



Biaryl formation: palladium catalyzed cross-coupling reactions between hypervalent silicon reagents and aryl halides

M. Penso^{a,*}, D. Albanese^b, D. Landini^b, V. Lupi^b

^a CNR—ISTM, Via Golgi 19, I-20133 Milan, Italy

^b Dipartimento di Chimica Organica e Industriale dell'Università, Via Venezian 21, I-20133 Milan, Italy

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Dedicated to Professor Renato Ugo on the occasion of his 65th birthday.

Abstract

Quaternary onium triorgano(difluoro)silicates $R^1_2R^2SiF_2^-Q^+$ were prepared by reaction of the corresponding quaternary onium hydrogendifluoride ($Q^+H_2F_2^-$) with a (triorgano)silane or a silyl enol ether. These silicates were isolated in very high yield and purity >99% by excluding halogenated solvents from the synthetic protocol. $Ph_3SiF_2^-Bu_4N^+$ (TBAT) was used as phenylating agent of aromatic halides in DMSO, at 120 °C and in the presence of 2.5% M equivalents of allyl palladium chloride dimer (APC) as a catalyst.

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1. Introduction

Aromatic cross-coupling catalyzed by palladium is one of the most important methods for the construction of aryl–aryl bonds [1]. Among these coupling reactions, notable protocols of general application are organoboranes (Suzuki) [2,3], organostannanes (Stille) [4,5], and hypervalent tin reagents [6,7] couplings. Although these procedures employ reagents stable and compatible with many functional groups, Stille coupling has its drawback in the toxicity of tin(IV) derivatives, whereas Suzuki methodology, that has largely supplanted the previous method, is limited by the availability of boronic acids.

In recent years, to overcome the problems connected with the use of B and Sn compounds, pen-

tacoordinate silicon derivatives, as both preformed and in situ prepared compounds, have been envisaged as reagents for cross-coupling reactions. After the pioneering works of Bréfort et al. [8], efforts have been made by several groups to find new and more reactive hypervalent silicon derivatives and to improve the efficiency of the transfer of aromatic or aliphatic units from these reagents to many substrates [9,10]. In particular, Hiyama and coworkers have described the cross-coupling with aryl halides of tris(diethylamino)sulfonium trimethyl-(difluoro)silicate (TASF) [11], alkyl(trifluoro)silanes [12], 2-cyclohexenylphenyl(difluoro)silane [13], aryl(halo)silanes [14,15], alkenylsilanes [15–17], and silanols [18]; Denmark group recently studied the use of alkenylsilacyclobutanes [19,20], alkenylsilanols [20–23], silyl hydrides [20], arylsilacyclobutanes [24], and siloxanes [25–27]. DeShong et al. optimized the conditions for the use of siloxanes in

* Corresponding author. Fax: +39-02-50314165.

E-mail address: michele.penso@unimi.it (M. Penso).

cross-coupling reactions with aryl halides and allylic benzoates [28–31]. These authors prepared for the first time tetrabutylammonium triphenyl(difluoro)silicate (TBAT) [32] and used it as fluorine source [32,33] and for the phenylation of allylic alcohol derivatives [34] and of aromatic substrates [35]. Finally, TBAT was successfully employed as a catalyst in allylation reactions by allyltrimethoxysilane [36].

In previously published papers, our group described two alternative syntheses of TBAT and related penta-coordinated onium difluorosilicates [37,38].

Here, we report our results on the synthesis optimization of difluorosilicates (**5**) and their use in palladium-catalyzed cross-coupling formation of unsymmetrical biaryls.

2. Experimental

2.1. Material

(Triorgano)silanes, silyl enol ethers, quaternary onium fluorides and hydrogenosulfates, aromatic halides, allyl palladium chloride dimer (APC), and potassium hydrogendifluoride purchased from Aldrich, Fluka, and Acros were used as such. Anhydrous solvents were from Fluka.

2.1.1. General method for the synthesis of triorgano(difluoro)silicates **5** from (triorgano)silanes **2**

The (triorgano)silane (**2**) (10 mmol) dissolved in benzene (10 ml) was added dropwise to a solution of quaternary onium hydrogendifluoride (**1**) (10 mmol) in benzene (5 ml) under nitrogen at 20–25 °C. After stirring for 0.5–20 h, the product is recovered by filtration, if it is a solid, or by distillation of the solvent, in the case of an oil (Table 1).

2.1.2. General method for the synthesis of triorgano(difluoro)silicates (**5**) from (trimethyl)silyl cyclopentenyl ether (**8**)

(Trimethyl)silyl cyclopentenyl ether (**8**) (10 mmol) was added dropwise to a solution of quaternary onium hydrogendifluoride (**1**) (10 mmol) in benzene (10 ml), under nitrogen at 20 °C. After stirring for 3 h the product is recovered by filtration, if it is a solid, or by distillation of the solvent, in the case of an oil (Table 2).

Table 1

Quaternary onium triorgano(difluoro)silicates prepared from triorganosilanes **2**^a

Product		Time (h)	Yield (%)
Ph ₃ SiF ₂ ⁻ Bu ₄ N ⁺	5a	0.5	99
Ph ₂ MeSiF ₂ ⁻ Bu ₄ N ⁺	5b	2	98
PhMe ₂ SiF ₂ ⁻ Bu ₄ N ⁺	5c	4	93
Ph ₃ SiF ₂ ⁻ PhCH ₂ N ⁺ Me ₃	5d	4	92
Ph ₂ MeSiF ₂ ⁻ PhCH ₂ N ⁺ Me ₃	5e	20	95
Ph ₃ SiF ₂ ⁻ C ₆ H ₁₃ P ⁺ Bu ₃	5f	0.5	94

^a Quaternary onium hydrogendifluoride (**1**) (1 M equivalent), silane **2** (1 M equivalent), benzene (1 M/l solution), under nitrogen at 25 °C.

2.1.3. Physical and spectroscopic data of silicates **5**

Tetrabutylammonium triphenyl(difluoro)silicate (**5a**): mp 155 °C (literature [39] 155–156 °C). ¹H NMR (acetone-d₆) δ 8.23 (dd, 6H, 7.8, 1.5), 7.26–7.17 (m, 9H), 3.89 (t, 8H, 8.5), 1.85–1.73 (m, 8H), 1.58–1.42 (m, 8H), 1.07 (t, 12H, 7.2); ¹³C NMR (acetone-d₆) δ 152.4 (t, 36), 138.4, 126.8, 126.7, 58.8, 24.2, 20.1, 13.8.

Tetrabutylammonium diphenylmethyl(difluoro)silicate (**5b**): mp 70 °C. ¹H NMR (acetone-d₆) δ 8.20 (dd, 4H, 7.8, 1.5), 7.63–7.54 (m, 2H), 7.37–7.29 (m, 4H), 2.51–2.41 (m, 8H), 1.78–1.70 (m, 8H), 1.63–1.60 (m, 8H), 1.56 (s, 3H), 1.06 (t, 9H, 8.1), 0.99 (t, 3H, 8.0).

Tetrabutylammonium phenyldimethyl(difluoro)silicate (**5c**): oil. ¹H NMR (acetone-d₆) δ 8.00–7.15 (m, 5H), 3.57 (t, 8H, 8.7), 1.93–1.87 (m, 8H), 1.58–1.48 (m, 8H), 1.09 (t, 12H, 7.2), 0.45 (s, 6H).

Benzyltrimethylammonium triphenyl(difluoro)silicate (**5d**): oil. ¹H NMR (acetone-d₆) δ 8.22 (dd, 6H, 7.8, 1.8), 7.65–7.60 (m, 5H), 7.26–7.17 (m, 9H), 4.59 (s, 2H), 3.51 (s, 9H).

Table 2

Quaternary onium triorgano(difluoro)silicates prepared from (trimethyl)silyl cyclopentenyl ethers (**8**)^a

Product		Yield (%) ^b
Ph ₃ SiF ₂ ⁻ Bu ₄ N ⁺	5a	87
Ph ₂ MeSiF ₂ ⁻ Bu ₄ N ⁺	5b	85
Me ₃ SiF ₂ ⁻ Bu ₄ N ⁺	5g	100 ^c
<i>t</i> -BuMe ₂ SiF ₂ ⁻ Bu ₄ N ⁺	5h	100 ^c

^a Quaternary onium hydrogendifluoride (**1**) (1 M equivalent), (trimethyl)silyl cyclopentenyl ether (**8**) (1 M equivalent), benzene (1 M/l solution), under nitrogen at 20 °C.

^b Isolated yield after filtration.

^c Yield of the crude **5** after distillation of the solvent.

Benzyltrimethylammonium diphenylmethyl(difluoro)silicate (**5e**): mp 147 °C. ¹H NMR (acetone-d₆) δ 8.50 (bs, 2H), 7.76–7.71 (m, 2H), 7.53–7.42 (m, 6H), 7.36–7.28 (m, 5H), 4.76 (s, 2H), 3.24 (s, 9H), 0.78 (s, 3H).

Hexadecyltributylphosphonium triphenyl(difluoro)silicate (**5f**): oil. ¹H NMR (acetone-d₆) δ 8.20 (dd, 6H, 7.8, 1.6), 7.26–7.18 (m, 9H), 2.51–2.41 (m, 8H), 1.79–1.70 (m, 8H), 1.63–1.56 (m, 8H), 1.41–1.39 (m, 24H), 1.06 (t, 9H, 6.9), 0.99 (t, 3H, 6.9).

Tetrabutylammonium trimethyl(difluoro)silicate (**5g**): oil. ¹H NMR (acetone-d₆) δ 3.55–3.35 (m, 8H), 1.90–1.15 (m, 16H), 1.05–0.70 (m, 12H), –0.20 (s, 9H). ¹⁹F NMR (acetone-d₆) δ –144.2.

Tetrabutylammonium *t*-butyldimethyl(difluoro)silicate (**5h**): oil. ¹H NMR (acetone-d₆) δ 3.50–3.30 (m, 8H), 2.05–1.20 (m, 16H), 1.15–0.80 (m, 12H), 0.18 (s, 9H), –0.18 (s, 6H). ¹⁹F NMR (acetone-d₆) δ –148.0.

¹⁹F NMR spectra of **5a–f** are reported in Table 3.

2.1.4. Cross-coupling phenylations of aromatic halides **10** promoted by onium (difluoro)silicates **5**. Representative procedure using TBAT (**5a**)

A solution of **10** (0.30 mmol), TBAT (**5a**) (324 mg, 0.60 mmol) and APC (2.7 mg, 0.0075 mmol) in anhydrous DMSO, was heated at 120 °C under nitrogen. After stirring for 1–26 h (TLC and/or GLC control) the reaction was quenched with brine (5 ml) and extracted with petroleum ether (PE, bp 40–60 °C, 3 × 3 ml). The organic phase was dried over MgSO₄, the solvent was evaporated under vacuum and the residue was purified

by flash chromatography. The chromatographic eluant and the physical data of nonsymmetric biaryls **11** (Table 6), homocoupling (**12b**) and methylation (**13b**) products (Table 8) are as following.

- Biphenyl (**11a**): PE; mp 69–70 °C (literature [40] 71 °C).
- 4-Nitrobiphenyl (**11b**): CH₂Cl₂–PE (1:5); mp 113 °C (literature [41] 114–114.3 °C).
- 4,4'-Dinitrobiphenyl (**12b**): CH₂Cl₂–PE (1:5); mp 238 °C (literature [42] 239–239.5 °C).
- 4-Nitrotoluene (**13b**): CH₂Cl₂–PE (1:5); mp 54 °C (literature [43] 54.5 °C).
- 2-Phenylnaphthalene (**11c**): PE; mp 101 °C (literature [44] 103–104 °C).
- 1-Phenylnaphthalene (**11d**): PE; mp 43 °C (literature [45] 45 °C).
- 1-Biphenyl-4-yl-ethanone (**11e**): CH₂Cl₂–PE (1:2); mp 119 °C (literature [46] 120–121 °C).
- 1-Biphenyl-2-yl-ethanone (**11f**): CH₂Cl₂–PE (2:3); mp 58 °C (literature [47] 56–58 °C).
- Biphenyl-2-carbaldehyde (**11g**): CH₂Cl₂–PE (2:3); *n*_D²⁰ 1.6252 (literature [48] *n*_D²³ 1.624).

2.2. Instrumentation

Melting points were determined on a Büchi 535 apparatus and are corrected. *n*_Ds were determined on an Atago 1T refractometer. NMR spectra were recorded on a Bruker AC 300 or AMX 300 spectrometers, operating at 300.133 and 300.132 MHz (¹H), 75.00 and 75.479 MHz (¹³C), 282.407 and 282.100 MHz (¹⁹F NMR), respectively. Potentiometric titrations were performed with a Metrohm 670 Titroprocessor by using a combined glass electrode isolated with a potassium chloride bridge or a combined silver electrode isolated with a potassium nitrate bridge. Karl–Fischer determinations were carried out with a Metrohm 684 KF coulometer or a 701 KF Titrino.

3. Results and discussion

3.1. Synthesis of difluorosilicates **5**

3.1.1. Preparation from triorganosilanes **2**

The general method for the preparation of difluorosilicates **5** containing at least one phenyl group

Table 3

¹⁹F NMR spectra of silicates **5** registered in chloroform-d, dichloromethane-d₂, and acetone-d₆

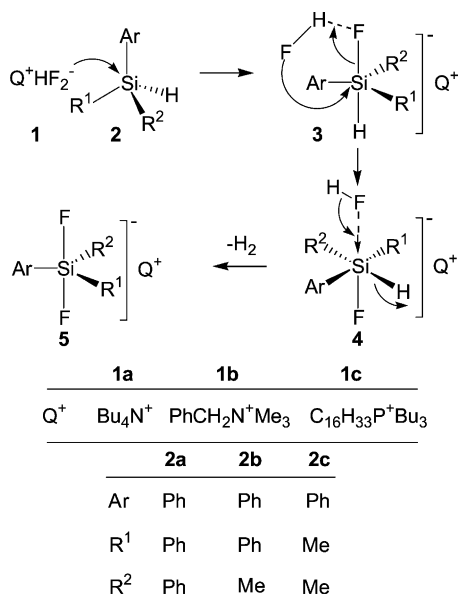
	¹⁹ F NMR (δ) ^a		
	CDCl ₃ ^b	CD ₂ Cl ₂ ^b	C ₃ D ₆ O
5a	–95.4	–94.6	–98.8
5b	–152.9	–157.3	–155.1
5c	– ^c	–153.0	–150.9
5d	–	–92.7, –148.7, –170.0 ^d	–97.8
5e	–	–147.5	–145.9
5f	–93.0, –128.6, –155.7, –170.1 ^d	–92.5, –126.5, –151.0, –169.8 ^d	–98.4

^a CFC1₃ as external standard; δ in ppm.

^b Registered in freshly distilled solvent.

^c The spectrum is complex with very broad signals.

^d Values in italics represent the decomposition by-product chemical shifts.

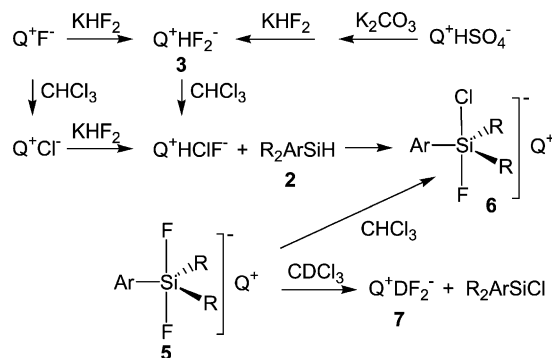


Scheme 1.

(Scheme 1) [35] is the reaction in benzene at 25 °C of a quaternary onium hydrogendifluoride (**1**) with 1 M equivalent of the corresponding triorganosilane **2**. When hydrogen evolution stopped, the product **5** was recovered from the crude by filtration, if solid, or by solvent evaporation, if it is an oil, in nearly quantitative yields (Table 1).

In this protocol, the purity of the quaternary hydrogendifluorides **1a–c** used is crucial (Scheme 1). In a optimization of our previously described procedure [49], these compounds were synthesized by reaction in water of the corresponding trihydrated quaternary ammonium fluoride, or alternatively of the quaternary phosphonium sulfate for the preparation of **1c**, with a stoichiometric amount of potassium hydrogendifluoride. The quaternary salt **1** was recovered by extraction with acetonitrile and distillation of the solvent. The crude was left under vacuum (2×10^{-4} mbar, 40 °C) until constant weight. The final products $Q^+HF_2^- \cdot 0.5H_2O$ (purity >99%) were analyzed by Karl–Fischer, argentometric, and acid/base titration.

As depicted in Scheme 1, and in analogy with several mechanisms proposed in literatures [50,51], the preparation of the difluorosilicate **5** probably involves three steps: (i) nucleophilic attack of the HF_2^- anion



Scheme 2.

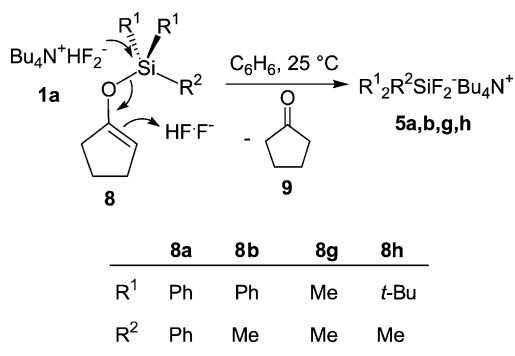
on silicon and formation of the monofluoro pentacoordinated derivative **3**; (ii) formation of the second Si–F bond through rearrangement of **3** to the hexacoordinated **4**; and (iii) elimination of hydrogen to produce **5**.

The presence of 0.5 M equivalents of water in the quaternary hydrogendifluorides does not affect the synthesis of quaternary difluorosilicates **1**. By contrast, it is of utmost importance that both procedures of preparation of **1** and **5** are conducted in the absence of halogenated solvents. In fact, the use of dichloromethane or chloroform produced partial displacement of fluorine, bearing to a less efficient pentacoordinated quaternary (triorgano)chlorofluorosilicate (**6**) (Scheme 2).

3.1.2. Preparation from (trimethyl)silyl cyclopentenyl ethers (**8**)

Since trialkylsilanes are unreactive with quaternary onium hydrogendifluorides (**1**) under the previously reported conditions, an alternative procedure for the synthesis of the corresponding trialkyl(difluoro)silicates was developed. A silyl cyclopentenyl ether **8** was reacted with a stoichiometric amount of **1a** (Scheme 3). The pentacoordinated silicates **5** are generated through a mechanism similar to that described in Scheme 1, via the corresponding hexacoordinated silicate and by elimination of cyclopentanone **9**.

Whereas the known silicates **5a** and **5b** are isolated in good yields by filtration (Table 2), the trimethyl(difluoro)silicate (**5g**) and *t*-butyldimethyl(difluoro)silicate (**5h**) are unstable at room temperature, and must be used, after distillation of the solvent, as



Scheme 3.

crude materials. The decomposition of TBAT [39] and other difluorosilicates [52] have previously been described.

3.1.3. ¹⁹F and ¹H NMR analyses

The silicate **6** (Scheme 2) is probably the intermediate of the onium deuteriodifluoride **7**, that was detected by ¹⁹F NMR analysis (δ_{DF_2} –145 to –160 ppm), formed in a deuteriochloroform solution of **5** stored for several hours at room temperature.

By examining the ¹⁹F NMR spectra of products **5a–f** (Table 3), we found that the stability of these silicates in deuteriochloroform and dichloromethane-*d*₂ is related to both the quaternary cation and the silicon substituents; tetrabutylammonium salts are more stable than benzyltrimethylammonium and phosphonium salts (e.g. **5a** > **5d**, **5f**), triphenyl- and diphenylmethyl- are more stable than phenyldimethyl(difluoro)silicates (e.g. in the series of tetrabutylammonium derivatives: **5a**, **5b** > **5c**). On the other hand, the silicates **5** are stable in acetone-*d*₆ solution, even after several hours, and all the spectra registered using this solvent show only one singlet.

In particular, the chemical shifts of the fluorine nuclei of (triphenyl)difluorosilicates **5a**, **5d**, and **5f** lie downfield (\sim –98 ppm) than those of **5b**, **5c**, and **5e**, containing alkyl substituents (–145.9 to –155.1 ppm). This behavior can probably be ascribed to the geometry of pentacoordinated silicon anion (Fig. 1), that is, a trigonal bipyramid having the fluorine atoms on the apical positions. The fluorine atoms are deshielded by the anisotropic influence of the axial benzene rings that, due to the steric hindrance, cannot completely rotate around the Si–C bonds (Fig. 1a).

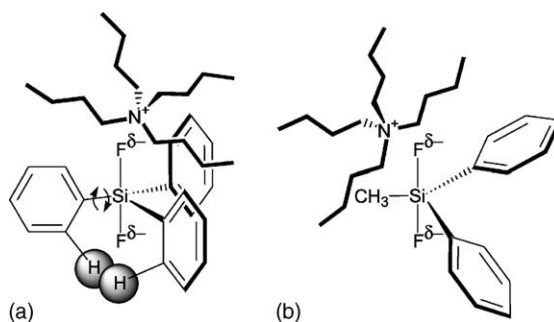


Fig. 1. Proposed structures of pentacoordinated difluorosilicates **5a** (a) and **5b** (b).

The partial rotation in the triphenyl(difluoro)silicate anion seems to be confirmed by the ¹H NMR spectrum of TBAT (**5a**) in CD₂Cl₂ (Table 4). The signal of α -methylene protons of the tetrabutylammonium cation is upfield than usually found for other quaternary ammonium salts ($\delta \sim$ 3.2 ppm) and, furthermore, several spectra of the same sample registered after short delays, show a random variation of the position of this signal in the range 2.32–2.70 ppm, whereas the ¹⁹F NMR spectrum remains unchanged. In this case, benzene rings shield the quaternary ammonium methylene protons that face them. The exerted shielding, and hence the chemical shift, change with the short rotations of the phenyls. Analogous results were obtained by the ¹H NMR analysis of benzyltrimethylammonium silicate (**5d**). On the contrary, the salts **5b**, **5c**, and **5e**, bearing methyl groups on the silicate anion, show ‘normal’ chemical shifts of the α -methylene signal, for example, for Ph₂MeSiF₂[–]Bu₄N⁺ (**5b**) in CD₂Cl₂ ($\delta_{\text{CH}_2\text{N}^+}$ 3.21 ppm). In this type of silicates, the cation can approach the anion from the methyl(s) side, resulting less influenced by the phenyl shielding.

In acetone-*d*₆ the ¹H NMR spectra of **5** do not show anomalous positions of the signals (Table 4). In all probability this solvent, due to its higher polarity, separates the ion pair by solvating the cation, so reducing the anisotropic effect of the aromatic rings.

3.2. Cross-coupling phenylation reactions promoted by difluorosilicates **5**

The palladium catalyzed phenylation of aromatic halides and triflates by TBAT (**5a**) has been stud-

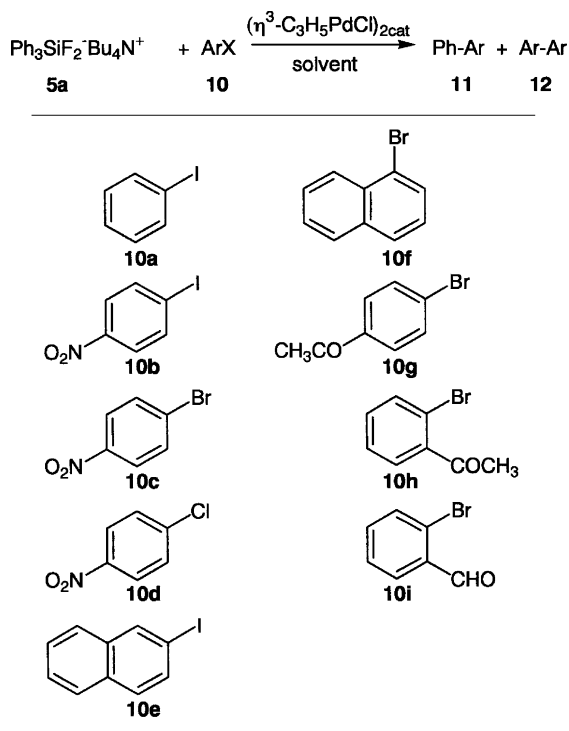
Table 4

Significant signals in ^1H NMR spectra of silicates **5** registered in acetone- d_6 and dichloromethane- d_2

Product	Solvent ^b	^1H NMR (δ) ^a			
		$\delta_{\text{CH}_2\text{N}^+}$ (t)	$\delta_{\text{CH}_2\text{N}^+}$ (s)	$\delta_{\text{PhCH}_2\text{N}^+}$ (s)	
$\text{Ph}_3\text{SiF}_2^- \text{Bu}_4\text{N}^+$	5a	$\text{C}_3\text{D}_6\text{O}$	3.39	–	–
		CD_2Cl_2	2.32–2.70	–	–
$\text{Ph}_2\text{MeSiF}_2^- \text{Bu}_4\text{N}^+$	5b	$\text{C}_3\text{D}_6\text{O}$	3.50	–	–
		CD_2Cl_2	3.21	–	–
$\text{PhMe}_2\text{SiF}_2^- \text{Bu}_4\text{N}^+$	5c	$\text{C}_3\text{D}_6\text{O}$	3.57	–	–
		CD_2Cl_2	3.24	–	–
$\text{Ph}_3\text{SiF}_2^- \text{PhCH}_2\text{N}^+\text{Me}_3$	5d	$\text{C}_3\text{D}_6\text{O}$	–	3.51	4.59
		CD_2Cl_2	–	2.64–2.85	4.02–4.28
$\text{Ph}_2\text{MeSiF}_2^- \text{PhCH}_2\text{N}^+\text{Me}_3$	5e	$\text{C}_3\text{D}_6\text{O}$	–	3.24	4.76
		CD_2Cl_2	–	3.22	4.74

^a TMS as external standard; δ in ppm; signal multiplicity is present in parenthesis.^b Registered in fresh distilled CD_2Cl_2 .

ied by Mowery and DeShong [35] and very good results are reported using APC or bis(dibenzylidenacetone)palladium as catalyst, and DMF as a solvent.



Scheme 4.

The cross-coupling of TBAT (**5a**) and 1-iodo-4-nitrobenzene (**10b**) was chosen as a model reaction (Scheme 4) to test the silicates **5**.

The effects of both the solvent and temperature were evaluated by carrying out a series of reactions in different solvents, at 40–120 °C and in the presence of 2.5% M equivalents of APC (Table 5). DMSO was the most effective in this aprotic dipolar solvent at 120 °C by using 2 M equivalents of TBAT, the substrate **10b** was completely converted in 1.5 h and 4-nitrobiphenyl (**11b**) was isolated in 89% yield. Under the same conditions, DMF is slightly less efficient, and 70% only of **11b** was produced. By contrast, very long reaction times were necessary and minor yields were obtained by using nonpolar solvents and lower reaction temperature. Dimethylsulfoxide and,

Table 5

Effect of the solvent and temperature on the phenylation of 1-iodo-4-nitrobenzene (**10b**) with TBAT (**5a**)^a

Solvent	T (°C)	t (h)	Yield (%) ^b
DMSO	120	1.5	89
DMF	120	1.5	70
CH_2Cl_2	40	48	30
CHCl_3	50	48	48
THF	50	48	53
C_6H_6	80	24	60

^a 1-Iodo-4-nitrobenzene (**10b**) (1 M equivalent), TBAT (**5a**) (2 M equivalents), solvent (0.4 M/l solution), under nitrogen.^b Isolated yield of 4-nitrobiphenyl (**11b**) after column chromatography.

Table 6

Effect of TBAT (**5a**) amount on the phenylation of 1-iodo-4-nitrobenzene (**10b**)^a

Entry	TBAT (molar equivalents)	<i>t</i> (h)	Yield (%) ^b
1	3	1.5	88
2	2	1.5	89
3	1.5	4.5	64
4	1.1	8	50
5	0.5	24	– ^c

^a 1-Iodo-4-nitrobenzene (**10b**) (1 M equivalent), DMSO (0.4 M/l solution), 120 °C, under nitrogen.^b Isolated yield of 4-nitrobiphenyl (**11b**).^c The reaction rate was very slow (conversion <50%) and hence the mixture was not worked up.

in a minor extent, dimethylformamide rapidly transform the dimeric species APC into the monomeric $\eta^3\text{-C}_3\text{H}_5\text{PdCl}$, that through a catalytic cycle involving the stable $\eta^3\text{-C}_3\text{H}_5\text{Pd(L)Cl}$ (L = DMF, DMSO) species, forms $\text{Pd}^0(\text{L})_n$, which most probably is the actual catalyst in the cross-coupling reactions [53]. The dissociation of the dimer is essentially due to the high reaction temperature and both the polarity and the strongly coordinating properties of these aprotic dipolar solvents [54].

The influence of the amount of TBAT was investigated by reacting **10b** at 120 °C, in anhydrous DMSO, with 0.5–3 M equivalents of **5a** (Table 6). We found, in line with the data of Mowery and DeShong [35], that the optimal quantity of TBAT is 2 M equivalents (entry 2), whereas a larger molar excess (entry 1) did not produce any yield enhancement. The yield of **11b** decreased by decreasing the amount of TBAT and, at the same time, the reaction rate slowed down (entries 3–5). On the contrary, the variation of allyl palladium

Table 7

Unsymmetrical biaryls **11** prepared by reaction of TBAT (**5a**) with aromatic halides **10**^a

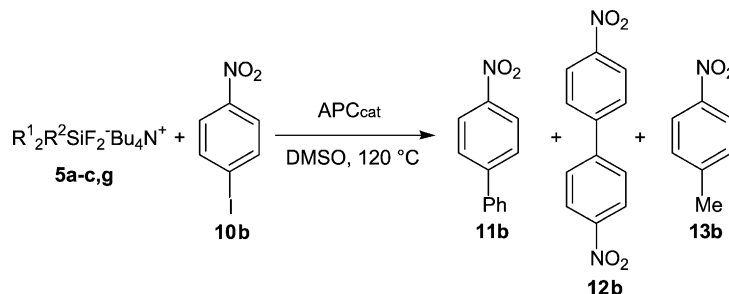
Substrate	<i>t</i> (h)	Product	Yield (%) ^b
$\text{C}_6\text{H}_5\text{I}$ (10a)	2	11a	85
4- $\text{NO}_2\text{C}_6\text{H}_4\text{I}$ (10b)	1.5	11b	89
4- $\text{NO}_2\text{C}_6\text{H}_4\text{Br}$ (10c)	4	11b	77
4- $\text{NO}_2\text{C}_6\text{H}_4\text{Cl}$ (10d)	26	11b	54
2- $\text{I-C}_{10}\text{H}_7$ (10e)	1	11c	83
1- $\text{Br-C}_{10}\text{H}_7$ (10f)	4	11d	66
4- $\text{CH}_3\text{CO C}_6\text{H}_4\text{Br}$ (10g)	4	11e	85
2- $\text{CH}_3\text{CO C}_6\text{H}_4\text{Br}$ (10h)	6	11f	61
2- $\text{CHO C}_6\text{H}_4\text{Br}$ (10i)	6	11g	90

^a ArX **10** (1 M equivalent), TBAT (**5a**) (2 M equivalents), APC (0.025 M equivalents), DMSO (0.4 M/l solution), under nitrogen for 120 °C.^b Isolated yields.

chloride amount, in the range 0.025–0.1 M equivalents, exerted minor influence on the reaction rate and products formation, and hence only 2.5% M of APC was used in the preparative reactions.

The optimal reaction conditions found were applied to the synthesis of a series of unsymmetrical biaryls (Table 7). Iodo and bromo derivatives were converted into the corresponding biaryls **11** in good yields, whereas the aromatic chlorides, for example, 1-chloro-4-nitrobenzene (**10d**), gave poor yields in long reaction times. Both substrates containing electron-withdrawing and electron-donating substituents were reactive and several functional groups are compatible with the conditions employed.

Finally, 1-iodo-4-nitrobenzene (**10b**) was reacted with several triorgano(difluoro)silicates to determine the products distribution of the palladium catalyzed coupling (Scheme 5).



Scheme 5.

Table 8

Products distribution of the coupling of 1-iodo-4-nitrobenzene (**10b**) with onium triorgano(difluoro)silicates **5**^a

Silicate 5	11b (%)	12b (%)	13b (%)
Ph ₃ SiF ₂ ⁻ Bu ₄ N ⁺ (5a)	89	–	–
Ph ₂ MeSiF ₂ ⁻ Bu ₄ N ⁺ (5b)	18	50 ^b	8
PhMe ₂ SiF ₂ ⁻ Bu ₄ N ⁺ (5c)	3	70 ^b	13
Me ₃ SiF ₂ ⁻ Bu ₄ N ⁺ (5g)	–	78 ^b	–

^a 1-Iodo-4-nitrobenzene (**10b**) (1 mmol), silicate **5** (2 M equivalents), APC (0.025 M equivalents), DMSO (2.5 ml), 120 °C.

^b Yield of the reaction 2ArX → Ar–Ar.

As previously described, with TBAT (**5a**) the aryl–aryl cross-coupled **11b** was the sole product isolated, whereas from the reactions with **5b** and **5c**, both homocoupled **12b** and methyl–aryl cross-coupled **13b** were produced together with **11b** (Table 8). In contrast, **5g** that contains three methyl groups on the silicate anion, gave only 4,4'-dinitrobiphenyl (**12b**) [38].

4. Conclusion

In conclusion, the described procedure enables a high yield synthesis of pure (>99%) onium triorgano(difluoro)silicates **5**. TBAT (**5a**) was successfully used as phenylating reagent of a wide variety of aryl iodides and bromides, in DMSO as a solvent and in the presence of 2.5% molar only of allyl palladium chloride as a catalyst. Under these conditions, also chloride derivatives were reactive and gave biaryls, even if in moderate yields.

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