C / Br	0

[a] Reactions of aryl bromide **1** (1.0 equiv) with HSi(OEt)$_3$ (1.5 equiv) were performed at 60 °C for 12 h in NMP by using 3 mol % Pd(dba)$_2$, (*t*-Bu)$_2$P(*o*-biphenyl) (**4**) (6 mol %), and *i*-Pr$_2$NEt (3 equiv). [b] Yields are isolated yields of purified (>95%) product.

was expected that 4-bromo-1,2-(methylenedioxy)benzene (Table 1, entry 3) would give a comparable (or greater) yield of siloxane than 4-bromoanisole (entry 1). Surprisingly, the opposite was observed. It was proposed that the presence of a substituent at the meta position resulted in the lower yield. Further exploration of the effect of substituent placement on the silylation of bromoanisoles was undertaken, and the results are summarized in Table 3. The yield of siloxane rapidly declined as the methoxy substituent shifted from the para (68%) to meta (25%) to ortho (0%) position. It was initially thought that coordination of the Lewis basic oxygen lone pair to palladium (or silicon) was responsible for this outcome. However, a noncoordinating *o*-methyl substituent also prevented silylation (Table 3, entry 6), indicating that steric interference may have a significant effect. It is proposed that both steric and electronic factors are responsible for the decreased yields with bromides when compared to their iodide counterparts. Attempts to improve the yield of *m*- or *o*-arylsiloxanes by altering the phosphine ligand were unsuccessful.

The modified reaction conditions were also applied to a variety of substituted aryl iodides in order to demonstrate the generality of the new ligand system and to determine the impact of arene substituent location on the silylation of iodides (Table 4). In agreement with the report of Masuda, electron-rich para-substituted aryl iodides underwent silylation more efficiently than the corresponding aryl bromides.[14] Similar yields of siloxanes were achieved with aryl iodides when either the Pd(dba)$_2$/ P(*t*-Bu)$_2$(*o*-biphenyl) (**4**) system or Masuda's Pd$_2$(dba)$_3$· CHCl$_3$/P(*o*-tol)$_3$ system was employed.

Aryl iodides were less sensitive to the electronic nature of the activating group than the corresponding bromides. For example, both 4-bromo- (Table 4, entry 8) and 4-chloroiodobenzene (Table 4, entry 9) gave comparable yields of siloxane to electron-rich aryl iodides (i.e., O-, N-, and alkyl-substituted). In contrast, only electron-rich aryl bromide analogues underwent silylation under these conditions. In the case of 4-bromoiodobenzene (Table 4, entry 8), the reaction required close monitoring for consumption of starting material because dehalogenation
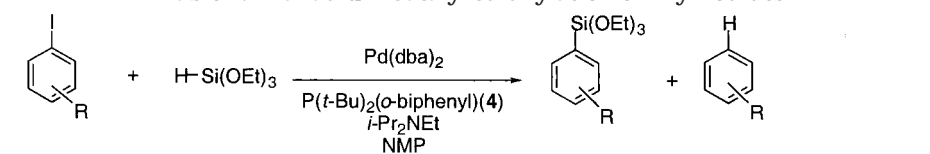
of the desired product, 4-(triethoxysilyl)bromobenzene, occurred under these conditions. Protection of other functionalities was unnecessary as shown by the excellent yields obtained with 4-iodoaniline (Table 4, entry 11) and 4-iodophenol (Table 4, entry 13). Prolonged reaction of iodoaniline not only lowered the yield of siloxane but also affected silylation of the unprotected amine nitrogen.
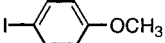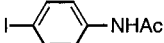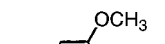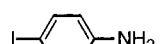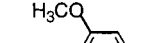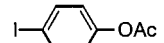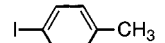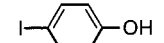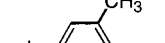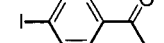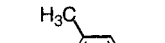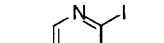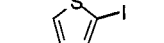
In contrast to the electron-rich aryl iodide systems, 4-iodoacetophenone was silylated in only 24% yield (Table 4, entry 14) (see other examples as well[14]). Recall that the bromo analogue failed to be silylated under these conditions (Table 2, entry 9). It is noteworthy that even the low yield was a triumph since the acetophenone analogue cannot be synthesized by the organometallic approach (Scheme 2) due to the presence of the reactive carbonyl group. Once again, the position of the substituent greatly impacted the reaction outcome: *o*-iodoanisole (Table 4, entry 3) or toluene (Table 4, entry 7) gave poor yields of product (10%, and 0%, respectively), whereas their *m*- and *p*-iodo arene counterparts gave acceptable yields.

The results from silylation of 2- and 3-iodopyridine are notable. While in all previous examples the Pd-mediated silylation reaction yielded either aryl siloxane or reduced starting material (Scheme 3), homocoupling of 2-iodopyridine was observed. [2,2′]Dipyridyl (**5**) was isolated in 15% yield from the attempted silylation of 2-iodopyridine (the reaction went to completion, with pyridine as the only other product). The homocoupling of 2-halopyridines in the presence of a palladium catalyst is a known reaction.[18] As a control, 2-iodopyridine was exposed to the standard silylation conditions *in the absence of triethoxysilane*, and [2,2′]dipyridyl (**5**) was isolated in quantitative yield (Scheme 4). In contrast, when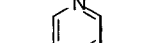 2-bromopyridine was used in the control experiment (Scheme 4), only a trace amount of the homocoupled product (**5**) was formed. The remainder of the reaction mixture was

(18) (a) Penalva, V.; Hassan, J.; Lavenot, L.; Gozzi, C.; Lemaire, M. *Tetrahedron Lett.* **1998**, *39*, 2559–2560. (b) Hassan, J.; Penalva, V.; Lavenot, L.; Gozzi, C.; Lemaire, M. *Tetrahedron* **1998**, *54*, 13793–13804. (c) Torii, S.; Tanaka, H.; Morisaki, K. *Tetrahedron Lett.* **1985**, *26*, 1655–1658.

Table 4. Palladium-Catalyzed Silylation of Aryl Iodides

| entry	aryl iodide (1)	% yield (2)[a,b]	entry	aryl iodide (1)	% yield (2)[a,b]
1	I—⟨⟩—OCH$_3$	86	10	I—⟨⟩—NHAc	68[d]
2	I—⟨⟩ (m-OCH$_3$)	52	11	I—⟨⟩—NH$_2$	77[d]
3	H$_3$CO, I (o-OCH$_3$)	10	12	I—⟨⟩—OAc	75[d]
4	I—⟨⟩—CH$_3$	80	13	I—⟨⟩—OH	70[d]
6	I—⟨⟩ (m-CH$_3$)	65	14	I—⟨⟩—C(=O)CH$_3$	24
7	H$_3$C, I (o-CH$_3$)	0[c]	15	2-iodopyridine	0[c]
8	I—⟨⟩—Br	68[d,e]	16	3-iodopyridine	10
9	I—⟨⟩—Cl	75[d]	17	2-iodothiophene	92

[a] Reactions of aryl iodide **1** (1.0 equiv) with HSi(OEt)$_3$ (**2**) (1.5 equiv) were performed at 60 °C for 12 h in NMP by using 3 mol % Pd(dba)$_2$, (*t*-Bu)$_2$P(*o*-biphenyl) (6 mol %), and *i*-Pr$_2$NEt (3 equiv). *[b]* Yields shown in parentheses are GC yields; all other yields are isolated yields of purified (>95%) product. *[c]* Yield confirmed by GCMS. *[d]* Reaction performed at room temperature. *[e]* Reaction stopped at 2 h.

Scheme 4
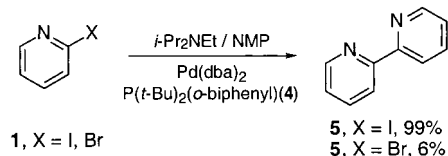
starting material. The results of the control experiments explain why no homocoupled product was observed in the attempted silylation of 2-bromopyridine, whereas homocoupling was a significant side reaction in the silylation of 2-iodopyridine.

Attempts to silylate 3-iodopyridine were problematic also. Although no homocoupled adduct was observed, we obtained only 10% of the desired product using either Masuda's conditions or our modified reaction conditions (Table 4, entry 16).These results were surprising since Masuda reported a 56% yield of 3-(triethoxysilyl)pyridine using Pd$_2$(dba)$_3$·CHCl$_3$/P(*o*-tol)$_3$ in NMP (1 h, 80 °C).[14] Again, it appears that the metal-coordinating ability of the pyridine nucleus is the culprit since 2-iodothiophene was readily silylated (92% yield, Table 4, entry 17).

Masuda has demonstrated that oxidative addition into the silane bond must be the key step in the mechanism of the transformation.[14] Subsequent metathesis of the Pd-(II) intermediate along the lines proposed by Kunai and Ishikawa results in either carbon−silicon or carbon−hydrogen bond formation.[19] The role of halogen (iodides vs bromides) in differentiating between carbon−silicon and carbon−hydrogen bond formation is obscure. Clearly, the difference in bond energies has a subtle effect upon which product is obtained. In addition, Kunai has shown that steric factors (*vide supra*, ortho vs meta vs para) play a significant role in which metathesis pathway is followed.

Conclusion

The Pd-mediated silylation of electron-rich aryl halides has been extended to include both iodides and bromides. For bromoarenes, the inclusion of Buchwald's phosphine

(19) Kunai, A.; Sakurai, T.; Toyoda, E.; Ishikawa, M.; Yamamoto, Y. *Organometallics* **1994**, *13*, 3233−3236.

ligand (**4**) is crucial. Although aryl iodides remain the substrates of choice for silylation, an acceptable yield of arylsiloxane may be obtained from the corresponding bromide. This is an advantage since aryl bromides are generally less expensive and more widely available.

The scope of the silylation protocol has been fully defined: the synthesis of aryl and heteroaryl siloxanes using HSi(OEt)$_3$ and a Pd catalyst is limited generally to electron-rich, para- and meta-substituted aryl bromides and iodides. This silylation method (Scheme 3) is an excellent companion to the more traditional organometallic approach (Scheme 2). Case in point, ortho-substituted arylsiloxanes are readily synthesized from the Grignard or lithium reagent.[15,20] Last, unlike the metalation approach, the Pd-catalyzed silylation technique can be performed in the presence of a wide range of functional groups, including carbonyl-containing electrophiles and protic moieties such as a phenol or primary amine.

Experimental Section

General Methods. All ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz instrument in CDCl$_3$, unless otherwise noted. Coupling constants (J) are given in Hz. Dimethylformamide (DMF) was distilled from molecular sieves. 1-Methyl-2-pyrrolidinone (NMP), toluene, pyridine, and acetonitrile (MeCN) were each distilled from calcium hydride. Tetrahydrofuran (THF) was distilled from sodium–benzophenone ketyl. Glassware used in the reactions was dried overnight in an oven at 120 °C. All reactions were performed under an atmosphere of argon.

Bis(dibenzylideneacetone)palladium (Pd(dba)$_2$) was purchased from Acros and used as received. 2-(Di-*tert*-butylphosphino)biphenyl (P(*t*-Bu)$_2$(*o*-biphenyl)) was purchased from Strem Chemical Co. and recrystallized from methanol (MeOH) prior to use. 2-(Dicyclohexylphosphino)biphenyl (P(cyh)$_2$(*o*-biphenyl)) was purchased from Strem Chemical Co. and recrystallized from absolute ethanol (EtOH) prior to use. All other phosphines and triphenylarsine were purchased from Aldrich, stored under argon, and used as received. Triethoxysilane (HSi(OEt)$_3$), diisopropylethylamine (*i*-Pr$_2$NEt), triethylamine (Et$_3$N), potassium acetate (KOAc), cesium carbonate (CsCO$_3$), 2,6-lutidine, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were purchased from Aldrich, stored in a desiccator, and used as received. *N*-(4-Bromophenyl)acetamide,[21] 2-iodopyridine,[22] 3-iodopyridine,[23] and 5-bromo-2-methoxypyridine[24] were each prepared according to the literature procedure. All other aryl halides were purchased from Aldrich and used as received. All compounds were determined to be >95% pure by GC and ^{1}H NMR unless otherwise noted. **CAUTION!** Triethoxysilane should be handled in a well-ventilated hood, and proper eye protection should be worn to prevent severe eye damage.

General Procedure for Synthesis of Siloxanes (2). Siloxane preparations and product isolations were performed under identical reaction conditions, the only variable being the reaction time and temperature as indicated in Tables 2–4. The following example is illustrative.

4-(Triethoxysilyl)anisole. 4-Bromoanisole (126 µL, 1.00 mmol) and *i*-Pr$_2$NEt (523 µL, 3.00 mmol) were added to a stirring solution of Pd(dba)$_2$ (17 mg, 0.03 mmol) and (*t*-Bu)$_2$P-(*o*-biphenyl)(**4**)(18 mg, 0.06 mmol) in 4 mL of NMP under an

atmosphere of argon. Triethoxysilane (277 µL, 1.5 mmol) was added, causing formation of yellow foam and a darkening of the reaction mixture. The reaction was heated at 60 °C (12 h). The black reaction mixture was extracted with 5 × 25 mL of pentane. The combined extracts were washed with 3 × 25 mL water to remove NMP, dried over MgSO$_4$, filtered, and concentrated. The resulting yellow oil was purified by bulb-to-bulb distillation (100 °C, 0.5 Torr) to give 184 mg (68% yield) of 4-(triethoxysilyl)anisole as a colorless oil. The IR and ^{1}H and ^{13}C NMR data were identical to published spectral data.[14]

4-(Triethoxysilyl)toluene: colorless oil. The IR and ^{1}H and ^{13}C NMR data were identical to published spectral data.[14]

4-(Triethoxysilyl)-1,2-(methylenedioxy)benzene: colorless oil; IR (CCl$_4$) 2976 (s), 2926 (m), 2886 (s), 1613 (w), 1503 (w), 1487 (m), 1422 (m), 1237 (m), 1168 (m), 1080 (s), 1045 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.24 (t, J = 6.8, 9H), 3.85 (q, J = 6.8, 6H), 5.95 (s, 2H), 6.86 (d, J = 7.6, 1H), 7.12 (s, 1H), 7.19 (d, J = 7.6, 1H); ^{13}C NMR (CDCl$_3$) δ 18.1, 59.9, 100.8, 108.8, 114.2, 123.9, 129.6, 147.6, 149.7; MS *m/z* 284 (100), 239 (39), 226 (28), 211 (10), 195 (14), 183 (25), 167 (18), 153 (13), 149 (24), 148 (14), 147 (75), 135 (12); HRMS for C$_{13}$H$_{20}$O$_5$Si calcd 284.1080, found 284.1083.

4-(Triethoxysilyl)acetanilide: colorless oil. The IR and ^{1}H and ^{13}C NMR data were identical to published spectral data.[14]

4-(Triethoxysilyl)aniline: colorless oil; IR (neat) 3469 (m), 3372 (s), 3223 (w), 2974 (s), 2926 (s), 2885 (s), 1624 (s), 1601 (s), 1509 (m), 1390 (m), 1295 (m), 1166 (s), 1074 (vs) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.23 (t, J = 7.0, 9H), 3.79 (s, 2H), 3.84 (q, J = 7.0, 6H), 6.67 (d, J = 8.3, 2H), 7.46 (d, J = 8.3, 2H); ^{13}C NMR (CDCl$_3$) δ 18.3, 28.6, 114.4, 118.4, 136.3, 148.6; MS *m/z* 255 (100), 210 (48), 153 (11), 147 (34), 136 (9), 135 (3); HRMS for C$_{12}$H$_{21}$O$_3$NSi calcd 255.1291, found 255.1292.

4-Acetoxy(triethoxysilyl)benzene: colorless oil. The IR and ^{1}H and ^{13}C NMR data were identical to published spectral data.[14]

4-(Triethoxysilyl)phenol: colorless oil; IR (CCl$_4$) 3606 (s), 3356 (vs), 2976 (s), 2926 (s), 2885 (s), 1602 (m), 1582 (w), 1506 (m), 1390 (w), 1261 (w), 1167 (m), 1125 (s), 1107 (s), 1080 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.24 (t, J = 7.2, 9H), 3.87 (q, J = 7.2, 6H), 6.23 (s, 1H), 6.85 (d, J = 8.3, 2H), 7.55 (d, J = 8.3, 2H); ^{13}C NMR (CDCl$_3$) δ 18.3, 59.0, 115.4, 121.2, 137.0, 158.1; MS *m/z* 256 (100), 241 (13), 220 (12), 211 (43), 210 (40), 183 (13), 167 (11), 163 (17), 155 (14), 147 (55), 119 (18); HRMS for C$_{12}$H$_{20}$O$_4$Si calcd 256.1131, found 256.1135.

Triethoxyphenylsilane: colorless oil. The IR and ^{1}H and ^{13}C NMR data were identical to an authentic sample, as well as published spectral data.[14]

4-(Triethoxysilyl)acetophenone: colorless oil; IR (neat) 2975 (s), 2927 (s), 2890 (s), 1728 (m), 1689 (s), 1497 (w), 1443 (m), 1390 (m), 1360 (m), 1263 (s), 1167 (s), 1079 (vs) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.26 (t, J = 7.0, 9H), 2.61 (s, 3H), 3.89 (q, J = 7.0, 6H), 7.79 (d, J = 8.0, 2H), 7.95 (d, J = 8.0, 2H); ^{13}C NMR (CDCl$_3$) δ 18.3, 26.8, 59.0, 127.4, 135.2, 137.4, 138.4, 198.5; MS *m/z* 282 (8), 268 (22), 267 (100), 239 (15), 238 (67), 237 (57), 223 (16), 209 (18), 193 (13), 181 (20), 165 (19), 163 (24), 147 (16), 138 (12), 135 (9); HRMS for C$_{14}$H$_{22}$O$_4$Si calcd 282.1287, found 282.1288.

4-Chloro(triethoxysilyl)benzene: colorless oil. An authentic sample was prepared in 76% isolated yield from 4-chloroiodobenzene using the general procedure for the synthesis of siloxanes given above; the IR and ^{1}H and ^{13}C NMR data were identical to published spectral data.[14] By GC, the reaction of 4-bromochlorobenzene with triethoxysilane using the general procedure for the synthesis of siloxanes given above yielded none of the desired product.

4-Bromo(triethoxysilyl)benzene: colorless oil; IR (neat) 2975 (s), 2926 (s), 2887 (s), 1575 (m), 1481 (m), 1442 (m), 1390 (m), 1379 (m), 1295 (w), 1165 (s), 1073 (vs) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.24 (t, J = 7.2, 9H), 3.86 (q, J = 7.2, 6H), 7.50–7.55 (m, 4H); ^{13}C NMR (CDCl$_3$) δ 18.4, 59.0, 125.5, 130.1, 132.3, 136.6; MS *m/z* 320 (5), 318 (5), 275 (26), 273 (22), 239 (16), 231 (11), 219 (11), 217 (12), 201 (10), 195 (33), 163 (12), 162 (18), 149 (11), 148 (21), 147 (100), 137 (10), 135 (32); HRMS for C$_{12}$H$_{19}$O$_3$^{79}BrSi calcd 318.0287, found 318.0295.

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(21) Bjornestedt, R.; Zhong, G.; Lerner, R. A.; Barbas, C. F., III. *J. Am. Chem. Soc.* **1996**, *118*, 11720–11724.

(22) Corcoran, R. C.; Bang, S. H. *Tetrahedron Lett.* **1990**, *31*, 6757–6758.

(23) Coudret, C. *Synth. Commun.* **1996**, *26*, 3543–3547.

(24) Kunishima, M.; Friedman, J. E.; Rokita, S. E. *J. Am. Chem. Soc.* **1999**, *121*, 4722–4723.

3-(Triethoxysilyl)anisole: colorless oil; IR (neat) 2975 (s), 2927 (m), 2887 (m), 1572 (m), 1482 (w), 1410 (w), 1391 (w), 1284 (w), 1249 (m), 1234 (m), 1167 (m), 1078 (vs) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.25 (t, J = 7.0, 9H), 3.81 (s, 3H), 3.87 (q, J = 7.0, 6H), 6.96–6.98 (m, 1H), 7.21–7.33 (m, 3H); ^{13}C NMR (CDCl$_3$) δ 18.3, 55.1, 58.8, 116.1, 119.8, 127.1, 129.2, 132.4, 159.0; MS m/z 270 (100), 256 (12), 255 (70), 226 (28), 225 (64), 211 (23), 197 (13), 182 (11), 181 (41), 169 (37), 168 (13), 167 (29), 163 (10), 154 (16), 153 (27), 149 (22), 147 (61), 139 (20), 137 (14), 136 (55), 135 (95); HRMS for C$_{13}$H$_{22}$O$_4$Si calcd 270.1287, found 270.1282.

2-(Triethoxysilyl)anisole: colorless oil; IR (neat) 3067 (m), 2967 (s), 2922 (s, 2891 (s), 2829 (m), 2780 (w), 2762 (w), 1590 (s), 1569 (s), 1459 (s), 1241 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.21 (t, J = 7.2, 9H), 3.79 (s, 3H), 3.84 (q, J = 7.2, 6H), 6.83 (d, J = 8.2, 1H), 6.95 (t, J = 7.2, 1H), 7.38 (m, 1H), 7.63 (dd, J = 1.6, 7.2, 1H); ^{13}C NMR (CDCl$_3$) δ 18.2, 55.1, 58.7, 109.6, 119.2, 120.5, 132.2, 137.5, 164.3; MS m/z 271 (M$^+$ + 1, 42), 225 (100), 195 (21), 181 (36), 139 (25), 119 (21), 91 (24), 77 (14); HRMS for C$_{13}$H$_{23}$O$_4$Si calcd 271.1366 (M$^+$ + 1), found 271.1354.

3-(Triethoxysilyl)toluene: colorless oil; IR (neat) 2975 (s), 2926 (s), 2885 (s), 1577 (w), 1480 (w), 1442 (m), 1390 (m), 1295 (w), 1225 (w), 1167 (s), 1104 (vs), 1079 (vs) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.25 (t, J = 7.2, 9H), 2.36 (s, 3H), 3.87 (q, J = 7.2, 6H), 7.23–7.29 (m, 2H), 7.46–7.48 (m, 2H); ^{13}C NMR (CDCl$_3$) δ 18.4, 21.7, 58.9, 128.0, 130.8, 131.4, 132.0, 135.6, 137.4; MS m/z 254 (41), 239 (6), 209 (52), 195 (6), 162 (44), 147 (100), 119 (53), 91 (42), 66 (6); HRMS for C$_{13}$H$_{22}$O$_3$Si calcd 254.1338, found 254.1331.

2-(Triethoxysilyl)toluene. By GCMS of the crude reaction mixture, the reaction of 2-bromotoluene with triethoxysilane using the general procedure for the synthesis of siloxanes given above yielded none of the desired product.

2-(Triethoxysilyl)thiophene: colorless oil. The IR and ^{1}H and ^{13}C NMR data were identical to published spectral data.[14]

3-(Triethoxysilyl)pyridine: colorless oil. An authentic sample was prepared in 10% isolated yield from 3-iodopyridine using the general procedure for the synthesis of siloxanes given above; the IR and ^{1}H and ^{13}C NMR data were identical to published spectral data.[14] In our laboratories, using the conditions given by Masuda,[14] we obtained a maximum isolated yield of 10% (Masuda reported a 56% yield). By GC, the reaction of 3-bromopyridine with triethoxysilane using the general procedure for the synthesis of siloxanes given above yielded none of the desired silylated product.

2-(Triethoxysilyl)pyridine. By GCMS of the crude reaction mixture, the reaction of 2-iodopyridine with triethoxysilane using the general procedure for the synthesis of siloxanes given above yielded pyridine as the major product and none of the desired silylated product. 2,2′-Dipyridyl (50 mg, 15%) was isolated; ^{1}H and ^{13}C NMR data were identical to an authentic sample.

5-Triethoxysilyl-2-methoxypyridine: colorless oil; IR (CCl$_4$) 2976 (s), 2927 (m), 2887 (m), 1589 (s), 1491 (w), 1442 (m), 1390 (w), 1356 (m), 1286 (s), 1082 (vs) cm^{-1}; ^{1}H NMR (CD$_3$CN) δ 1.20 (t, J = 7.0, 9H), 3.83 (q, J = 7.0, 6H), 3.87 (s, 3H), 6.73–6.75 (m, 1H), 7.76–7.78 (m, 1H), 8.32–8.35 (m, 1H); ^{13}C NMR (CD$_3$CN) δ 18.6, 53.9, 59.5, 111.5, 118.2, 145.5, 154.3, 166.5; MS m/z 272 (100), 240 (13), 226 (31), 170 (11), 163 (11), 136 (15), 119 (6), 91 (5), 79 (14); HRMS for C$_{12}$H$_{22}$O$_4$NSi calcd 272.1318, found 272.1311.

Supporting Information Available: ^{1}H NMR and ^{13}C NMR of 4-(triethoxysilyl)-1,2-(methylenedioxy)benzene, 4-(triethoxysilyl)aniline, 4-(triethoxysilyl)phenol, 4-(triethoxysilyl)-acetophenone, 4-bromo(triethoxysilyl)benzene, 3-(triethoxysilyl)-anisole, 2-(triethoxysilyl)anisole, 3-(triethoxysilyl)toluene, and 5-triethoxysilyl-2-methoxypyridine. This material is available free of charge via the Internet at http://pubs.acs.org.

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