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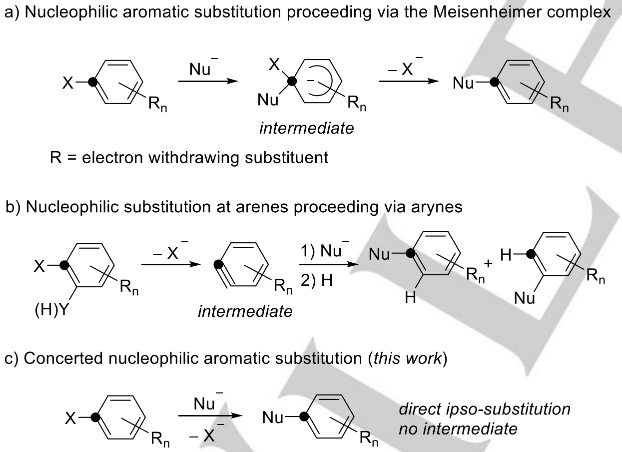
Silyldefluorination of Fluoroarenes via Concerted Nucleophilic Aromatic Substitution

Shubhadip Mallick, Pan Xu, Ernst-Ulrich Würthwein* and Armido Studer*

Abstract: The reaction of readily generated silyl lithium reagents with various aryl fluorides to provide the corresponding aryl silanes is reported. DFT calculations reveal that the nucleophilic aromatic substitution of the fluoride anion by the silyl lithium reagent proceeds via concerted *ipso* substitution. In contrast to the classical nucleophilic aromatic substitution, this concerted ionic silyldefluorination also occurs on more electron rich aryl fluorides.

Nucleophilic aromatic substitution proceeding via the so-called Meisenheimer complex is a well-established process for *ipso*-substitution of arenes (Scheme 1, a).[1] However, this addition/elimination sequence is only efficient for activated electron-deficient arenes. Alternatively, *ipso*-substitution products can be accessed via reactions that occur through arynes (Scheme 1, b). In such cases, elimination of the leaving group X precedes the addition step and isomeric products may result for substituted arynes.[2] In fact, 4-substituted arynes generally lead to a 1:1 mixture of regioisomers. The third option, that has gained some attention recently, is the concerted nucleophilic aromatic *ipso*-substitution, which can also occur on more electron-rich arenes (Scheme 1, c).[3] As for the nucleophilic aromatic substitution, these concerted transformations occur with complete regioselectivity and as recently discussed by Jacobsen, might be more abundant than expected.[3r]

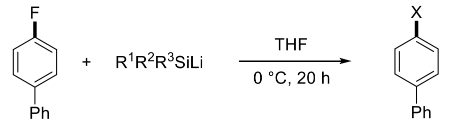


Scheme 1. Nucleophilic substitution at arenes.

Si-bearing compounds have found great attention in various fields of modern science and in organic chemistry they appear as valuable intermediates and reagents.[4] Along these lines, aryl silanes occupy a prominent role. They are generally prepared by the reaction of aryl Grignard or aryl lithium compounds with chlorosilanes.[5] Moreover, transition-metal catalyzed silylation of aryl halides has been intensively investigated.[6] Considering costs of transition metal catalysts, the direct silylation of aryl halides with silyl-metal compounds in the absence of any transition metal would be highly desirable.

It is well known that silyl anions, such as silyl lithium compounds react efficiently with various organic electrophiles,[7] but their reactivity towards aryl halides has not been well investigated. Strohmann and coworkers studied the reaction of Ph–X (X = Cl, Br, I) with chiral silyl lithium compounds and found that the less reactive chlorides and bromides are dehalosilylated under inversion of configuration at the chiral Si-center.[8a] These results indicated that the Si-lithium reagent first undergoes nucleophilic attack at the halogen atom of the halobenzene to give phenyl lithium along with the corresponding electrophilic halosilane which in turn reacts with PhLi to give the silylated product arene. Similar observations were disclosed recently by Ito.[8b] Herein we show that silyl lithium reagents react efficiently with various aryl fluorides to the corresponding aryl silanes via a different mechanism through concerted nucleophilic *ipso*-substitution, as also supported by theoretical studies.

The silyl lithium reagents were readily generated in THF from the corresponding chlorosilanes by treatment with elemental Li.[9] We commenced our studies by examining the reaction of *para*-fluorobiphenyl **1a** as a test substrate and the different SiLi-reagents **2a**-**e** (Scheme 2).



1a	**2a** ($PhMe_2SiLi$)	**3aa** (73%, 40%[a],[b], X = $SiPhMe_2$)
	2b (Ph_2t-BuSiLi)	**3ab** (70%[a],[c], X = $SiPh_2t$-Bu)
	2c ($Ph_2MeSiLi$)	**3ac** (45%[a],[b], X = $SiPh_2Me$)
	2d (Ph_3SiLi)	**3ad** (41%, X = $SiPh_3$)
	2e (Ph_2HSiLi)	**3ae** (27%, X = $SiPh_2H$)

Scheme 2. Variation of the silyl nucleophile. Reaction conditions: **1a** (0.3 mmol, 1.0 equiv), Si-reagent (0.6 mmol, 2.0 equiv), THF (1 mL) at 0 °C. [a] Reaction conducted with 1.5 equiv of the Si-lithium reagent. [b] Reaction conducted at –25 °C. [c] Reaction conducted at room temperature.

The best result was obtained upon running the *ipso*-substitution at 0 °C using 2 equiv of $PhMe_2SiLi$ (**2a**) for 20 hours to provide silylated biphenyl **3aa** in 73% isolated yield with complete regioselectivity. By using a smaller excess of reagent **2a**, yield slightly dropped (1.8 equiv: 70%, 1.6 equiv: 69%, 1.4 equiv: 65%, 1.2 equiv: 65%, 1.0 equiv: 63%). Note that at room

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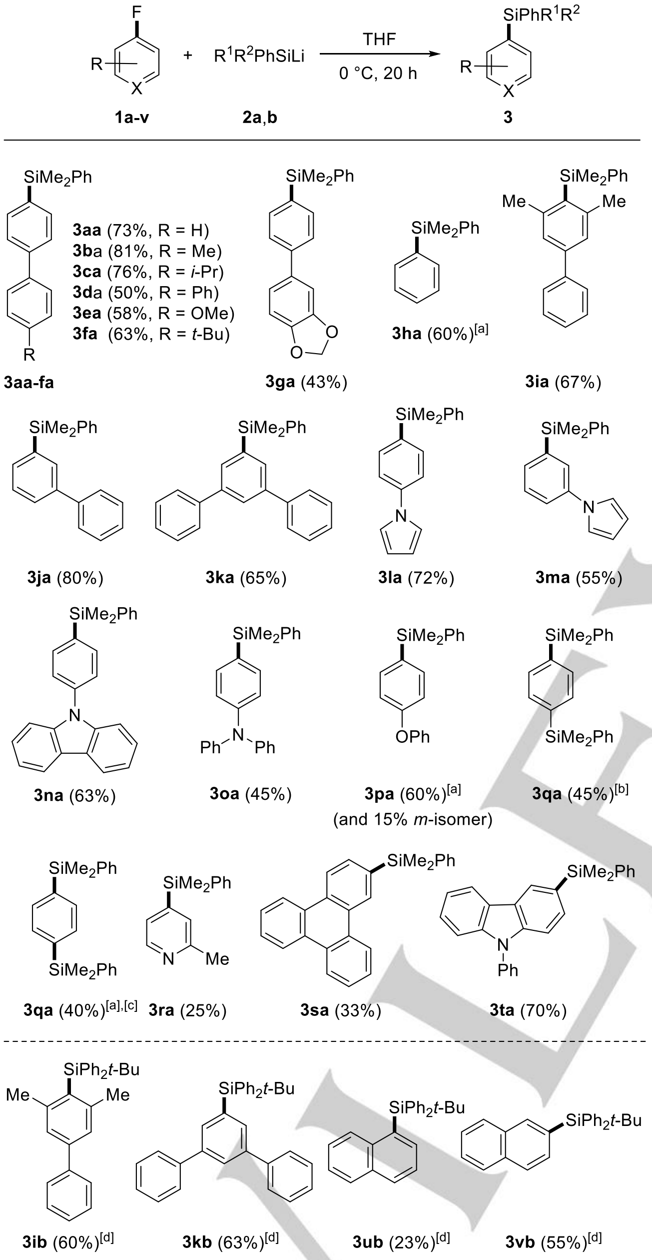
temperature, 5% of the *meta*-silylated biphenyl was formed as a side product indicating that at this temperature aryne generation competes with the direct *ipso*-substitution. Other silyl lithium reagents such as Ph_2*t*-BuSiLi (**2b**), $Ph_2MeSiLi$ (**2c**), Ph_3SiLi (**2d**) and Ph_2HSiLi (**2e**) can also be used in the silyldefluorination under slightly modified conditions to give the silylated biphenyls **3ab-ae** with complete regioselectivity. Ph_2*t*-BuSiLi provided a similar yield as **2a**, but the reagents **2c**-**e** showed lower efficiency.

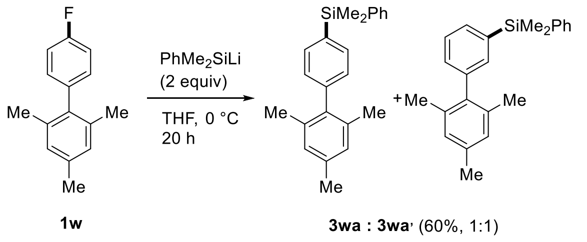


Scheme 3. Defluorosilylation of various fluoroarenes. Reaction condition: **1** (0.3 mmol, 1.0 equiv), Si-reagent (0.6 mmol, 2.0 equiv), THF (1 mL) at 0 °C. [a] Reaction conducted at –25 °C. [b] With 4-F-$C_6H_4SiMe_2Ph$ as substrate. [c] With 1,4-F_2-C_6H_4 as substrate using 4 equiv of **2a**. [d] Reaction conducted with Ph_2*t*-BuSiLi at rt.

We next investigated the scope and limitation of the novel method by testing various types of fluoroarenes (Scheme 3). For these studies we mainly used $PhMe_2SiLi$ (**2a**) as the silylating reagent. As expected, other *para*-fluorinated biphenyls **1b-g** reacted well with **2a** to give the corresponding aryl silanes **3ba-3ga** in 43-81% yields with excellent regioselectivity. The silyldefluorination is not restricted to fluorinated biphenyl derivatives and the non-activated fluorobenzene afforded dimethyldiphenylsilane (**3ha**) in 60% yield. A sterically hindered *ortho,ortho'*-dimethyl fluorobenzene reacted well to give the aryl silane **3ia** in 67% yield. *Meta*-substituents are tolerated in the starting fluorobenzenes as shown by the successful preparation of **3ja** (80%) and **3ka** (65%). Pyrrole-substituted fluorobenzenes **1l** and **1m** engage in the silyldefluorination and products **3la** and **3ma** were isolated in moderate to good yields. Also the *N*-*p*-fluorophenylcarbazole (**1n**) and *para*-fluoro-*N*,*N*-diphenylaniline (**1o**), which would not be a substrate in a classical nucleophilic aromatic substitution, were eligible substrates to afford **3na** and **3oa** in 63% and 45% yield, respectively. However, the electron-rich *para*-phenoxy derivative **1p** reacted with low regioselectivity and product **3pa** was isolated in 60% yield along with 15% of its *meta*-isomer. It is obvious that in this case a large fraction of the targeted product **3pa** (around 15% out of 60%) was formed *via* the corresponding aryne intermediate. *Para*-silylated fluorobenzene **1q** gave the bissilyl derivative **3qa** and the same compound was also prepared by double silyldefluorination of *para*-difluorobenzene (40%). The developed reaction is not restricted to fluoroarenes since *para*-fluoro-2-methylpyridine (**1r**) engaged in the substitution to give silylated pyridine **3ra**, albeit in only 25% yield. 2-Fluorotriphenylene **1s** and carbazole **1t** provided **3sa** and **3ta** in 33% and 70% yield, respectively.

For selected substrates, reactions were repeated using the bulkier Ph_2*t*-BuSiLi (**2b**) and the corresponding products were obtained in similar yields to those obtained with **2a** (see **3ib** and **3kb**). Naphthalene derivatives **1u** and **1v**, which surprisingly turned out to be unreactive towards $PhMe_2SiLi$, reacted with Ph_2*t*-BuSiLi to **3ub** and **3vb** which were isolated in 23% and 55% yield.

For the bulky fluoro biphenyl **1w** with a large torsion angle placing the two shielding methyl groups in direction to the *ipso*-carbon atom, the silyldefluorination provided products **3wa** and **3wa'** as a 1:1 mixture of isomers, indicating that substitution occurred exclusively *via* the corresponding aryne intermediate. This result shows that *ortho*-deprotonation of the fluorobenzene derivative with $Me_2PhSiLi$ can become the major reaction pathway if the transition state for the concerted substitution is not accessible.

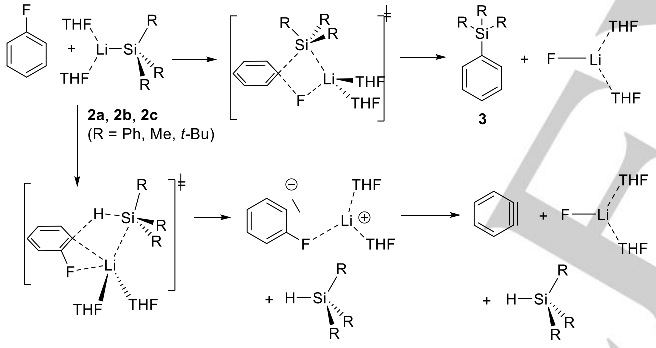


Scheme 4. Defluorosilylation of **1w** proceeds via the corresponding aryne.

To further address the reaction mechanism, DFT calculations (TPSSTPSS/def2-TZVP+PCM(THF)+GD3BJ dispersion correction as implemented in the GAUSSIAN 09 package of programs) were performed for the reaction of fluorobenzene with

PhMe$_2$SiLi (**2a**), Ph$_2$*t*-BuSiLi (**2b**) and Ph$_2$MeSiLi (**2c**). In the following, we report relative Gibbs free energies with respect to the educt complexes (ΔG298, kcal/mol) (see the Supporting Information for details).

As starting models for the calculations complexes of the silyl lithium compounds **2a**, **2b** and **2c** with two molecules of THF coordinating the lithium ion and fluorobenzene, also coordinating to the lithium ion, were chosen. First, we studied the nucleophilic *ipso*-substitution. By a continuous approach of the *ipso*-carbon atom of fluorobenzene to the silicon atom, the transition states for the nucleophilic *ipso*-substitution were localized (for **2a**: 18.8 kcal/mol; for **2b** 20.8 kcal/mol; for **2c** 19.4 kcal/mol) with a tetrahedral four coordinate *ipso*-phenyl carbon atom and Si–C distances of 2.557 Å (**2a**), 2.546 Å (**2b**), 2.581 Å (**2c**) along with Li–C-distances of 2.748 Å (**2a**), 2.887 Å (**2b**), 2.859 Å (**2c**). The Si–Li-distances were calculated as 2.676 Å (**2a**), 2.890 Å (**2b**), and 2.815 Å (**2c**), respectively (Scheme 5). Subsequently, in a very exothermic step (for **2a**: -61.5 kcal/mol; for **2b**: -58.4 kcal/mol and for **2c**: -59.8 kcal/mol compared to the energy of the starting complexes) diphenyldimethylsilane, triphenyl-*t*-butylsilane, and triphenyl-methylsilane respectively and Li–F (THF)$_2$ are formed. In case of **2b** by relaxation from the transition state a negatively charged fluoride-silane intermediate with five-coordinate silicon is formed as an intermediate (7.4 kcal/mol higher in energy compared to the product). Of course, further aggregation/oligomerrisation of LiF will considerably increase the exothermicity of this reaction even more.



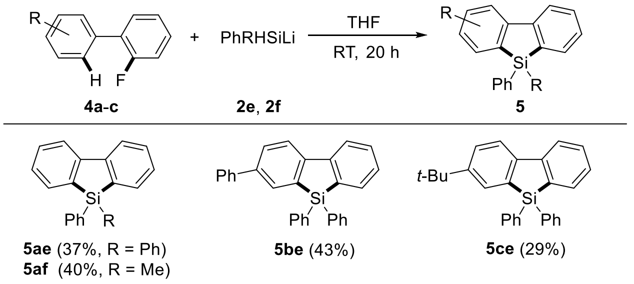
Scheme 5. Reaction mechanisms for the Si–F-exchange reaction and for the aryne formation, as studied by DFT-calculations.

For the formation of a possible aryne intermediate, a reaction pathway starting with the same initial complex as above involving an approach of the silicon atom to one of the two *ortho*-hydrogen atoms of the fluorobenzene was investigated. Here, transition states for the proton removal (for **2a** 21.7 kcal/mol, for **2b** 21.8 kcal/mol, for **2c**: 22.3 kcal/mol) were localized with a tetrahedral four coordinate *ipso*-carbon atom and calculated C··H (**2a** 1.504 Å, **2b** 1.530 Å, **2c** 1.485 Å), Si··H (**2a** 1.858 Å, **2b** 1.830 Å, **2c** 1.829 Å) and H··Li (**2a** 1.791 Å, **2b** 1.785 Å, **2c** 1.775 Å) distances. Relaxation from these transition states leads to aggregates of the respective hydrosilanes (PhMe$_2$SiH, Ph$_2$*t*-BuSiH or Ph$_2$MeSiH) and the o-fluorophenylanion coordinated to a lithium ion (solvated by two THF; relative energy for **2a**: -1.7 kcal/mol; for **2b**: 0.2 kcal/mol; for **2c**: -2.4 kcal/mol). By elongating the F–C-bond, the complexes of benzyne with the respective silane and solvated LiF are formed. This reaction step came out to be endothermic (relative energies for **2a**: 22.9; for **2b** 19.2 kcal/mol; for **2c** 22.3 kcal/mol), most likely because of neglecting the quite exothermic formation of LiF oligo- and polymers in our model reaction pathway.

In good agreement with the reaction conditions employed, all barriers are calculated to be higher for the aryne formation compared to the substitution reaction (difference to the substitution barrier: for **2a** (PhMe$_2$SiLi: 2.8 kcal/mol) for **2b** (Ph$_2$*t*-BuSiLi: 1.0 kcal/mol), and for **2c** (Ph$_2$MeSiLi: 2.9 kcal/mol)). Thus, in all cases, but especially in the first and third case, the substitution is calculated to be significantly favoured over the aryne formation.

To further support the suggested mechanism, we ran competition experiments using fluoroarenes with different electronic properties. To this end, a fluoroarene pair (1 equiv each) was reacted with **2a** (1 equiv) and product ratio was determined by GC analysis (see SI). Standard substrate **1a** was chosen as a reaction partner (σ_p = -0.01).[10] The 1-pyrryl-substituted fluoroarene **1l** was selected as the electron-poor arene in this series (σ_p = 0.37),[10] and the NPh$_2$-substituted fluorobenzene **1o** was included as the electron-rich substrate (σ_p = -0.22).[10] As expected for a concerted nucleophilic aromatic substitution, for the couple **1a**/**1o** the electron-poorer **1a** reacted with high chemoselectivity (**3a** (66%), **3o** (2%)). A similar result was achieved for the pair **1l**/**1o** (**3l** (59%), **3o** (3%)) and the pyrryl-biphenyl **1l** was slightly more reactive than **1a** ((**3l** (30%), **3a** (26%)). Moreover, a Hammett plot of $\log(k_{ArX}/k_{ArH})$ against σ_p considering four different aryl fluorides (para-substituent = H, Me, pyrrol and SiMe$_2$Ph) revealed a ρ-value of +3.2 (see SI for details), in line with the suggested concerted *ipso*-substitution.[3j,s]

Finally, the *ipso*-substitution reaction was applied to a novel synthesis of 9-silafluorenes, that are valuable compounds for the construction of functional materials.[11] Commercial *ortho*-fluorobiphenyls **4a-c** were chosen as the substrates. Reaction under standard conditions with the silyl lithium compounds **2e** and **2f**, both containing a Si–H bond, directly provided the corresponding 9-silafluorenes **5** (Scheme 6). The amazing and straightforward sequence likely proceeds *via* initial nucleophilic aromatic substitution to give *ortho*-silylbiphenyls as intermediates, which subsequently undergo oxidative cyclization to the isolated 9-silafluorenes.[12,13] The mechanism of the second Si–C bond forming step is currently not understood.[13]



Scheme 6. Preparation of 9-silafluorenes.

In summary, we showed that the reaction of various fluoroarenes with readily generated PhMe$_2$SiLi or Ph$_2$*t*-BuSiLi provides the corresponding silylated arenes in moderate to good yields offering a novel approach to silylated arenes. Theoretical studies showed that these transformations occur by a concerted nucleophilic aromatic substitution via a 4-membered asynchronous transition state. In contrast to nucleophilic aromatic substitutions the herein disclosed reaction also occurs on electron-rich fluoroarenes. We further found that *ortho*-deprotonation of the fluoroarene by $PhMe_2SiLi$ leading to the corresponding aryne can compete with the concerted *ipso*-substitution in selected cases. The *ipso*-substitution was successfully applied to a novel synthesis of 9-silafluorenes.

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Keywords: aromatic substitution • DFT calculations • fluoride • transition-metal-free • silylation

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Silyldefluorination of Fluoroarenes via Concerted Nucleophilic Aromatic Substitution

Just one step! Reaction of readily generated silyl lithium compounds with fluoroarenes provide the corresponding aryl silanes under very mild conditions. DFT calculations show that these transformations proceed via concerted nucleophilic aromatic substitution.