Transition Metal-Free Silylation of Unactivated C(sp 2)-H Bonds with tert-Butyl-Substituted Silyldiazenes

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Transition Metal-Free Silylation of Unactivated C(sp^2)–H Bonds with *tert*-Butyl-Substituted Silyldiazenes.

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ABSTRACT: Aromatic organosilanes bearing C(sp^2)–Si bonds have found increasing applications across the chemical science, yet are mostly produced by atom-uneconomical stoichiometric procedures. Catalytic alternatives using hydrosilanes as silicon sources have also been described but they display unfavorable thermodynamics and are mostly based on expensive catalytic systems, often derived from noble metals, or lack generality. Herein, we describe the use of an alternative silicon source, namely the *tert*-butyl-substituted silyldiazenes (*t*Bu–N=N–SiR$_3$), that are readily accessible from commercially available precursors and whose structure enables the C(sp^2)–H bond silylation of unactivated heteroaryl and aryl compounds under ambient, transition-metal free catalytic conditions.
Keywords: C–H silylation, diazene, metalation, homogeneous catalysis, rearrangement

Aromatic organosilanes have become invaluable chemical tools in drug discovery[1] and material science[2] or as intermediates in synthetic chemistry.[3] Most arylsilanes have traditionally been synthesized from the corresponding arylhalides (bromide or iodide).[4] The direct intermolecular silylation of C(sp^2)–H bonds represents an atom-economical alternative as it bypasses the substrate pre-functionalization step, yet poses significant reactivity and selectivity challenges. In this respect, the most common strategy relies on stoichiometric C–H metalation/silylation sequences mediated by organolithium (RLi) or Grignard reagents (RMgX), which nonetheless generate large amount of metallic wastes and display limited scope of application.

Recent research effort has therefore been devoted to uncover catalytic systems that facilitate the C–H silylation of various substrate classes, mainly using hydrosilanes (R$_3$Si–H) as silicon sources.[5] The catalytic dehydrogenative silylation of arenes bearing various directing groups[6] was first developed and later extended to unbiased substrates.[7] However, these developments mostly rely on expensive precious transition metals (typically Ir or Rh-based), which operate at high temperature often in conjunction with elaborated ligands. Beyond kinetic factors, the requirement of harsh reaction conditions in the typical dehydrogenative silylations may also be ascribed to unfavorable reaction thermodynamics.[8] For example, the silylation of *N*-methylindole with Et$_3$SiH is endergonic under standard conditions (ΔG = +2.2 kcal/mol)[9] and the equilibrium must usually be shifted to the product side, e.g. by hydrogenation of an olefin additives. Slightly improved silylation energetics can be reached with vinylsilanes[10] or disilanes[11] silicon sources, yet without genuine kinetic improvement.

Transition metal-free catalytic C(sp^2)–H silylation reactions with hydrosilanes have also been described,[12] though they exhibit somewhat limited generality and still suffer from unfavorable thermodynamics. For example, the use of potent Brønsted or Lewis acids catalysts[13] is restricted to electron-rich (hetero)aromatic substrates, while the
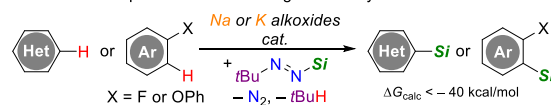
polarity of silyl radicals limits photocatalytic silylation strategies to electron-poor heterocycles.[14] In 2015, Grubbs, Stoltz and coworkers demonstrated that the combination of hydrosilanes (e.g. Et$_3$SiH) with catalytic amount of potassium-based Brønsted bases (e.g. *t*BuOK) allows the dehydrogenative silylation of a range of heteroarenes, including indole derivatives (Scheme 1, route 1A).[15] While operationally simple, cost-effective and scalable, this protocol is mostly restricted to aromatic heterocycles devoid of halides as well as electron withdrawing groups and barely expand to arenes.[16]

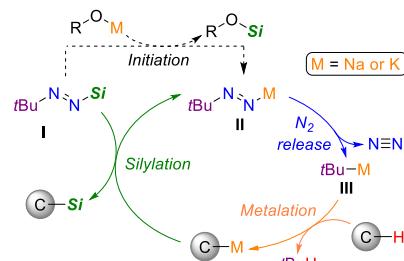**Scheme 1: Transition metal-free C–H silylation reactions with hydrosilanes (A) and CF$_3$SiMe$_3$ (B).**

1. Dehydrogenative (A) and deprotonative (B) silylations
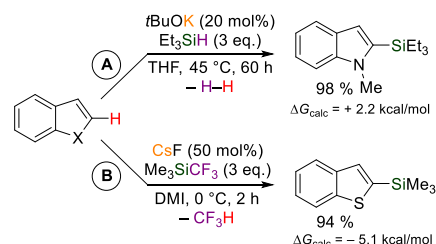
2. This work: deprotonative & denitrogenative silylation

Alternatively, Kondo and co-workers showed that replacing hydrosilanes by the more polarized silicon source Me_3SiCF_3 enabled the exergonic (Scheme 1, route 1B, ΔG = -5.1 kcal/mol on benzothiophene), fluoride-catalyzed deprotonative silylation of furan, thiophene or electron-poor difluoroaromatic derivatives.[17] The silylation of less acidic substrates such as indoles has remained, however, undescribed, presumably because of the lack of *kinetic* basicity of the generated CF_3^- anion.[18]

We have thus sought a novel silicon source that would display sufficient *thermodynamic* activation to enable exergonic C–H silylation reactions with most substrate classes, while being *kinetically* competent to cleave strong C–H bonds in a catalytic manner. Following the mechanistic hypothesis presented in Scheme 1, part of which having some literature precedent,[19] we reasoned that *tert*-butyl-substituted silyldiazenes (I, *t*Bu–N=N–*Si*) may meet these requirements through the release of N_2 upon treatment with a silaphilic Lewis base (e.g. *t*BuOK) and decomposition of the diazenido complex II. The denitrogenation step would not only provide formally a potent metalating agent –*t*BuM (III)– well poised to deprotonate most C–H bonds, but also ensure that the overall C–H silylation is exergonic (ΔG < -40 kcal/mol).[9] The reaction between the metalated substrate and starting diazene I will ultimately regenerate II, thereby providing an overall catalytic reaction. We herein demonstrate the feasibility of this approach through the $C(sp^2)$–H bond silylation of unactivated (hetero)aryl compounds under ambient, catalytic transition-metal free conditions and we provide mechanistic hints for the involvement of potent metalating agents.

At the outset of this study, we prepared a range of *tert*-butyl-substituted silyldiazenes[20] with silyl groups displaying various steric and electronic properties in a one pot two-steps sequence from commercially available *tert*-butylhydrazine hydrochloride (see the SI for details). The key step, which had previously been developed for aryldiazene derivatives,[21] relies on the oxidation of intermediate silylhydrazines (*t*Bu–NH–NH–*Si*) with di-*tert*-butyl azodicarboxylate (DBAD) that selectively delivers the diazenes as thermally-stable red liquids in yields up to 85 % after simple vacuum transfers (Scheme 2).

Scheme 2: Synthesis of *N-tert*-butyl-*N'*-silyldiazenes by oxidative dehydrogenation.
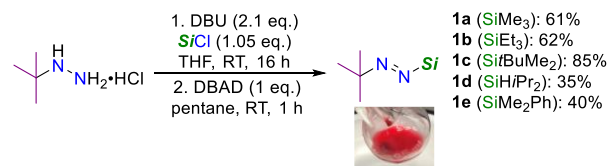

Yields refer to isolated yields over two steps from *t*BuNHNH$_2$·HCl. DBU = 1,8-Diazabicyclo[5.4.0]undec-7-ene.

The silylation of *N*-methylindole (2) as model substrate was first examined using Me_3Si-substituted diazene 1a as the corresponding silylated product would be difficult to prepare by conventional dehydrogenative methodologies because Me_3SiH is gaseous under standard conditions (b.p.= 6.7 °C). When 1a (1.2 eq.) was added dropwise to a solution of 2 and *t*BuOK (10 mol%) in THF at room temperature, the red color of the diazene vanished almost instantaneously while the rapid release of a gas, presumably N_2, was observed. Careful analysis by ^{1}H NMR after 1 h revealed the full conversion of the substate 2 and the quantitative formation of the C2-trimethylsilylated indole 2a, which was isolated in 73 % yield (Scheme 3). The formation of the C3-substituted isomer could not be detected within the limit of NMR. Further optimization of the reaction parameters (see Table S1 in the SI) showed that sodium *tert*-butoxide was almost as efficient as its potassium counterpart, while the lithium derivative was completely inactive. Importantly, widely available and cost-effective potassium hydroxide (KOH) was also an efficient catalyst, albeit the reaction time was extended to 8 h and the yield of 2a decreased to 71 % NMR yield.

Beyond the Me_3Si group, the silylation of 2 with other silyl groups proceeded smoothly (Scheme 3), including the bulky *t*BuMe$_2$Si or *i*Pr$_2$HSi moieties in 2c and 2e (75 % and 84 % isolated yields, respectively), thereby suggesting that the reaction is moderately sensitive to steric hindrance on the silicon atom. The presence of a protecting group on the nitrogen atom was found pivotal and can be as diverse as a phenyl group (3b), a cyclic alkane (4b) or more importantly a readily-cleavable Boc group (5a).

Scheme 3: $C(sp^2)$–H silylation of heteroarenes.
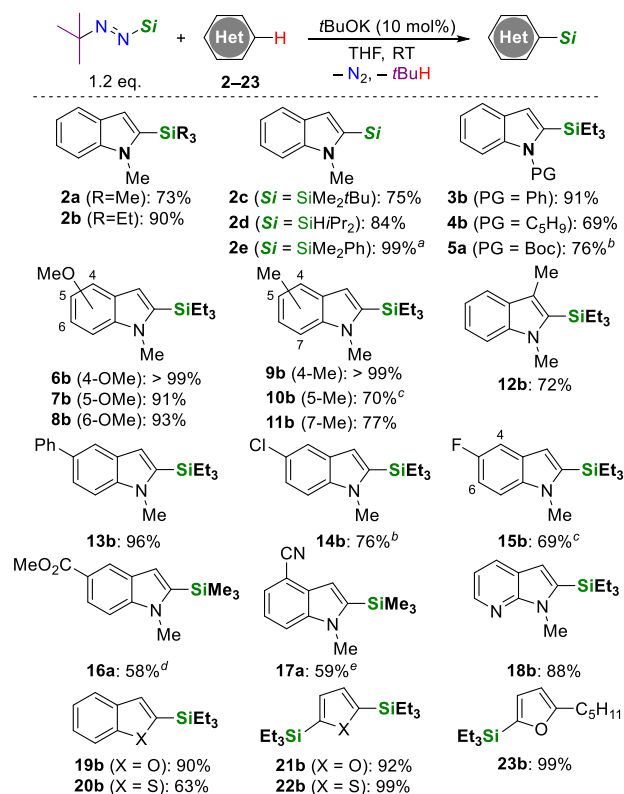
Reaction conditions: heteroarene (0.5 mmol), diazene (1.2 eq.), *t*BuOK (10 mol%) and THF (2.5 mL) at RT. Reaction time (generally <2 h) indicated in the SI. Yields refer to those of purified isolated products. [a]20 mol% *t*BuOK and 2.0 eq. 1e. [b]20 mol% *t*BuOK. [c]1.0 eq. 1b. [d]20 mol% *t*BuONa and 2.5 eq. 1a. [e]20 mol% *t*BuOK and 2.5 eq. 1a.

While keeping a methyl group on the nitrogen, the nature of the substituents on the indole core was also varied so as to probe the functional group tolerance of the C–H silylation protocol (Scheme 3). Pleasingly, both electron donating (**6**–**12**) and withdrawing (**13**–**17**) groups were well tolerated under ambient conditions, including methoxy, methyl, phenyl, chloro, fluoro, cyano or pyridyl substituents. Complex reaction mixtures of products were, however, obtained with indoles bearing bromide or iodide atoms at the 5-position. The introduction of a Me$_3$Si group in **16a**, which bears a methyl benzoate moiety prone to nucleophilic attack[19]*a* was also successful (58 % isolated yield) using *t*BuONa (20 mol%) as catalyst. In this case, the use of potassium salts led to a reaction mixture comprising products formally arising from the addition of a *t*Bu$^-$ anion to the ester. The formation of such products was prevented when *t*BuONa rather than *t*BuOK was used, thereby highlighting that simply varying the cation of the catalyst enables control over the selectivity of the silylation reaction. Finally, thiophene and furan derivatives (**19**–**23**) were all silylated exclusively in the 2 (and 5) position in good to excellent yields within 1 h at room temperature.

During the course of the heteroaromatic scope investigation, we noticed that when 5-fluoroindole **15** was reacted with diazenes **1a** or **1b** under the standard reaction conditions, the desired products (**15a** or **15b**) were produced along with minor amounts of bis-silylated compounds both at C2 and C4 or C6 (see Table S2 in the SI for details). The formation of the latter suggested that the *ortho*-silylation of fluoroarenes was energetically accessible, while requiring marginal reoptimization. This was confirmed when fluorobenzene **24** was reacted with excess **1a** (2.5 eq.) and 10 mol% *t*BuOK. The corresponding bis-silylated product **24a$_2$** was formed almost instantaneously at room temperature and isolated in 93 % yield with a complete regioselectivity for the *ortho* positions (Scheme 4). Importantly, the latter is the first example of a transition metal-free C–H silylation of a monofluoroaromatic compound, which had previously been prepared by stoichiometric directed ortho metalation (DoM) with LiTMP (TMP = 2,2,6,6-tetramethylpiperidine) followed by silylation.[22] The *para* or *meta* isomers, which are often co-produced with Ir or Rh-based catalysts and triethylsilane,[23] were not observed by ^{19}F NMR. The selective mono-*ortho*-silylation of **24** with decreased amount of **1a** or **1b** remained, however, only partially successful. For example, with 1 equiv **1b**, 12 % of **24b$_2$** was still produced (see Table S3 in the SI). Increasing the steric bulk around the silicon atom with **1c** nonetheless allowed to converge selectively toward the monosilylated product **24c**, which was isolated in 64 % yield.

Several substituted fluoroarenes bearing methoxy (**25-27**), hydroxy (**28**), phenoxy (**29**), chloro (**30**), methyl (**31**) or phenyl (**32**) groups were also successfully silylated, generally in good to excellent yields at room temperature (Scheme 4). The free hydroxy group in **28** was tolerated because it was first *in-situ* protected as a trimethylsilyl ether and the O- and C-silylated product **28a** was isolated in 63 % yield. The catalytic silylation of 4- or 2-fluoroanisole (**26** and **27**) selectively afforded the mono and difunctionalized products **26b$_2$** and **27b** in 93 and 80 % isolated yield

without any other regioisomers observed. Similarly, two Me$_3$Si groups could be quantitatively introduced in **25a$_2$**. While nitro-substituted 2– or 4-fluorobenzenes were found unreactive towards silylation, the presence of a chloride atom in **30** did not divert the selectivity of the reaction, though only the mono-silylated **30b** was formed in this case. The unsymmetrical 4-fluorodiphenylether **29** bearing only one fluorine atom also reacted preferentially by *ortho*-fluorine bis-silylation, whereas the reaction of unsubstituted Ph$_2$O (**33**) with **1a** afforded **33a** that stems from the monosilylation *ortho* to the oxygen atom. The silylation *ortho* to a methoxy group was also feasible provided the position *ortho* to the fluorine atom had been blocked by a SiEt$_3$ group (**27b → 34a**).

Scheme 4: C(sp^2)–H silylation of arenes.
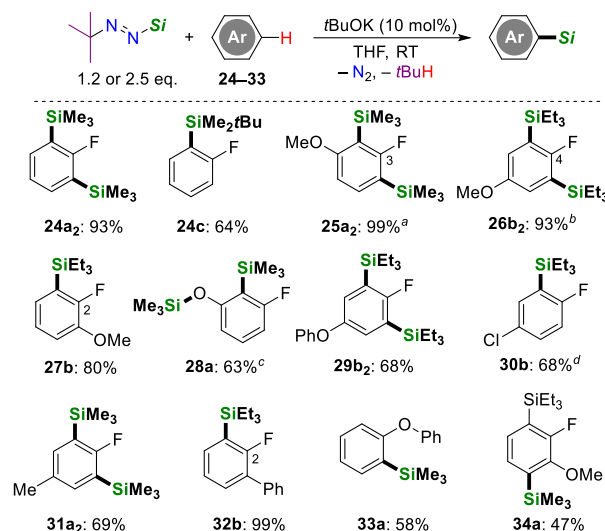
Reaction conditions: arene (0.5 mmol), diazene (1.2 eq. for mono- or 2.5 eq. for bis-silylation), *t*BuOK (10 mol%) and THF (2.5 mL) at RT. Reaction time (generally <2 h) indicated in the SI. Yields refer to those of purified isolated products. *a*3.5 eq. **1b**. *b*3.0 eq. **1b**. *c*20 mol% *t*BuOK and 2.8 eq. **1a**. *d*20 mol% *t*BuOK.

To illustrate the synthetic utility of this novel expeditive C–H silylation protocol, halogenation reactions by mild *ipso*-substitution were undertaken. **25a$_2$** was derivatized in high yields into the corresponding diiodo- and dibromoarene building blocks **35** and **36** with ICl and Br$_2$, respectively (Equation 1).[24] In addition, the bis-silylated fluorobenzene **24a$_2$** could be monobrominated selectively at room temperature (Equation 2) so that one Me$_3$Si group remains in **37** for further elaboration.
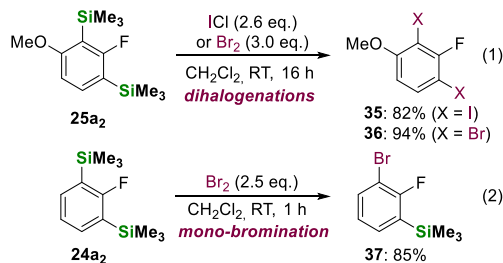
Collectively, these results allow us to delineate a preliminary scale of relative directing ability for the catalytic silylation of substituted arenes when reacted with *t*BuOK and *N*-*tert*-butyl-*N'*-silyldiazenes. Fastest silylations always took place *ortho* to the fluorine atom and the rate decreases in the order F > OPh > OMe ≈ OSiMe$_3$ ≈ Cl as determined by the aforementioned intramolecular competition experiments. Although the thorough elaboration of such a scale awaits further study, it is reminiscent of the one that had been established in several instances for stoichiometric *ortho*-metalation/functionalization reactions.[25] For example, Schlosser and coworkers have shown that 2-fluoroanisole can be carboxylated (and thus metalated) regioselectively at the most acidic position, that is in the neighborhood of the fluorine (rather than the oxygen) atom with super-bases.[26]. Because the catalytic silylation of arenes with *N*-*tert*-butyl-*N'*-silyldiazenes follows site selectivity trends consistent with the latter model, we questioned whether potent –anionic– metalating agent could be *in-situ* generated and sustain turnovers upon silylation.

Support for the involvement of *anionic* intermediates was gained when the *O*-fluoroaryl carbamate **38** was reacted with 1.5 eq. of diazene **1a** (Scheme 5). While the conversion remained low with 10 mol% *t*BuOK (< 30 %), the expected products silylated *ortho* to the fluorine atom were observed (**38a**: ca. 11 %) along with a silicon-free new species (ca. 9 %), whose formulation as the potassium phenolate complex **39** was confirmed from a separate stoichiometric reaction that allowed us to isolate **39** in 64 % yield. In fact, **39** results from a regioselective O→C 1,3-migration of the carbamoyl group -C(O)N(*i*Pr)$_2$ diagnostic of an anionic *ortho*-Fries (AoF) rearrangement,[27] which is usually triggered by strong Brønsted bases (e.g. LDA or *s*BuLi) as discovered by Snieckus[28] and later thoroughly studied by Collum.[29] Importantly, the reaction of *t*BuOK (1.1 eq.) with **38** alone led to the complete recovery of the latter, thereby demonstrating that the diazene played a central role in such rearrangement. Hence, the combination of *t*BuOK and **1a** generates a potassium-based metalating agent sufficiently activated to deprotonate **38** into the corresponding, yet uncharacterized, arylpotassium species,[30] which can further evolve by silylation or by AoF rearrangement. Interestingly, the latter rearrangement could be minimized using *t*BuONa as catalyst (bottom of Scheme 5) so that the mono-silylated product **38a** could be produced as a single regioisomer in 48 % isolated yield.

Overall, the scope as well as the preliminary mechanistic experiment hereinabove outlined both point to the facile generation of potent metalating agents from the silyldiazenes **1,** which have been exploited, for the first time, in catalytic C–H silylation reactions of both heteroarenes and fluoroarenes. Many of the described reactions had only been stoichiometrically realized with lithium or magnesium bases following traditional DoM/silylation sequences. The present methodology offers an alternative that proceeds rapidly under ambient conditions with non-pyrophoric reagents, while its catalytic nature allows one to conveniently control the reactivity and/or the regioselectivity of the process in an atom-economical manner, notably through the variation of the cationic part of the catalyst. Future work will be devoted to the concise study of the mechanism of the C–H silylation reaction, notably regarding the nature of the metalating agent generated *in-situ*, as well as to extend the scope to other substrate classes.

Scheme 5: Anionic *ortho*-Fries (AoF) rearrangement
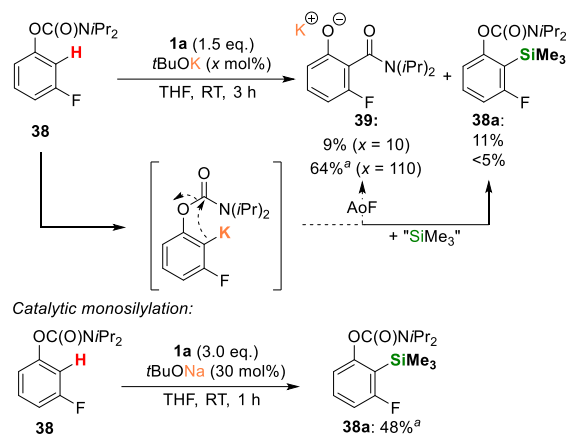
*a*Isolated yields after purification.

ASSOCIATED CONTENT

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Author Contributions

‡B.N. and F.L. contributed equally to this work.

Supporting Information

Experimental procedures and characterization data as well as computed thermodynamic data (PDF).

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