

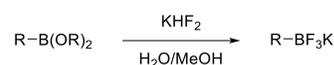


# Additive-free coupling of ammonium organotetrafluorosilicate salts and aryldiazonium salts

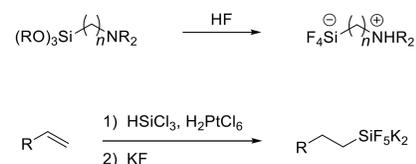
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## Introduction

Organotrifluoroborate salts have enjoyed substantial success over the past several years. This is, in part, due to their easy synthesis, high reactivity, and benchtop stability.<sup>1</sup>



However, the analogous, facile synthesis of organotetrafluorosilicates has recently been developed by our lab.<sup>2</sup> Organofluorosilicates have also been prepared by treating alkoxy silanes with water-free hydrogen fluoride in ether solution<sup>3</sup> or by reacting organotrichlorosilanes with KF.<sup>4</sup> Both of these syntheses rely on starting materials that are not readily synthetically available and require the use of dangerous reagents such as HF.



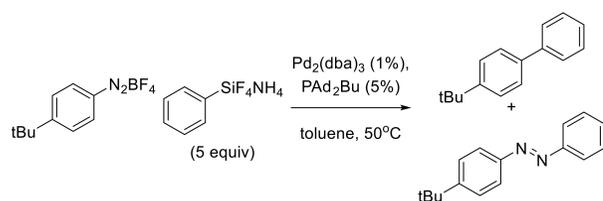
Several research groups have reported on the synthetically useful electrophilic cleavage reactions of the carbon-silicon bond, however, organofluorosilicates have not received much attention in part due to their inaccessibility.<sup>4,5</sup> Currently, there is one report of using alkoxy silanes to make organofluorosilicates, but they do not report a yield and their procedure has not been reproducible in our hands.<sup>6</sup>

Current best coupling reactions, like Suzuki couplings and Sonogoshira couplings, are limited by their use of basic conditions, which cannot tolerate base-sensitive functional groups. Organotetrafluorosilicate salts have not been explored as coupling partners until recently and show significant potential.<sup>7</sup> The activated silicon does not seem to require a base additive in order to couple effectively. Initial results show that tetrafluorosilicates will couple with aryldiazonium salts in the presence of a palladium catalyst, producing easily removable byproducts.

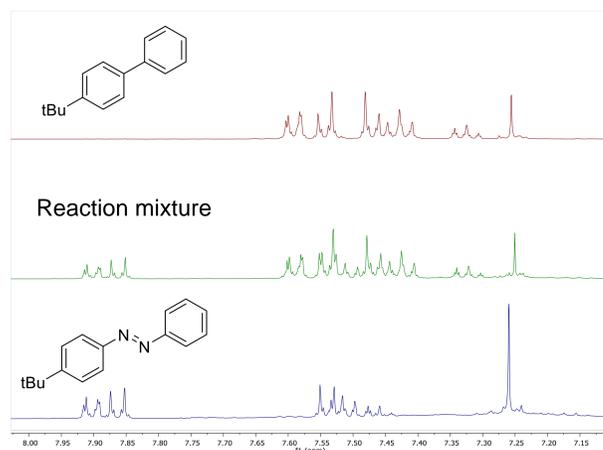
## Hypothesis

An ammonium organotetrafluorosilicate will tolerate coupling conditions, which will allow couplings to occur in mildly acidic conditions and without the need for a basic additive.

## Initial Findings



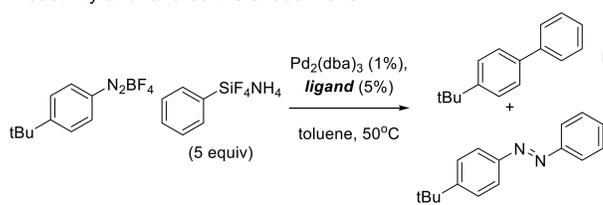
Most of the time, the reaction would only produce the coupling product, however, on occasion, seemingly randomly, it would produce two products. The second product turned out to be an azobenzene.



<sup>1</sup>H-NMRs of pure products and the reaction mixture

## Ligand Optimization

Initial optimization began with a selection of different ligands. Steric bulk favored the biaryl product. While steric bulk was also necessary for catalytic activity, a ligand with flexible steric bulk restored some reactivity and favored the azobenzene.

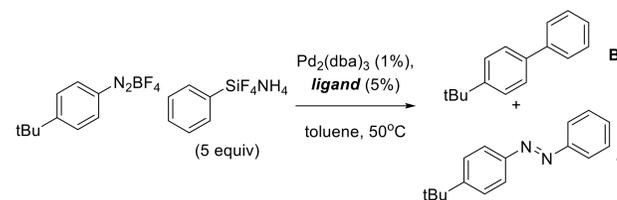


entry	ligand	A	B
1	PAd <sub>2</sub> Bu	3%	89%
2	PAd <sub>3</sub>	0%	98%
3	PtBu <sub>3</sub>	0%	100%
4	PCy <sub>3</sub>	4%	35%
5	PnBu <sub>3</sub>	<1%	0%
6	PBn <sub>3</sub>	19%	31%

yields determined by using 1,1,1,2-tetrachloroethane as an internal standard

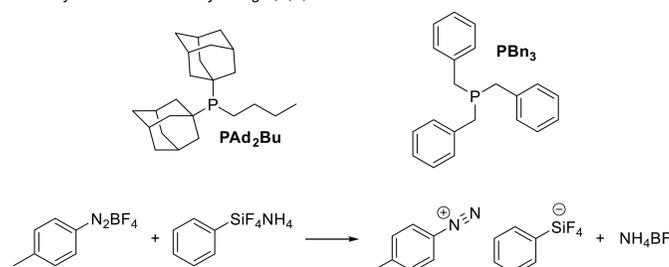
## Impact of Pre-Stirring

Since the results with PAd<sub>2</sub>Bu were inconsistent, pre-stirring different reaction components was explored. We found that stirring the substrates together was facilitated azobenzene formation.



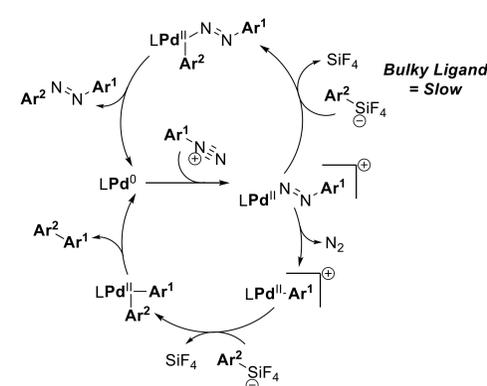
entry	pre-stirring conditions	ligand	A	B
1	ligand and Pd <sub>2</sub> (dba) <sub>3</sub> (5 min)	PAd <sub>2</sub> Bu	3%	93%
2	ligand, Pd <sub>2</sub> (dba) <sub>3</sub> , and PhSiF <sub>4</sub> NH <sub>4</sub> (5 min)	PAd <sub>2</sub> Bu	8%	90%
3	ligand, Pd <sub>2</sub> (dba) <sub>3</sub> , and ArN <sub>2</sub> BF <sub>4</sub> (5 min)	PAd <sub>2</sub> Bu	<1%	12%
4	PhSiF <sub>4</sub> NH <sub>4</sub> and ArN <sub>2</sub> BF <sub>4</sub> (15 min)	PAd <sub>2</sub> Bu	10%	60%
5	PhSiF <sub>4</sub> NH <sub>4</sub> and ArN <sub>2</sub> BF <sub>4</sub> (1 hour)	PAd <sub>2</sub> Bu	20%	28%
6	PhSiF <sub>4</sub> NH <sub>4</sub> and ArN <sub>2</sub> BF <sub>4</sub> (15 min)	PBn <sub>3</sub>	4%	11%
7	PhSiF <sub>4</sub> NH <sub>4</sub> and ArN <sub>2</sub> BF <sub>4</sub> (1 hour) ligand and P <sub>2</sub> (dba) <sub>3</sub> (separately)	PBn <sub>3</sub>	35%	32%

yields determined by using 1,1,1,2-tetrachloroethane as an internal standard



## Proposed Mechanism

We believe this reaction proceeds by a fairly standard mechanism where the significant point of deviation is the transmetalation step.



## Future Directions

1. Continue optimizing the azobenzene coupling using other ligands with flexible steric bulk.
2. Use the coupling to establish a substrate scope that includes other functional groups such as carbonyls, acids, and phenols.

## Conclusions

We have shown that an organotetrafluorosilicate can participate in coupling reactions. We expect the reaction to be highly tolerant of a variety of functional groups. Future work will focus on continuing to develop the Pd-catalyzed coupling of aryltetrafluorosilicate salts with aryldiazonium salts by exploring the substrate scope of both the biaryl and azobenzenes.

## Acknowledgements

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