Preparation and Palladium-Catalyzed Cross-Coupling of Aryl Triethylammonium Bis(catechol) Silicates with Aryl Triflates

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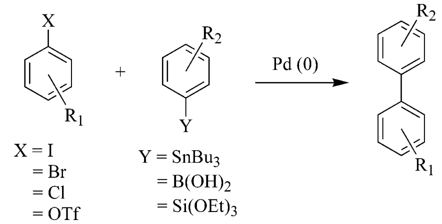
Pentavalent aryl and heteroaryl bis(catechol) silicates undergo palladium-catalyzed cross-coupling with aryl and heteroaryl triflates in the presence of a fluoride source in excellent yields. These solid, air-stable bis(catechol) silicates are prepared from a high-yielding displacement reaction between catechol and an aryl siloxane in the presence of an amine base. The cross-coupling reaction is tolerant of a wide range of electron-donating and electron-withdrawing groups. Several examples of di-ortho-substituted triflates are successfully coupled with these reagents.

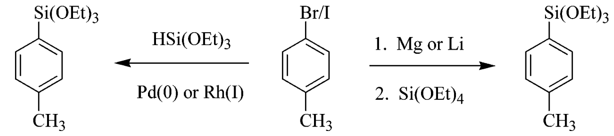
Introduction

Palladium-catalyzed cross-coupling reactions of aryl halides or triflates to form unsymmetrical biaryls are one of the most useful tools in synthetic organic chemistry. Several of the most common methods for performing these transformations are the Stille (organostannane), Suzuki−Miyaura (organoboron), and Hiyama (organosilicon) reactions (Scheme 1).[1−5] The more established Suzuki−Miyaura and Stille reactions have benefited from high yields and wide functional group tolerances. Despite these advantages, organosilicon reagents have emerged as a viable alternative for the synthesis of unsymmetrical biaryls, due in part to the inherent drawbacks in the Stille and Suzuki−Miyaura methodologies.[6−23] For example, Stille couplings require the use of toxic organotin reagents, while the boronic acid derivatives utilized in Suzuki couplings can be difficult to synthesize and purify.

SCHEME 1



SCHEME 2



Our laboratory has focused on the use of aryl trialkoxysiloxanes as alternatives to the organotin and organoboron compounds. These siloxanes can be readily synthesized via metalation (Li or Mg) of the corresponding aryl halide followed by nucleophilic attack upon readily available tetraalkyl orthosilicates or through palladium-[24,25] or rhodium-catalyzed[26] silylation (Scheme 2). In the presence of a fluoride activator, aryl siloxanes undergo Pd(0)-catalyzed cross-coupling with aryl iodides,[21] bromides,[21,22] and chlorides.[22] In addition, Fu has recently

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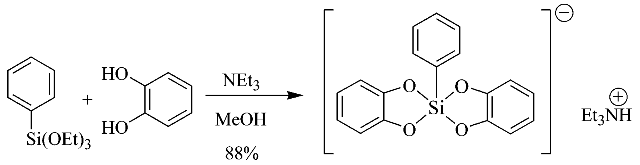
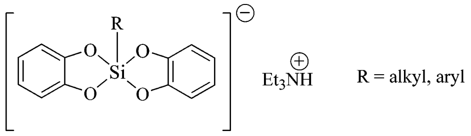
SCHEME 3



extended this methodology to include couplings with alkyl bromides and iodides.[9]

One limitation of the siloxane-based methodology is that aryl siloxanes do not couple efficiently to aryl triflates due to competing hydrolysis of the triflate under the basic reaction conditions. However, the use of aryl triflates is advantageous because they can easily be derived from the corresponding phenol and are often more accessible than the analogous aryl halide.[27] Recent studies in our laboratory have demonstrated that siloxane derivatives can be employed for the coupling of aryl triflates under strictly controlled conditions.[28] Nonetheless, we sought to develop new silicon-based reagents that would give better yields and show greater functional group tolerance and synthetic utility than the siloxane based approach. In this paper, we describe the preparation and coupling reactions of aryl bis(catechol) silicate anions with aryl triflates.



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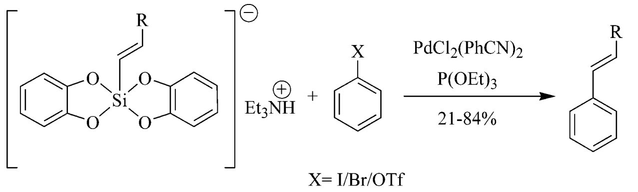
Pentavalent bis(catechol) silicates (**1**) were first synthesized by Frye in 1962.[29] They are readily prepared in excellent yields from alcoholic solutions of catechol, the respective siloxane, and triethylamine (Scheme 3).[29]

The structure[30−52] and reactivity[53−63] of these complexes have been studied extensively. However, their use as carbon−carbon bond-forming reagents remains relatively unexplored.[64−67] In one of the few examples of their use in cross-coupling reactions, Hosomi[65,68] has shown that pentacoordinate alkenylsiliconates in the presence of a suitable palladium catalyst in refluxing dioxane will couple in good yields with electron-deficient aryl iodides (60−84%) and in poor to moderate yields with aryl bromides, triflates, and electron-rich aryl iodides (21−57%) (Scheme 4).

SCHEME 4



In addition to low yields, these reactions suffered from long reaction times (30−110 h). It is within this context that we sought to develop a methodology for the efficient cross-coupling of bis(catechol) silicates with aryl triflates. Additionally, we have extended the scope of the coupling to electron-rich aryl iodides.[68]

Results and Discussion

Aryl bis(catechol) silicates are readily prepared in excellent yield by the reaction of their siloxane counter-

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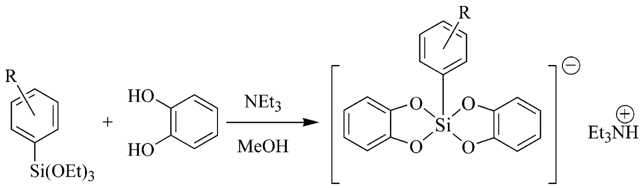
TABLE 1. Synthesis of Triethlyammonium Aryl Bis(catechol) Silicates from Aryl Siloxanes[a]

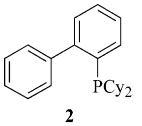


entry	R	yield (%)
1	H	88
2	2-OCH_3	82
3	3-OCH_3	94
4	4-OCH_3	86
5	2-CH_3	83
6	3-CH_3	90
7	4-CH_3	88
8	3,4-methylenedioxy	82
9	4-CO_2Et	89

[a] Reactions were perfomed at room temperature overnight.

parts with 2 equiv of catechol in the presence of triethylamine (see Table 1). The silicates are white, air stable, crystalline solids that can be recrystallized from methanol–ether (when necessary). The salts are freely soluble in warm ethereal solvents (THF, dioxane) and DMF.

Employing the protocol established in our laboratory for siloxane couplings, the bis(catechol) silicates did not cross-couple well with aryl bromides (Table 2, entries 1–4) or chlorides (data not shown). With bromides, the yields of coupled product were <40% and chlorides gave no product at all. For comparison, the analogous reaction with the aryl trialkoxysiloxane afforded 90% of the respective unsymmetrical biaryl.[21] The bis(catechol) silicates did couple successfully with aryl iodides (Table 2, entries 5 and 6). However, the best coupling substrates for the bis(catechol) silicates were aryl triflates (Table 2, entries 7–16). As summarized in Table 2 (entries 9, 14–16), the best conditions for the cross-coupling with anisoyl triflate were 5 mol % palladium catalyst and 5 mol % dicyclohexylphosphinobiphenyl (Buchwald phosphine) **2** in refluxing dioxane, although satisfactory yields can be obtained at lower temperatures in refluxing THF. It is likely that this electron-rich phosphine facilitates rapid oxidative addition into the aryl triflate, while at the same time its steric bulk allows it to readily disassociate and allow transmetalation with the hypervalent silicate species. Employing a similar ligand to **2**, di-*tert*-butylphosphinobiphenyl (**3**)[69] provided only a 23% yield of the cross-coupled product (Table 3, entry 12), providing further evidence that phosphine **2** combines the optimal combination of steric and electronic effects to promote the reaction.



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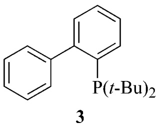

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The poor yields of coupled product obtained in DMF versus THF or dioxane indicate that increasing the polarity of the reaction solvent has an adverse effect upon the reaction. This result can be attributed to the ability of the solvent to coordinate to the palladium and disrupt the catalytic cycle.

Two notable features of this reaction were discovered during the course of the optimization studies. It was found that catechol could be quantitatively recovered from the crude cross-coupling reaction mixture by extraction with aqueous base (1 M NaOH), followed by acidification and re-extraction of the aqueous layer. Also, approximately 50% of the phosphine **2** could be recovered during chromatographic separation of the reaction products.

Efficient cross-coupling reactions with aryl triflates is very gratifying because previously we had reported that siloxanes failed to undergo cross-coupling with triflates due to facile hydrolysis of the triflate under the coupling conditions.[21,22] Subsequently, we had reported a revised protocol using silatrane analogues that allows for cross coupling with electron-rich aryl triflates in fair to good overall yields.[28] The silicate methodology discussed above, however, is more general and consistently gives higher yields of product than the silatrane method.

Having established that iodides and triflates are effective coupling substrates with aryl bis(catechol) silicates, a systematic investigation of the scope and limitations of the reaction was undertaken. The results summarized in Table 3 indicate that ortho-, meta-, and para-substituted electron-rich aryl iodides (entries 1–3) couple with phenyl bis(catechol) silicate. In addition, meta- and para-substituted bis(catechol) silicates were successfully coupled with iodobenzene (Table 3, entries 5 and 6). However, the ortho-substituted silicate coupled in poor yield (entry 4). This is most likely due to steric crowding around the silicon atom, which hinders transmetalation of the aryl ring to the palladium.

The analogous study was performed with aryl triflates to evaluate the functional group and steric tolerances of the reaction. The results are summarized in Table 4. The data indicates that this new methodology is applicable to a wide range of aryl triflates. Attempted coupling of very strongly electron-deficient triflates (Table 4, entry 12) proceeded in only moderate yield, with the remainder of the mass balance being 4-nitrophenol (hydrolysis product). Coupling of unprotected 4-aniline triflate was not successful (Table 4, entry 9); however, when the amine was acylated, cross-coupling proceeded in excellent yield (Table 4, entry 7). The inability of the cross-coupling reaction to proceed in the presence of a free amino group is attributed to coordination of the amine to the palladium and poisoning of the catalyst.

Entries 16 and 17 are of particular interest. These di-ortho-substituted aryl triflates coupled in only moderate yield (Table 4, entry 17), or not at all (entry 16) when the reaction was run in THF. However, when the reaction was run at a higher temperature (refluxing dioxane), these substrates coupled in excellent yields. This result indicates that it is possible to couple more stericly demanding substrates by switching the solvent to dioxane and performing the reaction at a higher temperature.[70] It is thought that the higher reaction temperature achieved in refluxing dioxane facilitates oxidative addi-

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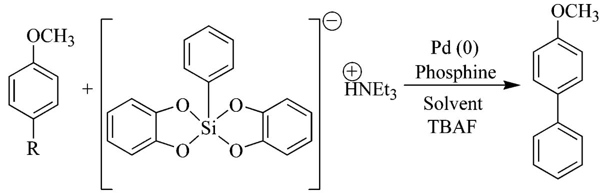
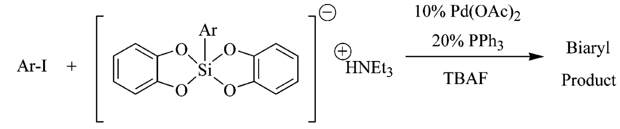
TABLE 2. Optimization of the Palladium-Catalyzed Cross-Coupling Reaction of Triethylammonium Bis(catechol) Phenyl Silicate with Aryl Triflates



entry	R	silicate complex (equiv)[a]	PdL$_n$ (mol %)	phosphine (mol %)	solvent (T, °C)	yield (%)
1	Br	2.0	Pd(OAc)$_2$ (10)	PPh$_3$ (20)	DMF (90)	40
2	Br	2.0	Pd(OAc)$_2$ (10)	PPh$_3$ (20)	DMF (150)	40
3	Br	2.0	Pd(dba)$_2$ (10)	**2** (10)	DMF (90)	38
4	Br	2.0	Pd(dba)$_2$ (10)	**2** (10)	THF (65)	7
5	I	2.0	Pd(OAc)$_2$ (10)	PPh$_3$ (20)	DMF (90)	87
6	I	2.0	Pd(dba)$_2$ (10)	**2** (10)	THF (65)	9
7	OTf	2.0	Pd(OAc)$_2$ (10)	PPh$_3$ (20)	DMF (90)	75
8	OTf	2.0	Pd(OAc)$_2$ (10)	PPh$_3$ (20)	THF (65)	0
9	OTf	2.0	Pd(dba)$_2$ (10)	**2** (10)	THF (65)	96
10	OTf	2.0	Pd(dba)$_2$ (10)	none	THF (65)	11
11	OTf	2.0	Pd(dba)$_2$ (10)	PPh$_3$ (10)	THF (65)	0
12	OTf	2.0	Pd(dba)$_2$ (10)	**3** (10)	THF (65)	23
13	OTf	1.0	Pd(dba)$_2$ (10)	**2** (10)	THF (65)	49
14	OTf	1.5	Pd(dba)$_2$ (10)	**2** (10)	THF (65)	95
15	OTf	1.5	Pd(dba)$_2$ (5)	**2** (5)	THF (65)	93
16	OTf	1.5	Pd(dba)$_2$ (5)	**2** (5)	dioxane (101)	97

[a] For each equivalent of the catechol complex, 1.0 equivalent of TBAF was added.

TABLE 3. Palladium-Catalyzed Cross-Couplings of Triethylammonium Bis(catechol) Phenyl Silicate with Aryl Iodides



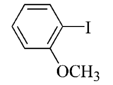
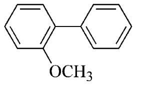
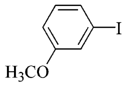
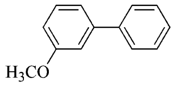
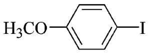
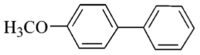
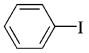
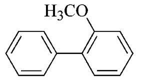
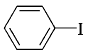
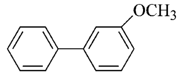
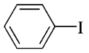
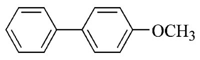
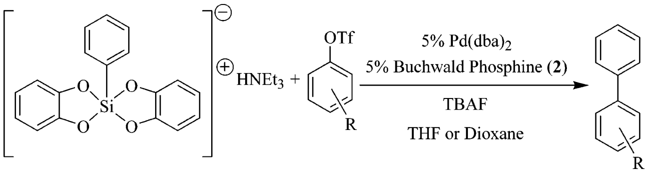
Entry	Ar-I	Ar	Biaryl Product	Yield (%)
1		phenyl		74
2		phenyl		82
3		phenyl		86
4		2-methoxyphenyl		29
5		3-methoxyphenyl		84
6		4-methoxyphenyl		81

TABLE 4. Palladium-Catalyzed Cross-Couplings of Triethylammonium Bis-catechol Phenyl Silicate with Aryl Triflates[a]



entry	R	yield[b] (%)	bromide[c]
1	4-OCH$_3$	96	88
2	2-OCH$_3$	95	
3	4-CHO	98	
4	4-COCH$_3$	96	86
5	2-COCH$_3$	93	
6	4-CO$_2$CH$_3$	94	93
7	4-NHAc	92	77
8	4-*tert*-butyl	95	
9	4-NH$_2$	0	90
10	4-CN	91	24
11	2-CN	89	
12	4-NO$_2$	46[d]	58
13	1-naphthyl	86	
14	2,6-dimethoxy	0[e] (0)[f]	
15	2-CH$_3$	92	
16	2,6-dimethyl	96[e] (0)[f]	
17	2-methoxy-6-formyl	86[e] (64)[f]	

[a] Reactions were perfomed for 6 h. [b] Reaction was performed in refluxing THF as solvent unless otherwise noted. [c] Yields are obtained using the corresponding aryl bromide in place of the triflate, coupling to phenyltrimethoxysilane.[21,22] [d] Remainder of mass balance was hydrolyzed triflate. [e] Yield in refluxing dioxane. [f] Yield in refluxing THF.

tion of the palladium into these hindered systems. This assertion is supported by the fact that at lower temperatures (THF), the triflate is recovered quantitatively (Table 4, entries 14 and 16). However, 2,6-dimethoxyphenyl trifluoromethanesulfonate (Table 4, entry 14) would not couple with the silicate, even in refluxing dioxane. The triflate was recovered.

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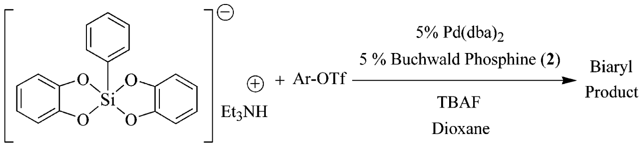
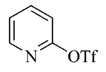
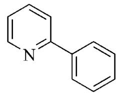
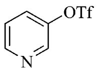
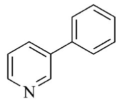
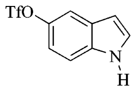
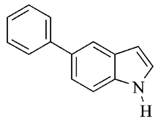
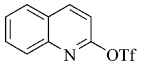
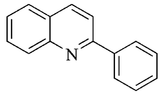
(70) It was noted by a reviewer that the effect seen by switching the solvent from THF to dioxane may not be entirely attributable to the increased temperature of the reaction. Rather, the difference in dielectric constant (2.21 for dioxane, 7.58 for THF) may play a greater role. However, two experimental results indicate that temperature, not polarity may, be the significant factor. When the coupling reactions were performed in dioxane at the reflux temperature of THF, no improvement in the yield of product was observed. In addition, when toluene was used as the solvent (dielectric constant of 2.15 at reflux), no cross-coupling was observed.

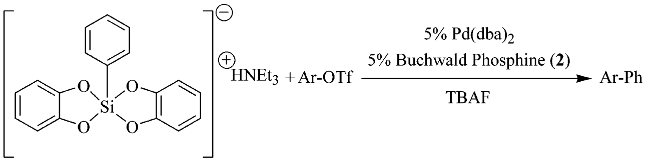
TABLE 5. Palladium-Catalyzed Cross-Couplings of Triethylammonium Bis-catechol Phenyl Silicate with Heteroaryl Triflates[a]

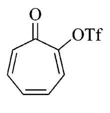
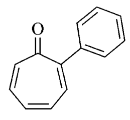
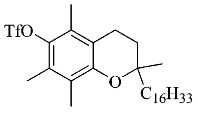
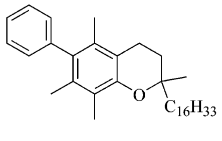
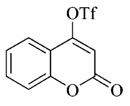
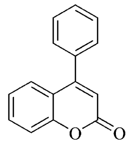


Entry	Ar-OTf	Biaryl Product	Yield[b]	Bromide Yield[c]
1			73 (51)	76
2			78 (53)	62
3			69 (51)	40
4			91[d]	75

[a] Reactions were run using 1.5 equiv of triethylammonium bis(catechol) phenyl silicate, 1.5 equiv of TBAF, 5 mol % of Pd(dba)$_2$, and 5 mol % of **2** in refluxing dioxane for 6 h. [b] Value in parentheses is the yield obtained in refluxing THF. [c] Bromide yield refers to the coupling of phenyl trimethoxysilane with the corresponding heteroaryl bromide.[22,23] [d] Reaction run in refluxing THF.

TABLE 6. Palladium-Catalyzed Cross-Coupling of Triethylammonium Bis-catechol Phenyl Silicate with Highly Functionalized Triflates



Entry	Ar-OTf	Ar-Ph	Yield (%)
1	 **4**	 **5**	89[a]
2	 **6**	 **7**	90[b]
3	 **8**	 **9**	0[c]

[a] Solvent was THF. [b] Solvent was dioxane. [c] Triflate was hydrolyzed under all conditions investigated.

The coupling of bis(catechol) silicates with heteroaryl triflates was also investigated. Palladium-catalyzed cross-coupling reactions of heteroaryl halides with aryl siloxanes proceed in only moderate yields and we were therefore interested to see if we could improve on the yield by employing a coupling between heteroaryl triflates and aryl bis(catechol) silicates.[18,71] The results are presented in Table 5.

The coupling of pyridyl triflates with triethylammonium bis(catechol) phenyl silicate in refluxing dioxane gave the desired cross-coupled products in yields that were comparable to the equivalent heteroaryl bromide/siloxane reactions (Table 5, entries 1 and 2).[22] However, the coupling of unprotected 5-indole trifluoromethanesulfonate (Table 5, entry 3) proceeded in a significantly higher yield than that observed in the corresponding siloxane reaction.[18] In addition, the coupling of 2-quinoline trifluoromethanesulfonate (Table 5, entry 4) proceeded in excellent yield.

The scope and limitations of triflate coupling were extended to the highly functionalized triflates shown in Table 6. the first coupling was 2-tropolone trifluoromethanesulfonate (4) with bis(catechol) phenyl silicate (Table 6, entry 1). The tropolone ring system is present in the colchicine family of alkaloids, and these compounds have shown promise as anti-cancer agents by binding to cellular tubulin in a Taxol-like mechanism.[72] Thus, there is interest in developing novel analogues. Tropolone 4 cross coupled in excellent yield with triethylammonium bis(catechol) phenyl silicate to produce the functionalized tropone **5**, thus demonstrating the ability to add aryl functionality to the tropolone system.

Similarly, the triflate of α-tocopherol (**6**) (vitamin E) was chosen to evaluate the ability of the bis(catechol) silicates to cross couple with highly hindered systems (Table 6, entry 2). When triflate **6** was allowed to couple with bis(catechol) phenyl silicate in refluxing dioxane, the desired cross-coupled product **7** was obtained in excellent yield.

Attempts to couple 5-coumarin trifluoromethanesulfonate (**8**) yielded none of the desired cross-coupled product **9** (Table 6, entry 3). Instead, the triflate was quantitatively hydrolyzed. This example clearly demonstrates that the reaction conditions that are appropriate for the coupling of aryl triflates are not suitable for the coupling of vinyl triflates.

Having demonstrated the scope and limitations of the reaction with various triflate substrates, attention was turned to a systematic investigation of substituent effects on the aryl bis(catechol) silicates. These results are presented in Table 7. In summary, the presence of electron-rich (Table 7, entries 5 and 6) and electron-deficient (entry 7) functionalities is well tolerated. The presence of functional groups in the meta and para positions of the aryl ring do not adversely affect the cross-coupling yields. However, when a substituent is present in the ortho position, the yield drops dramatically (Table 7, entries 1 and 4). The yield can be increased slightly by performing the reaction at a higher temperature (refluxing dioxane). This outcome is not entirely unex-

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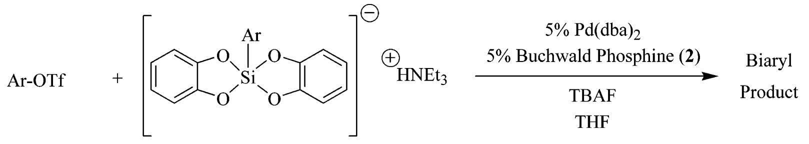
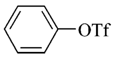
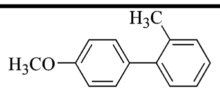
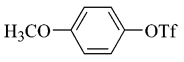
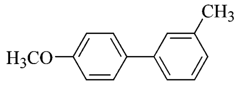
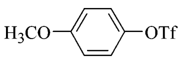
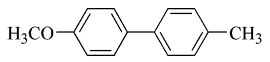
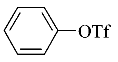
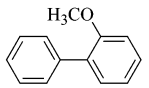
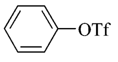
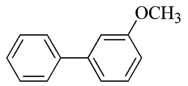
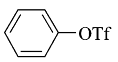
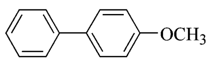
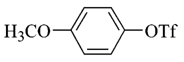
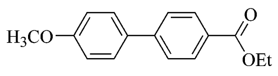
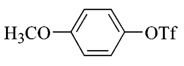
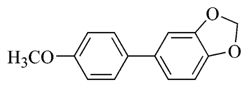
(71) Handy, C. J. *Preparation and NMR Studies of Hypervalent Silicates and Their Use in Palladium-Catalyzed Cross Coupling Reactions*; PhD Dissertation, University of Maryland, College Park, 2002.

TABLE 7. Palladium-Catalyzed Cross-Couplings of Aryl Triethylammonium Bis-catechol Silicates with Aryl Triflates



Entry	Ar-OTf	Ar	Biaryl Product	Yield (%)
1		*o*-tolyl		40[a] (20)[b]
2		*m*-tolyl		97
3		*p*-tolyl		92
4		*o*-anisole		41[a] (21)[b]
5		*m*-anisole		87
6		*p*-anisole		91
7		*p*-ethyl benzoate		94
8		3,4-methylenedioxybenzene		89

[a] Yield obtained in refluxing dioxane. [b] Yield obtained in refluxing THF.

pected as a similar result was obtained in the coupling of the aryl iodides (Table 3, entry 4).

Another interesting system that would further define the scope of the bis(catechol) silicate coupling technology was the coupling of a heteroaromatic triflate with a heteroaromatic bis(catechol) silicate. Quinoline−pyridyl moieties are found in multiple natural products such as streptonigrin[73] and camptothecin.[74] We, therefore, designed a template that would probe the feasibility of applying the bis(catechol) silicate coupling technology to these systems. Pyridyl derivative **11** is readily available in excellent yield from the respective pyridyl siloxane **10** (Scheme 5).[25] Having obtained the desired heteroaromatic bis(catechol) silicate **11**, a simple triflate was chosen to probe the feasibility of the coupling reaction. Accordingly, heteroaromatic bis(catechol) silicate **11** was coupled with 4-methoxyphenyl trifluromethanesulfonate **12** to yield the heteroaromatic biaryl **13** in 96% yield (Scheme 5).

Encouraged by the high yield obtained in this reaction, the coupling of 2-quinoline trifluoromethanesulfonate **14** with heteroaromatic bis(catechol) silicate **11** was attempted (Scheme 5). We were pleased to find that this coupling proceeded smoothly to produce the quinolopyridine **15** in 97% yield. It is anticipated that an analogous coupling reaction will be applicable to the total synthesis of streptonigrin and related substances.

A final feature of the cross-coupling reaction that was explored was the fluoride activation source. The typical fluoride source was tetrabutylammonium fluoride (TBAF) in THF solution (Acros) containing 5% water. It was observed that this reagent gave extensive hydrolysis of triflates derived from phenols bearing strong electron-withdrawing groups (Table 4, entry 12). A variety of alternative fluorides was investigated and the results are summarized in Table 8.

In the absence of a fluoride source, the cross-coupling reaction does not occur (entry 1). Alkali fluoride salts were ineffective as fluoride sources for the coupling reactions (entries 2−6). TBAF trihydrate, available as a crystalline solid, was as effective as the 1.0 M solution of TBAF in THF in promoting the cross-coupling reaction (entries 7 and 8). Tetramethylammonium fluoride trihydrate (TMAF) was also found to have similar activity (entry 9). It is interesting to note that the use of anhydrous TMAF actually lowered the yield of the cross-coupling reaction, with the remainder of the triflate

---

(72) Nicolaou, K. C.; Dai, W. M.; Guy, R. K. *Angew. Chem., Int. Ed. Engl.* **1994**, *106*, 15−44.

(73) Godard, A.; Marsais, F.; Ple, N.; Trecourt, F.; Turck, A.; Queguiner, G. *Heterocycles* **1995**, *40*, 1055−1091.

(74) Hutchinson, C. R. *Tetrahedron* **1981**, *37*, 1047−1065.

SCHEME 5

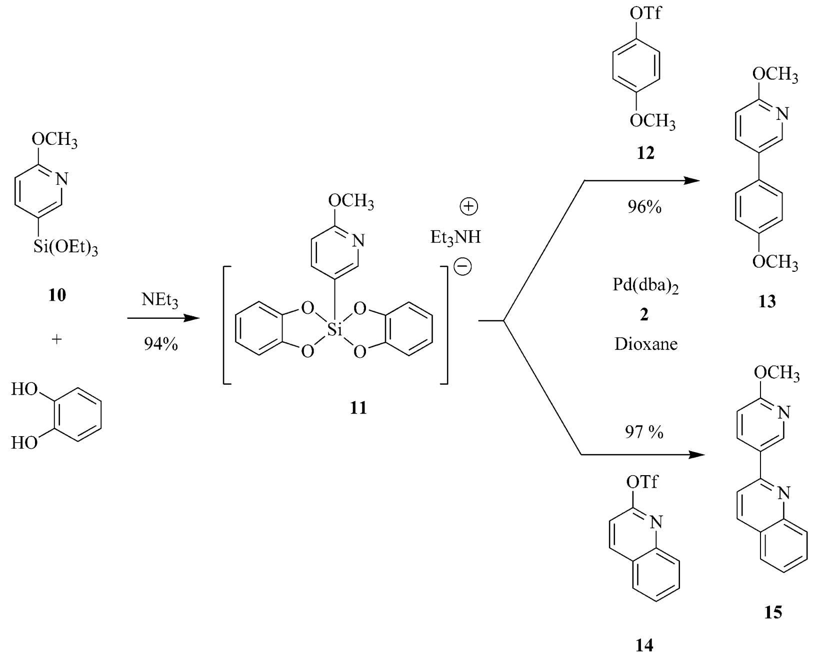
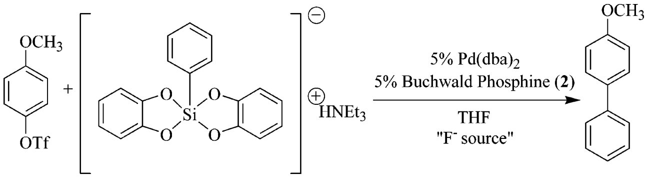


TABLE 8. Effect of Varying the Fluoride Source on Cross-Coupling Efficiency of Triethylammonium Bis-catechol Phenyl Silicate with 4-Methoxyphenyl Trifluoromethanesulfonate



entry	"F^- source"	yield (%)
1	none	0^a
2	KF	29^a
3	NaF	0^a
4	CsF	3^a
5	LiF	0^a
6	$NaBF_4$	30^a
7	$TBAF\cdot3H_2O$	94
8	TBAF (1.0 M in THF)	95
9	$TMAF\cdot3H_2O$	96
10	TMAF (anhydrous)[b]	74^c
11	$NaOSiMe_3$	33^a

[a] Remainder of triflate was unreacted. [b] Commerically available "anhydrous" TMAF contains less than 3% water. [c] Remainder of triflate was hydrolyzed.

undergoing hydrolysis (entry 10). It is plausible that the water present in the hydrated TMAF is serving to moderate the bacicity of the fluoride ion in solution and slow the rate of hydrolysis of the triflate. A similar effect was noticed in the coupling of aryl triflates and nonaflates with silanols.[7]

Denmark had previously reported that silanolates were effective promoters in the cross-coupling of organosilanols.[75] However, this reagent was not effective when extended to the coupling of bis(catechol) silicates with aryl triflates (Table 8, entry 11).

Conclusion

Aryl siloxanes efficiently couple to aryl iodides, bromides, and chlorides to provide unsymmetrical biaryl derivatives. However, the cross-coupling of aryl triflates to aryl siloxanes has been largely unsuccessful due to hydrolysis of the triflate under the reaction conditions. The studies reported in this paper demonstrate that pentacoordinate aryl bis(catechol) silicates serve as siloxane surrogates and couple to a wide range of aryl and heteroaryl triflates in excellent yields. the application of this methodology to the synthesis of heteroaromatic natural products is underway and will be reported in due course.

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Supporting Information Available: Experimental procedures for the preparation and characterization of all compounds is provided. ^{1}H NMR spectra are available for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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